

# Simultaneous photooxidation and photoreduction of phenol and Cr(VI) ions using titania modified with nanosilica

Daria Kądziołka<sup>1</sup>, Joanna Grzechulska-Damszel<sup>1</sup>, Beata Schmidt<sup>2\*</sup>

West Pomeranian University of Technology in Szczecin, Faculty of Chemical Technology and Engineering, Pułaskiego 10, 70-322 Szczecin, Poland

<sup>1</sup>Department of Inorganic Chemical Technology and Environment Engineering

<sup>2</sup>Department of Chemical Organic Technology and Polymeric Materials

\*Corresponding author: e-mail: Beata.Schmidt@zut.edu.pl

The photocatalytic process of phenol oxidation and Cr(VI) reduction in the presence of nano-silica modified titania was carried out. The activity of composites was tested using two different light sources. The photocatalysts with 10% of nanosilica showed the highest activity. The calcination temperature (200–800 °C) significantly determined the sensitivity of the obtained materials to the light source used. Photocatalysts alternately adsorbed and desorbed Cr(VI) ions from the reaction mixture during irradiation. In the one-component mixture, complete oxidation of phenol was observed using material calcined at 650 °C, after 3 h of UV-VIS irradiation. In the reaction mixture of Cr(VI) and phenol, the highest activity was demonstrated by photocatalyst calcined at 300 °C. The concentration of phenol decreased in proportion to the decrease of chromium ions. The obtained titania-silica composites showed oxidizing properties towards phenol and reductive properties toward Cr(VI) ions.

**Keywords:** photocatalysis, titanium dioxide, nanosilica, water purification.

## INTRODUCTION

Titanium(IV) oxide (TiO<sub>2</sub>) is a photocatalyst commonly used in advanced oxidation processes (AOPs), mainly in the removal of anthropogenic pollutants (e.g. aromatic and carboxylic acids, pesticides, herbicides, phenol derivatives, textile dyes or drug residues) from water<sup>1–4</sup>. TiO<sub>2</sub> is characterized by high photochemical stability and good mechanical strength for most of the reaction conditions. The band gap energy of titania semiconductor (3.2 eV for anatase) corresponds to the range of UVA radiation (300–388 nm), which is about 4% of solar radiation<sup>5</sup>. Due to the constant increase in energy costs, the use of artificial light sources emitting UVA radiation increases the costs of the photocatalytic process.

Obtaining a titanium semiconductor, the photocatalytic activity of which is in the range of visible radiation (>400 nm), would allow the use of the main part of the solar spectrum and/or the use of artificial energy sources that are cheaper to produce and operate. To enhance the photocatalytic activity in visible light, titanium(IV) oxide is subjected to various modification processes, e.g. by using secondary oxides, including nanosilica (nano-SiO<sub>2</sub>)<sup>6,7</sup>. Studies performed by many research groups have shown that enrichment of titanium dioxide with nanosilica directly prevents agglomeration and growth of TiO<sub>2</sub> particles, improves the thermal stability of the photocatalyst and increases the efficiency of the photocatalytic process<sup>8,9</sup>. It was proved that the photocatalytic properties of the TiO<sub>2</sub>-SiO<sub>2</sub> composite depend on the selection of the preparation method and the percentage content of nanosilica in the final material<sup>10,11</sup>.

The group of impurities subjected to photocatalytic removal from water includes phenol and chromium(VI) compounds. The physical and chemical properties of phenol determine its use in the chemical, petrochemical, biotechnological and food industries. Industrially synthesized phenol is used primarily in the production of phenolic resins, synthetic fibers and fungicides<sup>12,13</sup>. Potassium dichromate is often used in the chemical or

textile industries as an oxidant<sup>14,15</sup>. The wide spectrum of phenol and potassium dichromate applications generates a real threat for drinking water contamination with these compounds<sup>16</sup>. In environmental toxicology, the maximum permissible concentration in drinking waters is 0.1 and 0.2 mg/dm<sup>3</sup>, for chromium(VI) ions and phenol, respectively. The European Union (EU) and the World Health Organization (WHO) have recognized phenol and potassium dichromate as carcinogenic and toxic to humans<sup>17–20</sup>.

In this work, modifications of titanium(IV) oxide with nanosilica were carried out. Titania/silica composites were characterized using UV-VIS/DR, FTIR and XRD methods. The effect of silica addition and thermal treatment conditions on photocatalytic performance was examined. The obtained materials were applied in the photocatalytic reaction of phenol and Cr(VI) removal from water. Modification of titania with silica revealed the benefits such as better sedimentation properties of obtained material together with activity under VIS light. These facts were not widely mentioned in the literature before. The process of chromium(VI) removal was found to be accelerated by the presence of phenol in the reaction mixture. The coexistence of the photoreduction/ photooxidation processes in the reaction mixture of both model pollutants significantly accelerated the process.

## EXPERIMENTAL

### Materials

Titanium dioxide (Grupa Azoty Zakłady Chemiczne “Police” S.A., Poland), was a precursor to obtain TiO<sub>2</sub> starting material. The analytical grade nanosilica (7–14 nm) was purchased from Plasmachem, Germany. The phenol (POCh, Poland) and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Chempur, Poland) were the sources of model pollutants. The 1,5-diphenylcarbazine (Chempur, Poland), ammonia water (Chempur, Poland) and ethanol (Stanlab, Poland) were used also in analytical grade.

### Synthesis of photocatalysts

The raw titania containing sulfuric acid residue was rinsed with ammonia water followed by distilled water until neutral pH. The obtained slurry was then dried and thus the starting material (s.m.) was obtained. Modifications of TiO<sub>2</sub> were performed with the use of nanosilica in the presence of ethanol. Nanosilica (in an amount of 2.5 to 15 wt.%, with respect to TiO<sub>2</sub>) was added to ethanol and then homogenized in an ultrasonic bath for 60 minutes. Titania was then added to the prepared suspension and the mixture was stirred for 60 minutes using a magnetic stirrer (500 rpm). The obtained material was dried (time 24 hours, temperature 100 °C) and then calcined in a muffle furnace for 8 hours using temperatures ranging from 200 to 800 °C.

The prepared titania/silica materials were assigned as, for example, Ph/ 10% 300 – Ph is for the photocatalyst, 10% means the amount of silica added to titania (weight %) and 300 indicates the temperature of thermal treatment. Reference materials were prepared without the addition of silica. The course of the photocatalytic process was also investigated for the raw (untreated) TiO<sub>2</sub>.

### Photocatalysts characterization

FT/IR-4200 spectrometer (Jasco, Japan) with the equipment for powdered samples (Pike Technologies, USA) was used to record FTIR spectra in the wavelength range 4000–500 cm<sup>-1</sup>.

XRD analysis was done using PANalytical Empyrean diffractometer (Malvern Panalytical, UK) with CuK $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ).

The UV-Vis/DR spectra were measured in a range of 200 to 800 nm using UV-Vis/DR spectrophotometer (Jasco V-650, Japan). Spectralon white diffuse reflectance standard was used as a reference.

Analysis results of three photocatalysts samples are presented in this paper. These are for the starting material (s.m.); titania modified with 10% of silica calcined at 300 °C and titania modified with 10% of silica calcined at 650 °C since they showed the highest photocatalytic activity under UV-VIS and VIS illumination, respectively.

### Photocatalytic reaction

The photocatalytic activity of titania/silica composites was tested in the reaction of the photocatalytic oxidation

of phenol and chromium(VI) ions reduction in water. The oxidation state of chromium ions was determined using the colorimetric method with 1,5-diphenylcarbazide. The model solutions of impurities were prepared: phenol (20 mg/dm<sup>3</sup>), potassium dichromate (10 mg/dm<sup>3</sup>) and a mixture of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (10 mg/dm<sup>3</sup>) and phenol (20 mg/dm<sup>3</sup>) in a ratio of 1 : 1. The tests were carried out at pH 6.5  $\pm$  0.1. The photocatalyst in the amount of 0.2 g/ dm<sup>3</sup> and the model impurity solution were placed in a glass beaker (500 ml) and stirred using a magnetic stirrer (550 rpm) until the adsorption equilibrium of the substrates on the surface of the photocatalyst was established. Next, the reaction mixtures were illuminated using a UV-VIS (six lamps, 20 W each, Philips) or VIS (LED Osram Parathom 5W) light source – Figure 1. Using the same experimental conditions, tests were performed without the use of a light source, in the dark.

The radiation spectra of applied light sources was measured with a LB-901 radiometer (LAB-EL, Warsaw, Poland). The radiometer was equipped with CMP3 (Kipp & Zonen, The Netherlands) sensor with the spectral range of 300 to 2800 nm and UV sensor PD204AB Cos (Macam Photometrics Ltd., USA) with the spectral range of UV-A and UV-B radiation.

Samples of about 5 ml were periodically drawn from the reactor, centrifuged to remove solid particles and then analyzed with respect to phenol concentration, chromium ions concentration and total organic carbon content.

The decrease in the concentration of the pollutants was the basis for the assessment of the effectiveness of the processes carried out. The degree of degradation of the test substances was calculated as follows:

$$R = [(C_0 - C_t) / C_0] \cdot 100\%$$

where:

$C_o$  – concentration of pollutant in the reaction mixture after adsorption [mg/dm<sup>3</sup>];

$C_t$  – concentration of pollutant in the reaction mixture after the certain time of illumination [mg/dm<sup>3</sup>].

Changes in the concentration of phenol were observed using V-630 UV-VIS spectrometer (Jasco, Japan) after centrifugation (3000 rpm, 15 min) and separation of the photocatalyst from the reaction mixture. A linear dependence between the concentration of phenol and the absorption peak at 269 nm was observed thus the phenol concentration was monitored at this wavelength<sup>21</sup>. Total

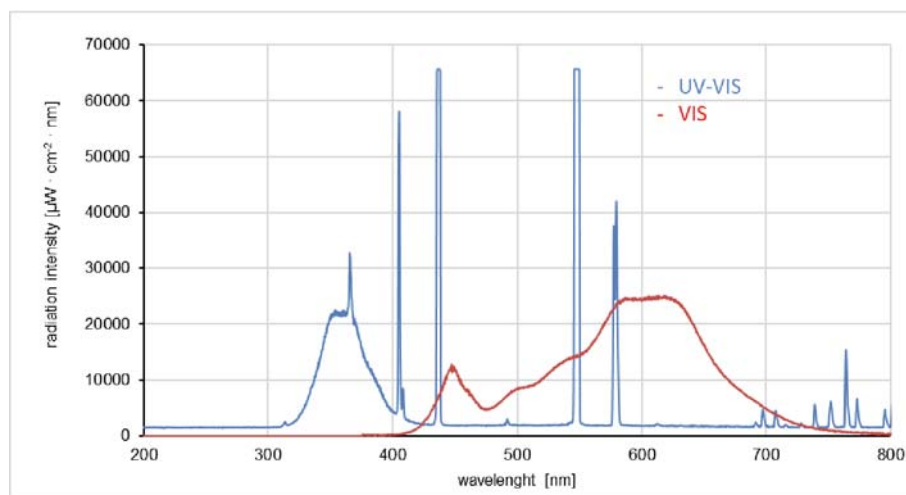


Figure 1. The spectrum of UV-VIS and VIS light sources

organic carbon (TOC) content in the reaction mixture was measured using TOC analyzer (multi N/C 2000, Analytik Jena, Germany) to monitor the mineralization degree during the photooxidation of phenol. Cr(VI) ions were determined according to the diphenylcarbazide colorimetric method at 540 nm<sup>22, 23</sup>.

Experiments were performed in triplicate to ensure reproducibility of the results.

## RESULTS

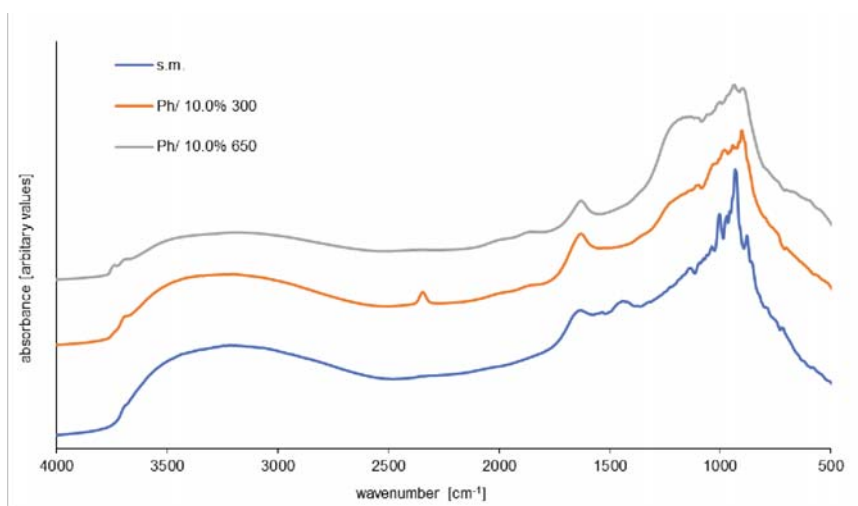
### Physicochemical properties of titania-silica materials

Figure 2 presents FTIR spectra of starting material (s.m.) and photocatalysts modified with 10% of silica thermally treated at 300 and 650 °C. The peaks centered at 1627 cm<sup>-1</sup> and 3384 cm<sup>-1</sup> are characteristic of  $\delta$ -H<sub>2</sub>O bonding and vibration of hydroxyl groups<sup>24</sup>. The peak at 732 cm<sup>-1</sup> is for O–Ti–O bonding in anatase. Peaks at 970 cm<sup>-1</sup> and 1100 cm<sup>-1</sup> belong respectively to Si–O–Ti and Si–O–Si asymmetric stretching<sup>25, 26</sup>. There is no peak at 2900 cm<sup>-1</sup> (C–H) for Ph/ 10.0% 300 and Ph/ 10.0% 650 °C, which means that all organic matter (from ethanol) was removed from the samples after calcination<sup>27, 28</sup>.

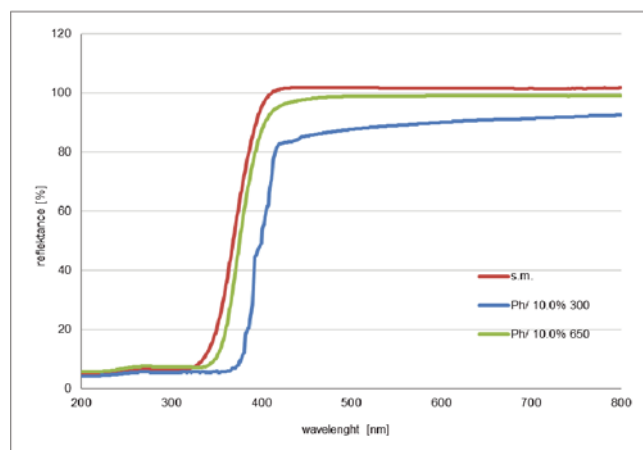
UV-VIS/DR spectra of s.m. and the best-acting photocatalysts are presented in Figure 3. Based on the analysis it was found that the starting TiO<sub>2</sub> and the modified photocatalysts absorb UV radiation well. The addition of silica revealed changes in absorption spectra. The photocatalyst containing 10.0% of nano-silica thermally treated at 300 °C showed absorption in the visible light range also. The presence of nano-SiO<sub>2</sub> resulted in the shift of the absorption spectrum maximum to 385 nm for Ph/ 10.0% 300 photocatalyst and 376 nm for Ph/ 10.0% 650, compared to 369 nm observed for the starting material (titania without silica). Table 1 summarizes the bandgap energies  $E_g$  determined according to the Kubelka-Munk method<sup>29</sup>.

**Table 1.** Band gap energies of starting material (s.m.) and photocatalysts modified with 10% of SiO<sub>2</sub> treated at 300 and 650 °C

| Photocatalyst | Bandgap Energy $E_g$ [eV] |
|---------------|---------------------------|
| s.m.          | 3.36                      |
| Ph/ 10.0% 300 | 3.57                      |
| Ph/ 10.0% 650 | 3.79                      |

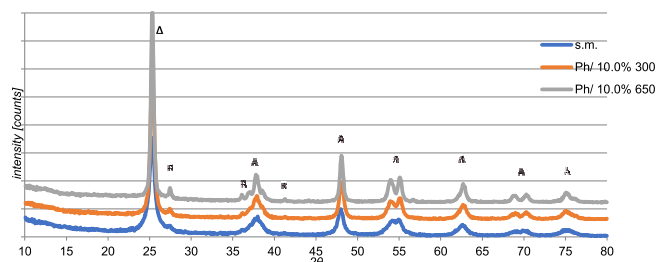


**Figure 2.** FTIR spectra of starting material (s.m.) and photocatalysts modified with 10% of silica thermally treated at 300 and 650 °C



**Figure 3.** UV-VIS absorption spectra of starting material (s.m.) and photocatalysts modified with 10% of SiO<sub>2</sub> treated at 300 and 650 °C

Figure 4 shows the results of XRD analysis. Crystallite size was changed from 9 nm to 18 and 16 nm, respectively for Ph/ 10.0% 300 and Ph/ 10.0% 650 – based on Scherrer formula<sup>30, 31</sup>. An increase in the intensity of anatase reflections was found, for the nano-SiO<sub>2</sub> modified photocatalysts. The peaks become less broad and sharper showing increasing crystallinity of material with increasing treatment temperature. It can be also seen that rutile phase reflections appear with the increase of treatment temperature. It is known that during the calcination of titania, at the temperature of about 400 °C amorphous titania starts to transform to anatase and further rising of the temperature above 600 °C anatase transformation to rutile phase occurs<sup>32</sup>. In a hybrid material, like titania and silica together, the silica material stabilizes the different phases of titania. Silica suppresses the transformation of



**Figure 4.** XRD spectra of starting material (s.m.) and photocatalysts modified with 10% of SiO<sub>2</sub> treated at 300 and 650 °C

amorphous titania to anatase and anatase to rutile by decreasing the mobility of titania atoms like an anchor.

The specific surface area of selected photocatalysts was determined by analyzing the nitrogen adsorption isotherm by the Brunauer-Emmett-Teller (BET) method (ISO 9277:2010, Gemini 2360, V 2.01, Micromeritics) at the P/P0 range of 0.05–0.25 using multipoint BET equation. The average pore width was calculated by the Barrett-Joyner-Halenda (BJH) method. The starting material for the photocatalysts preparation showed a surface area of 231 m<sup>2</sup>/g (Tab. 2). The presence of 10% silica caused the surface area decrease to 191 m<sup>2</sup>/g. As can be seen from Table 2, the increase of treatment temperature resulted in gradual decrease of surface area. After calcination at 650 °C, the surface area of the treated material was only 49 m<sup>2</sup>/g. This can be connected with the phase transformation of titania.

**Table 2.** BET surface area of starting material (s.m.) and photocatalysts modified with 10% of SiO<sub>2</sub> treated at 300, 550, 600 and 650 °C

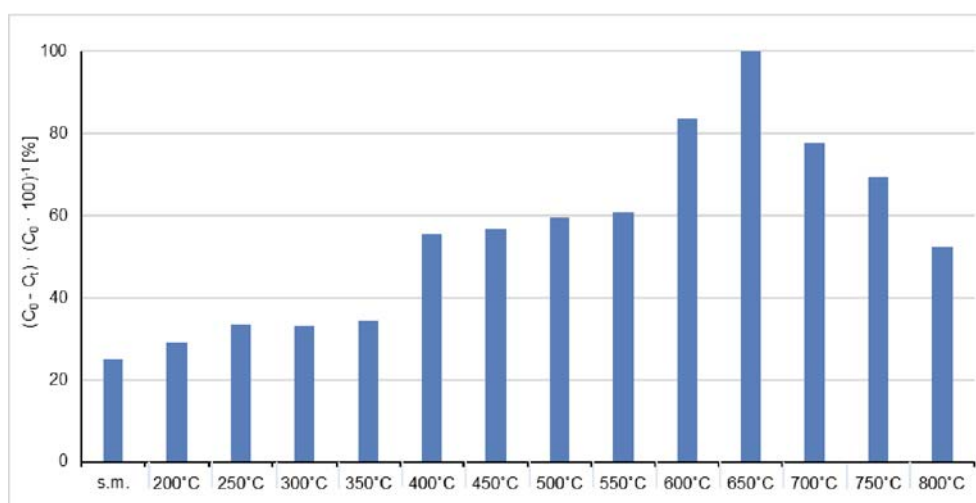
| Photocatalyst | BET Surface area [m <sup>2</sup> /g] |
|---------------|--------------------------------------|
| s.m.          | 231                                  |
| Ph/ 10.0% 300 | 191                                  |
| Ph/ 10.0% 550 | 69                                   |
| Ph/ 10.0% 600 | 63                                   |
| Ph/ 10.0% 650 | 49                                   |

### Photocatalytic properties of titania-silica materials

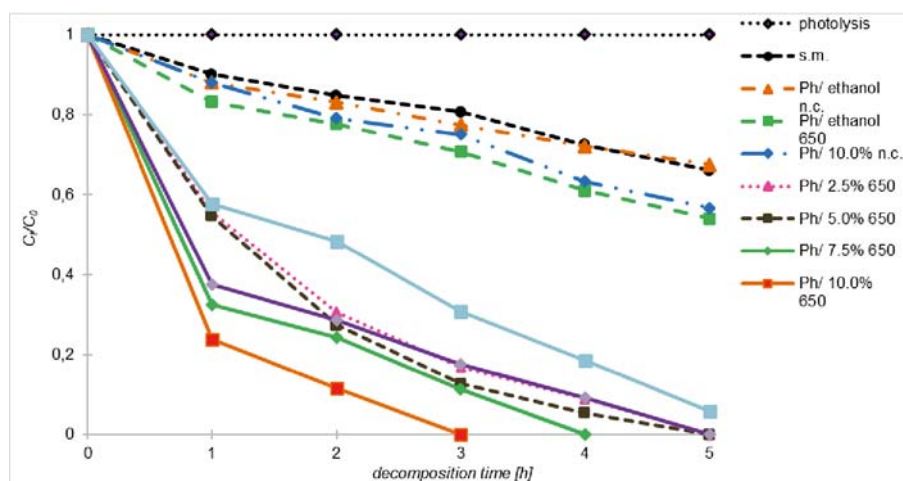
The photolytic decomposition of model pollutants was not observed for both UV-Vis and Vis light sources. The control tests were also performed without the use of any light source, in the dark. There were no changes in the impurities concentration in the reaction mixtures. The adsorption equilibrium time was established as 60 minutes for the phenol solution and 120 minutes for the chromium and phenol/chromium mixture solutions.

The obtained TiO<sub>2</sub>/SiO<sub>2</sub> composites showed high photocatalytic activity under UV-VIS light towards phenol decomposition (Figs. 5–7). It is well known that the addition of silica to TiO<sub>2</sub> might significantly increase the photocatalytic activity since the Ti–O–Si bonds activate the catalytic centers of composite oxides in the oxidation of organic compounds<sup>32–38</sup>. The calcination temperature and the amount [wt.%] of SiO<sub>2</sub> additive directly affected the efficiency of phenol oxidation in the reaction mixtures.

The starting material (s.m.) decomposed only about 25% of phenol from the reaction mixture with the starting concentration of 20 mg/dm<sup>3</sup> (Fig. 5). Increase in the calcination temperature revealed the increase in the photocatalytic activity of titania-silica composites. The photocatalyst modified with 10% of SiO<sub>2</sub> and calcined at 650 °C (Ph /10% 650) showed the highest activity



**Figure 5.** Photocatalytic decomposition [%] of phenol (20 mg/dm<sup>3</sup>) after 3 hours of exposure to UV-VIS light in the presence of the photocatalyst Ph/10.0% (0.2 g/dm<sup>3</sup>) modified in the temperature range from 200 to 800 °C



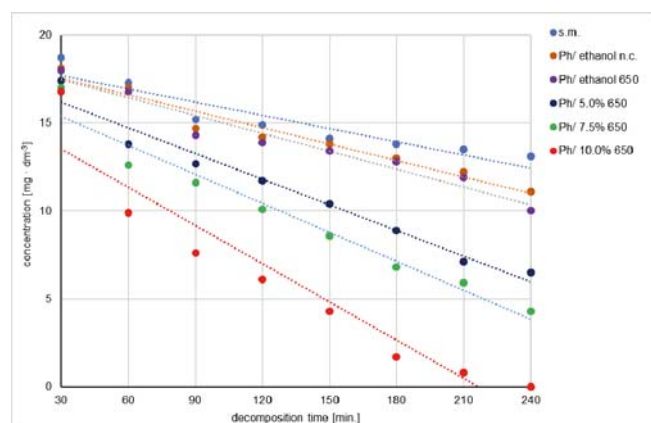
**Figure 6.** Changes in phenol concentration (initial concentration: 20 mg/dm<sup>3</sup>) during irradiation with UV-VIS light in the presence of a photocatalyst (0.2 g/dm<sup>3</sup>)

under UV-VIS light. Exceeding 650 °C, the photocatalytic activity toward phenol decomposition began to decrease.

Figure 5. Photocatalytic decomposition [%] of phenol (20 mg/dm<sup>3</sup>) after 3 hours of exposure to UV-VIS light in the presence of the photocatalyst Ph/10.0% (0.2 g/dm<sup>3</sup>) modified in the temperature range from 200 to 800 °C

Figure 6 presents the results of the experiments applying titania-silica composites with different amounts of nanosilica from 2.5 to 10% of nanomaterial calcined at 650 °C compared to the reference materials and photolysis. Photolysis showed no decomposition of phenol at all. The reference materials: s.m., Ph/ethanol n.c. (titania in ethanol not calcinated), Ph/ethanol 650 (titania in ethanol calcinated at 650 °C without silica), Ph/ 10% n.c. (titania with addition of 10% silica not calcinated) – showed significantly lower photoactivity comparing to the materials with varying amounts of silica calcined at 650 °C. The complete decomposition of phenol took place after three hours of the process for the sample Ph/ 10% 650.

As can be seen from Figure 7, the increasing amount of silica additive resulted in the increasing mineralization of phenol. The complete removal of TOC was obtained after four hours of the experiment.



**Figure 7.** Changes in the concentration of TOC during photocatalytic degradation of phenol under irradiation with UV-VIS light in the presence of s.m. and SiO<sub>2</sub> modified photocatalysts

Gobara et al.<sup>39</sup> reported that the photocatalytic decomposition of trichlorophenol on TiO<sub>2</sub>-SiO<sub>2</sub> composite depends on the TiO<sub>2</sub>/SiO<sub>2</sub> ratio. Sirimahachai et al.<sup>34</sup> established that composite oxide shows the best photocatalytic activity at about 50% of SiO<sub>2</sub> content. From the results of Chiara et al.<sup>40</sup> it can be seen that the best activity was at TiO<sub>2</sub>/SiO<sub>2</sub> 80/20 ratio.

In these studies, the best photocatalytic activity was observed for the composite oxides containing 10% of SiO<sub>2</sub>.

In the single-component solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (10 mg/dm<sup>3</sup>) in the presence of photocatalysts, an alternating

decrease and increase in the concentration of chromium(VI) ions was observed depending on the duration of exposure to a given light source (Table 3), however, on every case, the concentration of chromium(VI) was lower than the starting concentration. It can be observed that the presence of silica in materials resulted in higher decrease in Cr(VI) concentration.

In the reaction mixture of phenol (20 mg/dm<sup>3</sup>) and chromium(VI) (10 mg/dm<sup>3</sup>) in the ratio 1: 1, a total loss of chromium was observed using 0.2 g/dm<sup>3</sup> of photocatalyst containing 10.0 % of nano-silica and calcined at the temperature of 300 °C. The necessary exposure time was 1 and 3 hours, respectively for the UV-VIS (Fig. 8) and VIS (Fig. 9) light sources. It takes longer illumination with VIS light in contrary to the UV-VIS to obtain the complete removal of chromium. The loss of phenol was similar in both cases (approx. 80%) – Fig. 8 and 9. The photocatalysts calcined above 450 °C showed no significant activity under VIS light (Fig. 9).

Papadam et al.<sup>41</sup> studied the photocatalytic removal of chromium(VI) by TiO<sub>2</sub> at the presence or absence of organic compounds. A definite synergic effect was observed between photocatalytic reduction of chromium(VI) and the presence of organics in the reaction mixture. The photocatalytic reduction of chromium and other metal ions occurs via conduction band electrons and the presence of valence band holes scavengers, like organic compounds that can be oxidized, facilitate the process<sup>42</sup>.

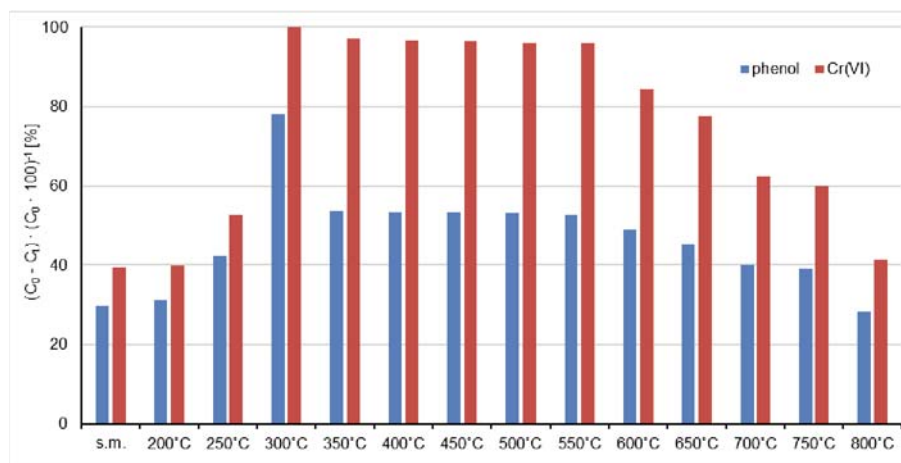
The stability and possible reuse of photocatalytic materials are important aspects for its application. The addition of silica to titania increased sedimentation properties. Since the materials could be easily recovered from the reaction mixture, the tests of reuse have been done. Figure 10 presents the results of this experiment. It was found that the application of the spent photocatalyst did not show any significant decrease in activity during the three subsequent tests.

#### SUMMARY

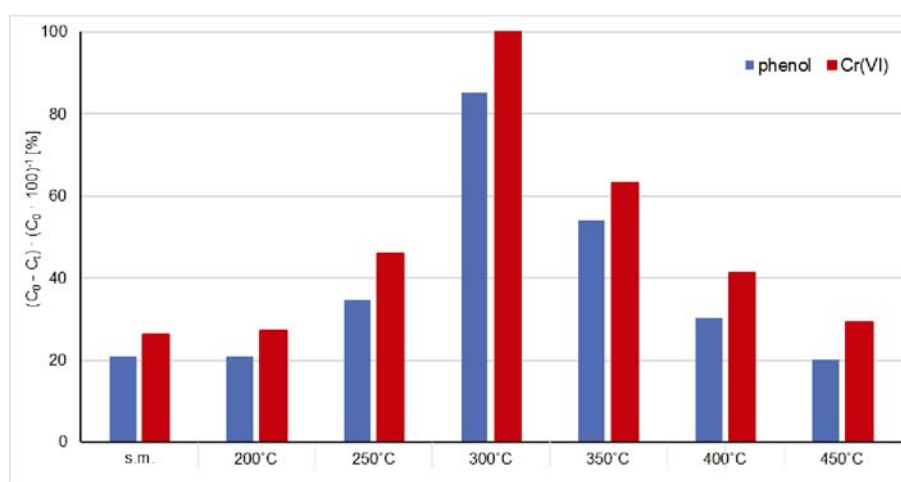
The doping of TiO<sub>2</sub> with nano-silica results in a significant increase in sedimentation of the photocatalyst particles - a centrifugation process is enough to separate the photocatalyst particles from the solution. Titania modified with nano-SiO<sub>2</sub> shows high UV-VIS photocatalytic activity towards phenol decomposition. Modification of titania using nano-silica gives a material showing photocatalytic properties toward Cr(VI) ions in the reaction mixture of Cr(VI) and phenol in the ratio 1: 1. The coexistence of the photoreduction/photooxidation processes in the reaction mixture of both model pollutants significantly accelerated the process. The visible light source used in the research is an inexpensive commercial product, commonly used in households, and the obtained results prove that the application of such an inexpensive light

**Table 3.** Cr(VI) concentration in the reaction mixture illuminated with UV-VIS and VIS light in the presence of photocatalysts

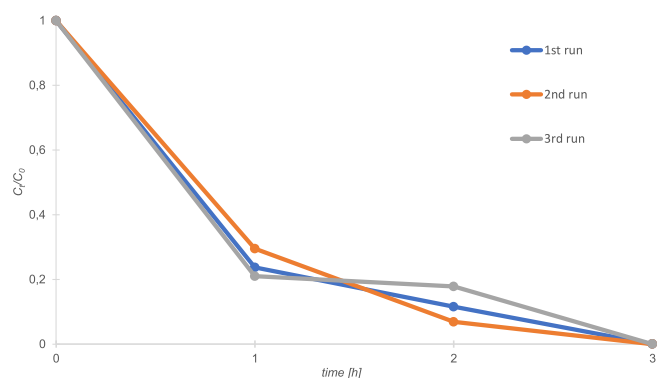
| Source of light | Photocatalyst    | Concentration Cr(VI) [mg · dm <sup>-3</sup> ] |     |     |     |     |      |      |      |      |  |
|-----------------|------------------|---|-----|-----|-----|-----|------|------|------|------|--|
|                 |                  | 0 h   | 1 h | 2 h | 4 h | 8 h | 12 h | 16 h | 20 h | 24 h |  |
| UV-VIS          | s.m.             | 10.0  | 9.4 | 7.8 | 8.1 | 6.9 | 9.2  | 7.1  | 5.9  | 8.2  |  |
|                 | Ph/ ethanol n.c. |   | 8.8 | 6.9 | 7.7 | 6.8 | 7.9  | 8.2  | 7.4  | 6.8  |  |
|                 | Ph/ 10.0% n.c.   |   | 3.8 | 4.0 | 3.5 | 6.7 | 3.9  | 4.7  | 6.1  | 5.2  |  |
|                 | Ph/ 10.0% 300    |   | 4.1 | 5.6 | 4.9 | 5.7 | 6.4  | 5.2  | 6.3  | 5.9  |  |
|                 | Ph/ 10.0% 650    |   | 3.1 | 4.9 | 6.3 | 3.9 | 6.7  | 4.1  | 6.2  | 5.7  |  |
| VIS             | Ph/ 10.0% 300    | 6.3   | 5.1 | 4.7 | 5.6 | 5.5 | 6.2  | 4.7  | 5.9  |      |  |



**Figure 8.** Photocatalytic decomposition of phenol (20 mg/dm<sup>3</sup>) and Cr(VI) (10 mg/dm<sup>3</sup>), in ratio 1:1, after 1 h of illumination with UV-VIS light source over Ph/ 10.0% (0.2 g/dm<sup>3</sup>) modified in the temperature range 200–800 °C



**Figure 9.** Photocatalytic decomposition of phenol (20 mg/dm<sup>3</sup>) and Cr(VI) (10 mg/dm<sup>3</sup>), in ratio 1:1, after 3 h of illumination with VIS light source over Ph/ 10.0% (0.2 g/dm<sup>3</sup>) modified in the temperature range 200–450 °C



**Figure 10.** Photocatalytic removal of phenol (20 mg/dm<sup>3</sup>) after 3 h of illumination with UV-VIS light source over Ph/ 10.0% 650 (0.2 g/dm<sup>3</sup>)

source can result in measurable benefits in the removal of pollutants and treatment of drinking water.

## LITERATURE CITED

- Al-Hajji, L.A., Ismail, A.A., Bumajdad, A., Alsaidi, M., Ahmed, S.A., Al-Hazza, A. & Ahmed, N. (2021). Photodegradation of powerful five estrogens collected from waste water treatment plant over visible-light-driven Au/TiO<sub>2</sub> photocatalyst. *Environ. Technol. Innov.* 24, 101958. DOI: 10.1016/j.eti.2021.101958.
- Jihyun, R. & Eunsung, K. (2016). Heterogeneous photocatalytic degradation of sulfamethoxazole in water using

a biochar-supported TiO<sub>2</sub> photocatalyst. *J. Environ. Manage.* 180, 94–101. DOI: 10.1016/j.jenvman.2016.05.016.

3. Rejek, M. & Grzechulska-Damszel, J. (2018). Degradation of sertraline in water by suspended and supported TiO<sub>2</sub>. *Pol. J. Chem. Technol.* 20(2), 107–112. DOI: 10.2478/pjct-2018-0030.

4. Rejek, M., Grzechulska-Damszel, J. & Schmidt, B. (2021). Synthesis, Characterization, and Evaluation of Degussa P25/Chitosan Composites for the Photocatalytic Removal of Sertraline and Acid Red 18 from Water. *J. Polym. Environ.* 29, 3660–3667. DOI: 10.1007/s10924-021-02138-x.

5. Ochiai, T. & Fujishima, A. (2012). Photoelectrochemical properties of TiO<sub>2</sub> photocatalyst and its applications for environmental purification. *J. Photochem. Photobiol. C.* 13, 247–262. DOI: 10.1016/j.jphotochemrev.2012.07.001.

6. Nilchi, A., Janitabar-Darzi, S. Mahjoub, A.R. & Rasouli-Garmarodi, S. (2010). New TiO<sub>2</sub>/SiO<sub>2</sub> nanocomposites – Phase transformations and photocatalytic studies. *Colloids Surf. A.* 361, 25–30. DOI: 10.1016/j.colsurfa.2010.03.006.

7. Czech, B. & Tyszczyk-Rotko, K. (2018). Visible-light-driven photocatalytic removal of acetaminophen from water using a novel MWCNT-TiO<sub>2</sub>-SiO<sub>2</sub> photocatalysts. *Sep. Purif. Technol.* 206(29), 343–355. DOI: 10.1016/j.seppur.2018.06.025.

8. Dahl, M., Liu, Y. & Yin, Y. (2014). Composite titanium dioxide nanomaterials. *Chem. Rev.* 114, 853–9889. DOI: 10.1021/cr400634p.

9. Shchelokova, E.A., Tyukavkina, V.V., Tsyryatyeva, A.V. & Kasikov, A.G. (2021). Synthesis and characterization of SiO<sub>2</sub>-TiO<sub>2</sub> nanoparticles and their effect on the strength of self-cleaning cement composites. *Constr. Build. Mater.* 283, 122769. DOI: 10.1016/j.conbuildmat.2021.122769.

10. Stokova, V., Gubareva, E., Ogurtsova, Y., Fediuk, R., Zhao, P., Vatin, N. & Vasilev, Y. (2021). Obtaining and properties of photocatalytic composite material of the SiO<sub>2</sub>-TiO<sub>2</sub> system based on various types of silica raw materials. *Nanomaterials* 11, 1–26. DOI: 10.3390/nano11040866.
11. Pakdel, E., Daoud, W.A., Seyedin, S., Wang, J., Razal, J.M., Sun, L. & Wang, X. (2018). Tunable photocatalytic selectivity of TiO<sub>2</sub>/SiO<sub>2</sub> nanocomposites: Effect of silica and isolation. *Colloids Surf. A* 552, 130–141. DOI: 10.1016/j.colsurfa.2018.04.070.
12. Udom, I., Myers, P.D., Ram, M.K., Hepp, A.F., Archibong, E., Stefanakos, E.K. & Goswami, D.Y. (2014). Optimization of photocatalytic degradation of phenol using simple photocatalytic reactor. *Am. J. Analyt. Chem.* 5, 743–750. DOI: 10.4236/ajac.2014.511083.
13. Trinh, D.T.T., Le, S.T.T., Channei, D., Khanitchaidecha, W. & Nakaruk, A. (2016). Investigation of intermediate compounds of phenol in photocatalysis process. *Int. J. Chem. Eng. Appl.* 7(4), 273–276. DOI: 10.18178/ijcea.2016.7.4.588.
14. Rashmi, A., Brundabana, N. & Kulamani, P. (2018). Cr(VI) remediation from aqueous environment through modified-TiO<sub>2</sub>-mediated photocatalytic reduction. *Beilstein J. Nanotechnol.* 9, 1448–1470. DOI: 10.3762/bjnano.9.137.
15. Brasili, E., Bavasso, I., Petruccelli, V., Vilardi, G., Valletta, A., Bosco, C.D., Gentili, A., Pasqua, G. & Di Palma, L. (2020). Remediation of hexavalent chromium contaminated water through zero-valent iron nanoparticles and effects on tomato plant growth performance. *Sci. Rep.* 10, 1–11. DOI: 10.1038/s41598-020-58639-7.
16. Suma, N., Prakash, B.S.J. & Iyngar, P. (2011). Oxidation of phenol, o-nitro phenol, o-chloro phenol and trichloroethylene present in water using surfactant immobilized manganate and impregnated metal cations. *Silicon* 3, 13–26. DOI: 10.1007/s12633-010-9063-6.
17. Madhuranthakam, C.M.R., Thomas, A., Akhter, Z., Fernandes, A.Q. & Elkamel, A. (2021). Removal of chromium(VI) from contaminated water using untreated mooring leaves as biosorbent. *Pollutants* 1, 51–64. DOI: 10.3390/pollutants1010005.
18. Nasiri, E.F., Kebria, D.Y. & Qaderi, F. (2018). An experimental study on the simultaneous phenol and chromium removal from water using titanium dioxide photocatalyst. *Civ. Eng. J.* 4(3), 585–593. DOI: 10.28991/cej-0309117.
19. WHO (1996). Guidelines for drinking-water quality. 2<sup>nd</sup> ed. Vol 2: Health criteria and other supporting information. Geneva: World Health Organization.
20. WHO (1994). Phenol: health and safety guide.
21. Lopes, P.R.M., Montagnolli, R.N., Bidoia, E.D. (2011). Analytical methods in photoelectrochemical treatment of phenol. *J. Braz. Chem. Soc.* 22(9), 1758–1764. DOI: 10.1590/S0103-50532011000900019.
22. Santos, E.J., Sabatke, M., Herrmann, A.B., Sturgeon, R.E. (2021). Evaluation of sample preparation procedures for determination of Cr(VI) in Cr<sub>2</sub>O<sub>3</sub> pigments by Vis spectrophotometry. *Braz. Arch. Biol. Technol.* 64, 1–12. DOI: 10.1590/1678-4324-75years-2021200455.
23. Borges, S.S., Korn, M. & Costa Lima, J.L.F. (2002). Chromium(III) determination with 1,5-diphenylcarbazide based on the oxidative effect of chlorine radicals generated from CCl<sub>4</sub> sonolysis in aqueous solution. *Anal. Sci.* 18, 1361–1366. DOI: 10.2116/analsci.18.1361. DOI: 10.2116/analsci.18.1361.
24. Kapridaki, C., Maravelaki, N-P. (2015). TiO<sub>2</sub>-SiO<sub>2</sub>-PDMS nanocomposites with self-cleaning properties for stone protection and consolidation. *Geol. Soc. Spec. Publ.* 416, 285–292. DOI: 10.1144/SP416.6.
25. Rowlette, P. & Wolden, C. (2009). Digital control of SiO<sub>2</sub>-TiO<sub>2</sub> mixed-metal oxides by pulsed PECVD. *ACS App. Mater. Interfaces*, 1(11), 2586–91. DOI: 10.1021/am900506y.
26. Cani, D., van der Waal, J.C. & Pescarmona, P.P. (2021). Highly-accessible, doped TiO<sub>2</sub> nanoparticles embedded at the surface of SiO<sub>2</sub> as photocatalysts for the degradation of pollutants under visible and UV radiation. *Appl. Catal. A.*, 621(5), 1–10. DOI: 10.1016/j.apcata.2021.118179.
27. Praveen, P., Viruthagiri, G., Mugundan, S. & Shanmugam, N. (2014). Structural, optical and morphological analyses of pristine titanium di-oxide nanoparticles – synthesized via sol-gel route. *Spectrochim. Acta A* 117, 622–629. DOI: 10.1016/j.saa.2013.09.037.
28. Chien-Lin, T., Yi-Kwan, C., Shuai-Han, W., Zih-Wei, P. & Jong-Liang, L. (2010). 2-Ethanolamine on TiO<sub>2</sub> investigated by in situ infrared spectroscopy. Adsorption, photochemistry and its interaction with CO<sub>2</sub>. *J. Phys. Chem. C* 114(27), 11835–43. DOI: 10.1021/jp9117166.
29. Wanghui, C., Chika, T., Razavi, K., Masayoshi, F., Takashi, S. (2016). SiO<sub>2</sub>/TiO<sub>2</sub> double-shell hollow particles: fabrication and UV-VIS spectrum characterization. *Adv. Powder Technol.* 27(3), 812–818. DOI: 10.1016/j.appt.2015.10.016.
30. Bo, Z., Dong, R., Jin, C. & Chen, Z. (2017). Facile synthesis of SiO<sub>2</sub>@TiO<sub>2</sub> crystallite photocatalysts with enhanced interaction level and high light absorption efficiency. *Nanotechnol. Environ. Eng.* 2(17), 1–11. DOI: 10.1007/s41204-017-0028-5.
31. Chen, W.H., Takai, C., Khosroshahi, H.R., Fuji, M. & Shirai, T. (2016). SiO<sub>2</sub>/TiO<sub>2</sub> double-shell hollow particles: fabrication and UV-Vis spectrum characterization. *Adv. Powdered Technol.* 27, 812–818. DOI: 10.1016/j.appt.2015.10.016.
32. Hendrix, Y., Lazaro, A., Yu, Q. & Brouwers, J. (2015). Titania-Silica Composites: A Review on the Photocatalytic Activity and Synthesis Methods. *World J. Eng.* 5, 161–177. DOI: 10.4236/wjnse.2015.54018.
33. Llano, B., Hidalgo, M.C., Rios, L.A. & Navio, J.A. (2014). Effect of the type of acid used in the synthesis of titania-silica mixed oxides on their photocatalytic properties. *Appl. Catal. B* 150–151, 389–395. DOI: 10.1016/j.apcatb.2013.12.039.
34. Sirimahachai, U., Ndiege, N., Chandrasekharan, R., Wongnawa, S. & Shannon, M.A. (2010). Nanosized TiO<sub>2</sub> particles decorated on SiO<sub>2</sub> spheres (TiO<sub>2</sub>/SiO<sub>2</sub>): synthesis and photocatalytic activities. *J. Sol-Gel Sci. Technol.* 56 (1), 53–60. DOI: 10.1007/s10971-010-2272-z.
35. Balachandran, K., Venkatesh, R., Sivaraj, R. & Rajiv, P. (2014). TiO<sub>2</sub> nanoparticles versus TiO<sub>2</sub>/SiO<sub>2</sub> nanocomposites: a comparative study of photo catalysis on acid red 88. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 128, 468–474. DOI: 10.1016/j.saa.2014.02.127.
36. Kibombo, H.S., Peng, R., Rasalingam, S. & Koodali, R.T. (2012). Versatility of heterogeneous photocatalysis: synthetic methodologies epitomizing the role of silica support in TiO<sub>2</sub> based mixed oxides. *Catal. Sci. Technol.* 2, 1737–1766. DOI: 10.1039/C2CY20247F.
37. Seriani, N., Pinilla, C., Cereda, S., De Vita, A. & Scandola, S. (2012). Titania-silica interfaces, *J. Phys. Chem. C* 116, 11062–11067. DOI: 10.1021/jp301584h.
38. Ren, J., Li, Z., Liu, S., Xing, Y. & Xie, K. (2008). Silica-titania mixed oxides: Si–O–Ti connectivity, coordination of titanium, and surface acidic properties. *Catal. Lett.* 124, 185–194. DOI: 10.1007/s10562-008-9500-y.
39. Gobara, H., El-Salamony, R., Mohamed, D., Mishrif, M., Moustafa, Y. & Gendy, T. (2014). Use of SiO<sub>2</sub>-TiO<sub>2</sub> nanocomposite as photocatalyst for the removal of trichlorophenol: a kinetic study and numerical evaluation, *Chem. Mater. Res.* 6, 63–81.
40. de Chiara, M.L.V., Pal S., Licciulli, A., Amodio, M.L. & Colelli, G. (2015). Photocatalytic degradation of ethylene on mesoporous TiO<sub>2</sub>/SiO<sub>2</sub> nanocomposites: effects on the ripening of mature green tomatoes. *Biosyst. Eng.* 132, 61–70. DOI: 10.1016/j.biosystemseng.2015.02.008.
41. Papadam, T., Xekoukoulotakis, N.P., Poullos, I. & Mantzavinos, D. (2007). Photocatalytic transformation of acid orange 20 and Cr(VI) in aqueous TiO<sub>2</sub> suspensions. *J. Photochem. Photobiol. A* 186, 308–315. DOI: 10.1016/j.jphotochem.2006.08.023.
42. Acharya, R., Naik, B. & Parida, K. (2018). Cr(VI) remediation from aqueous environment through modified-TiO<sub>2</sub>-mediated photocatalytic reduction. *Beilstein J. Nanotechnol.* 9, 1448–1470. DOI: 10.3762/bjnano.9.137.