

*Ph.D. Thesis*

# **Decontamination of environmental pollutants by UV- and visible light-active titanium dioxide-based photocatalysts**

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*Szeged  
2014*

## 1. INTRODUCTION AND AIMS OF THE RESEARCH

Heterogeneous photocatalysis is nowadays an intensively investigated research topic. The production and behavior of visible light-active titanium dioxide-based photocatalysts are investigated in many publications. These photocatalysts can be applied in economic water purification processes, in which solar irradiation is applied, and also for the preparation of indoor self-cleaning/air-cleaning surfaces. The immobilization of the photocatalysts is a crucial question in these processes. The aims of my research were to investigate essential aspects of the practical applicability of heterogeneous photocatalysis: the production of differently modified, visible light active, titanium dioxide based photocatalysts, possible immobilization methods, the detailed characterization of these photocatalysts, and their comparison with commercial photocatalysts.

For the determination of the particle sizes and the crystal phase distributions of the investigated titanium dioxides, X-ray diffraction (XRD) measurements were carried out. The dopant contents of the modified titanias were measured by X-ray photoelectron spectroscopy (XPS). The specific surface areas were determined by nitrogen adsorption. For the specification of the light absorption of the photocatalysts, diffuse reflectance spectroscopy (DRS) was applied. Pictures of the photocatalyst nanoparticles were taken by transmission electron microscopy (TEM) for determination of the size distributions and shapes of the nanoparticles. The photocatalytic activities were determined with different light sources (UV, VIS and solar irradiations) and different model pollutants (phenol and *Escherichia coli* bacteria).

Connections were explored between the photocatalytic efficiencies of different titanium dioxides and the photocatalytically produced reactive species by electron spin resonance (ESR) measurements.

The photocatalytic efficiencies of the investigated photocatalysts were characterized in outdoor photocatalytic experiments, in which solar irradiation was applied for the activation of the photocatalysts. The wavelength dependence of the photocatalytic efficiency of the promising titanium dioxides was investigated in details.

Attempts were made to develop different methods for the immobilization of the photocatalysts, and the produced photocatalytically active, durable surface was applied in a self-designed and home-made, fixed-bed, recirculating flow reactor. A further aim was to produce a pilot-scale photoreactor in which the developed photocatalytically active and durable surface was utilized. This photoreactor can provide the basis for a mobile, water purifier apparatus, which needs only solar light for operation.

## 2. METHODS

### 2.1. Determination of photocatalytic efficiencies

For the determination of photocatalytic efficiencies, home-made photoreactors were applied, which were equipped with UV- (6 of *Vilber-Lourmat T-6L UV-A* type, 6 W fluorescent tubes), or visible light-emitting (4 of *Düwi 25920/R7S* type, 24 W energy-saving, compact fluorescent tubes) light sources. In some cases, different colored 5050 SMD LED strips (14.4 W) were applied for the activation of the photocatalysts.

### 2.2. Determination of disinfection efficiencies

The photocatalytic efficiencies of the investigated photocatalysts were also determined by the inactivation of *Escherichia coli* K12 bacteria in some cases. The experiments were carried out in the photoreactor, which was equipped with visible light-emitting light sources. The numbers of the colony forming units of the treated waters were determined by counting the grown colonies (on agar-agar gels) from the taken samples.

### 2.3. Flow reactor equipped with immobilized photocatalysts

The produced photocatalytically active surfaces were applied in a self-designed, home-made, fixed-bed, recirculating flow reactor. For the activation of the immobilized photocatalysts, UV fluorescent tubes (*Lightech UVA*; 4×40 W) or visible light-emitting reflectors (*Jen CE-82*; 2×500 W) were applied.

### 2.4. Liquid chromatography

The concentrations of the model contaminants were determined by *high-performance liquid chromatography* (HPLC) with *Agilent 1100 series* equipment.

### 2.5. Electron spin resonance (ESR) measurements

For the investigation of the reactive species produced by the activated photocatalysts, ESR measurements were carried out with a *Bruker Biospin ESP300E* spectrometer. The reactive oxygen species scavengers applied were 2,2,6,6-tetramethyl-4-piperidinol (TMP-OH) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO). In some cases, heavy water and sodium azide were also used.

### 2.6. Determination of photon fluxes

The photon fluxes in the applied photoreactors were determined by *ferrioxalate actinometry*, which is one of the most commonly used light intensity determination methods in photochemistry.

In the case of the light sources, when  $\lambda > 550$  nm, the light intensity was determined with an *Apogee MQ-200* PPF (photosynthetic photon flux)-meter.

## 2.7. Characterization of the photocatalysts

Pictures used for the characterization of the shape, the size distribution and (in some cases) the size of the nanoparticles were taken with a *Philips CM 10* (100 kV) *transmission electron microscope*.

XRD measurements were carried out with a *Rigaku Miniflex II* diffractometer ( $\lambda_{\text{Cu K}\alpha} = 0.15406$  nm, 40 kV and 30 mA).

The *DR spectra* of the samples were determined with a *JASCO-V650* diode array spectrophotometer, equipped with an *ILV-724* DR module ( $\lambda = 220\text{-}800$  nm; resolution: 0.5 nm; scanning speed: 100 nm/min).

The *specific surface areas* of the photocatalysts were measured by nitrogen adsorption at 77 K, using a *Micromeritics* gas adsorption analyzer (*Gemini Type 2375*). The specific surface areas were calculated via the BET method.

For the investigation of the dopant contents and the surfaces of the photocatalysts, XPS was applied. For the measurements, a *Specs* spectrometer was used, equipped with a *Phoibos 150 MCD 9* electron analyzer. The X-ray photoelectron source was the  $\text{K}\alpha$  radiation of a Mg anode ( $h\nu = 1253.6$  eV).

The *FT-IR measurements* were made with a *Bruker Equinox 55* spectrometer with an integrated *FRA 106* Raman Module. Samples were ground with KBr and pressed into thin pellets (thickness  $\approx 0.3$  mm), and IR spectra were recorded with a spectral resolution of  $2\text{ cm}^{-1}$  in the  $400\text{-}4000\text{ cm}^{-1}$  region.

A *Horiba Jobin Yvon XGT-5000* X-ray fluorescent spectrometer, equipped with a Rh X-ray source, was used to measure the element contents of some photocatalyst samples. The records were made at 30 kV excitation voltage, 0.5 mA anode current and 1000 s measuring time.

### 3. NOVEL SCIENTIFIC RESULTS

#### **1. Gold and silver-containing TiO<sub>2</sub>/noble metal nanocomposites do not have higher photocatalytic efficiency than the basic photocatalyst in the cases of phenol and *E. coli* model pollutants [1, 2].**

XRF measurements proved that a TiO<sub>2</sub>/Au nanocomposite (containing 0.96 wt% gold) and a TiO<sub>2</sub>/Ag nanocomposite (containing 0.94 wt% silver) were successfully synthesized. In the case of phenol as model contaminant, and UV irradiation, the noble metal-containing titanium dioxide nanocomposites showed slightly lower photocatalytic performances than that of the basic titanium dioxide [1]. In the case of visible light irradiation, the TiO<sub>2</sub>/Ag nanocomposite displayed similar efficiency to that of the basic titanium dioxide, while the TiO<sub>2</sub>/Au nanocomposite did not exhibit significant photocatalytic activity [2]. In the case of *E. coli* as model contaminant (only visible light irradiation was investigated), the TiO<sub>2</sub>/Ag nanocomposite showed similar efficiency to that of the basic titanium dioxide, while the TiO<sub>2</sub>/Au nanocomposite did not exert any disinfection property [2]. On the basis of these results, it can be concluded that, for the decontamination of the investigated model contaminants, it is not appropriate to deposit the applied titanium dioxide with the investigated noble metals. It should be noted that with oxalic acid as model contaminant, and UV irradiation, the TiO<sub>2</sub>/noble metal nanocomposites give an excellent photocatalytic performance [1], as it was also described in 2003 by Szabó-Bárdos *et al.* [3].

#### **2. Under visible light irradiation, those photocatalysts exert photocatalytic disinfection property, which generates hydroxyl radical [2]. The photocatalytic disinfection efficiency of the prepared, iodine-doped titanium dioxide was not caused exclusively by photocatalytic effects [4].**

The results of photocatalytic experiments with phenol and *E. coli* as model contaminants, and the results of ESR measurements are presented in **Table 1**. It can be seen that the titanium dioxides that displayed disinfection properties under visible light irradiation, also generated hydroxyl radicals. Those titanium dioxides which did not generate hydroxyl radicals, did not exhibit a disinfection effect; however, in some cases these titanium dioxides demonstrated a very high photocatalytic performance in the case of phenol decomposition.

Photocatalysts	$r_{0,phenol}$ ( $\times 10^{-8}$ M/s)	t Sterilization (min)	ESR measurements		
			with TMP-OH as scavenger	with DMPO as scavenger	with DMPO as scavenger
			$^1O_2$	$O_2^{\bullet-}$	$OH^{\bullet}$
TiO <sub>2</sub> -VLP7000	29,9	-	High	-	-
TiO <sub>2</sub> -I	5,0	20	-	-	Yes
TiO <sub>2</sub> -AR	4,2	20	-	-	High
TiO <sub>2</sub> -P25-NS	3,7	-	Not measured		
TiO <sub>2</sub> -N	2,4	-	-	-	-
TiO <sub>2</sub> -Fe	1,7	-	Not measured		
TiO <sub>2</sub> -TP-S201	1,5	60	Not measured		
TiO <sub>2</sub> -P25	1,4	60	-	-	Yes
TiO <sub>2</sub> -P25-Ag	1,3	60	Not measured		
TiO <sub>2</sub> -P25-Au	0,4	-	Not measured		
TiO <sub>2</sub> -AA	0,4	-	Not measured		

**Table 1.**

*Photocatalytic performances and the results of the ESR measurements*

Iodine-doped titanium dioxide was synthesized by *Hong et al.* [5] by the dropwise addition of titanium(IV) butoxide into iodic acid solution ( $c = 0.15$  M). In my research a series of iodine-doped titanium dioxides were synthesized with different  $n_I/n_{Ti}$  ratios (0.0, 0.1, 0.5, 1.3 and 2.6) [4]. The photocatalyst with  $n_I/n_{Ti} = 0.5$  had the highest photocatalytic activity for both UV and VIS irradiation. XPS measurements proved that this titanium dioxide has 0.67 at% iodine on the surface of the particles, in the form of  $I^-$  (61%) and  $I^{+7}$  (39%). The generation of elemental iodine in the visible light-irradiated suspension, which can contribute to the high disinfection performance of this titanium dioxide was proved by spectrophotometry [4].

**3. Non-doped, rutile-phase titanium dioxide with small particle size was synthesized via the HCl-promoted hydrolysis of titanium(IV) butoxide followed by crystallization at low temperature (40 °C). The calcination of this titanium dioxide with increasing temperature (400-1000 °C) resulted in increasing particle size, increasing absorption of visible light and decreasing specific surface area [6]. The photocatalytic activity of the home-made rutile (calcinated at 900 °C) was much lower than that of Aldrich rutile, even though these titanium dioxides have very similar structural properties [6].**

For the preparation of rutile-phase titanium dioxide with small particle size, the preparation method described by *Tang et al.* [7] was modified. The HCl hydrolysis of titanium(IV) butoxide at a molar ratio  $Ti(OC_4H_9)_4:H^+:H_2O = 1:3:50$  resulted in pure rutile-phase titanium dioxide [6]. With the utilization of HCl, possible nitrogen incorporation can be excluded.

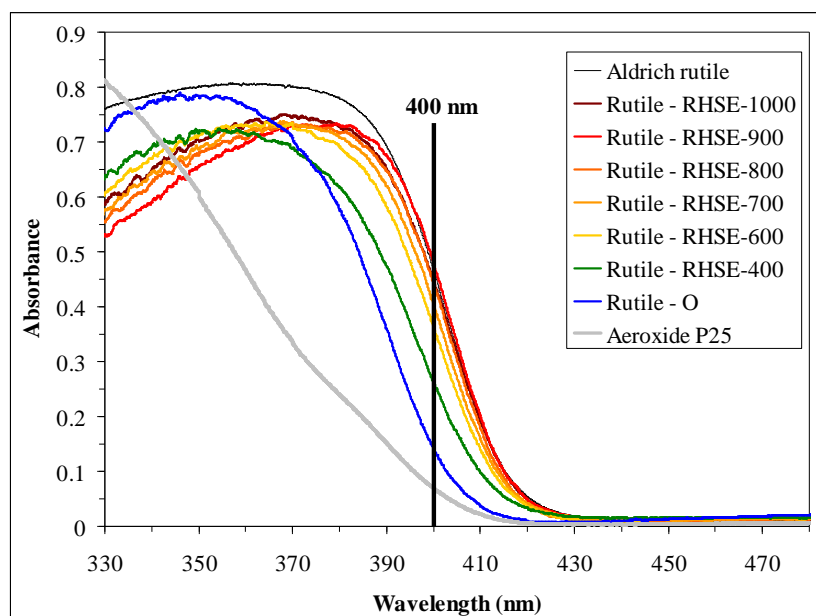
XRF and TEM measurements proved that rutile-phase titanium dioxides (**Table 2**) with increasing particle sizes can be prepared by calcination (with increasing temperature: 400-1000 °C) of home-made nano rutile (average particle size: 5.2 nm; specific surface area: 197 m<sup>2</sup>/g).

Photocatalyst	Phase distribution				Specific surface area (m <sup>2</sup> /g)	R <sub>0, phenol</sub> (10 <sup>-10</sup> M/s)	R <sub>0, phenol</sub> (10 <sup>-12</sup> mol/m <sup>2</sup> /s) (surface normalized)
	Anatase		Rutile				
	Content (wt%)	Particle size (nm)	Content (wt%)	Particle size (nm)			
Rutile - O	-	-	100	5,2	197	8,7	4,4
Rutile - RHSE-400	-	-	100	12,9	62	3,2	5,2
Rutile - RHSE-600	<1	-	>99	39,1	34	3,1	9,1
Rutile - RHSE-700	<1	-	>99	69,3	12	3,1	25,8
Rutile - RHSE-800	<1	-	>99	135 <sup>TEM</sup>	7	2,0	28,6
Rutile - RHSE-900	<1	-	>99	245 <sup>TEM</sup>	3	1,9	63,3
Rutile - RHSE-1000	<1	-	>99	290 <sup>TEM</sup>	1	1,8	175,0
Aldrich rutile	4	315 <sup>TEM</sup>	96	315 <sup>TEM</sup>	3	41,6	1386,7
Aeroxide P25	90	25,4	10	40,0	49	12,3	25,1

**Table 2.**

*Phase distributions, particle sizes, specific surface areas and photocatalytic efficiencies*

The visible light absorption of the synthesized photocatalysts increased in the sequence of increasing calcination temperature, as can be seen in **Figure 1**, which shows the red-shifted light absorption onset (measured by DRS) of the photocatalysts.



**Figure 1.**

*Light absorption of the investigated photocatalysts (DRS)*

The photocatalytic efficiency slightly decreased in the sequence of increasing calcination temperature because of the combined effect of the decreasing specific surface area and the decreasing visible light absorption. However, the surface-normalized photocatalytic efficiency decreased strongly in the same sequence.

The commercial (Aldrich) rutile has very similar structural properties to those of the self-prepared Rutile-RHSE-900 photocatalyst, but it has significantly higher photocatalytic efficiency. The only difference between the IR spectra of these photocatalysts is the appearance of a new band for Aldrich rutile at  $687\text{ cm}^{-1}$ , which indicates Ti-O-O-Ti groups [8, 9] on the surface of this titanium dioxide. These groups result in an oxygen-rich surface, which could be an electrophilic entity. This “peroxidized” surface can attract electrons, which can then be easily captured by molecular oxygen, resulting in a higher rate of radical generation.

**4. In the case of rutile-phase titanium dioxide, the presence of  $\text{Ti}^{3+}$  and low-binding-energy oxygen (which indicates defects) have no significant importance for the photocatalytic performance under visible light irradiation [6] (in contrast with the UV-irradiated, anatase-phase titanium dioxides [10]).**

In the Ti2P XPS spectrum of Aldrich rutile, only  $\text{Ti}^{4+}$  was detected, while the O1s spectrum revealed the usual components: oxide oxygen from titanium dioxide (530.3 eV), surface OH group oxygen (532 eV), and oxygen from  $\text{H}_2\text{O}$  (532.8 eV) [6]. In the case of the self-prepared Rutile-RHSE-900, the Ti2p XPS spectrum demonstrated a small amount of  $\text{Ti}^{3+}$  (13 at%: peaks at 457.3 eV and 461.9 eV), along with  $\text{Ti}^{4+}$  (87 at%: peaks at 459.1 eV and 464.8 eV). The O1s spectrum of this material indicated (besides the usual oxygen signals) a low-binding-energy oxygen species (at 528.8 eV, 12 at%). On the basis of recent publications [10, 11], this interesting form of oxygen indicates defects, or oxygen atoms adjacent to  $\text{Ti}^{3+}$ . In the case of anatase-phase titanium dioxides, the presence of this special species enhanced the photocatalytic activity [10] under UV irradiation (for phenol degradation). Nevertheless, Rutile-RHSE-900 (which contains  $\text{Ti}^{3+}$  and the described low-binding-energy oxygen species) has significantly lower photocatalytic efficiency than Aldrich rutile (under visible light irradiation) [6].

**5. The intensity of commercially available lamps in the wavelength range from 400 nm to 420 nm is crucial for the effective application of photocatalysts in indoor air/surface cleaning processes [2].**

Photocatalytic disinfection experiments (with *E. coli* bacteria) were also carried out with  $\text{K}_2\text{Cr}_2\text{O}_7$  (5 mM) light filtration, which resulted in reduction of the light intensity under 420 nm to

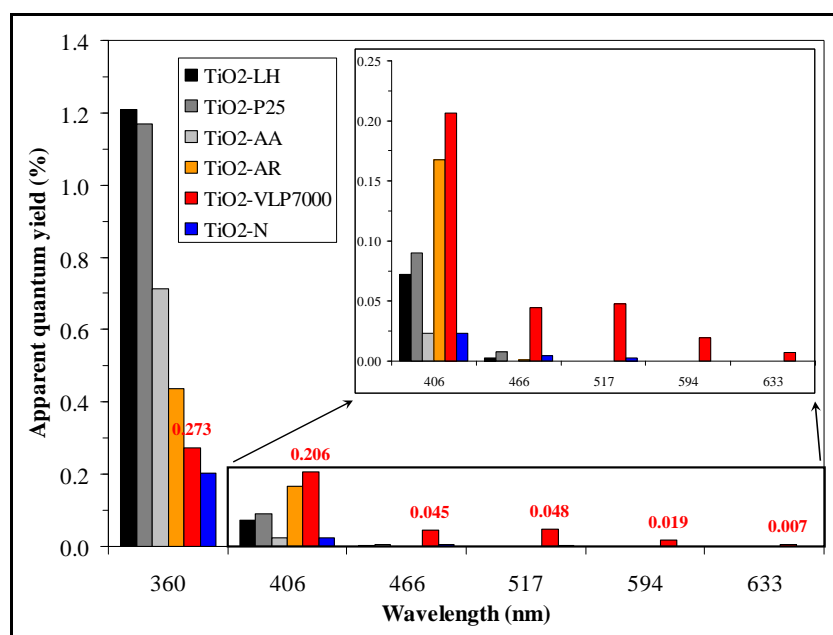


4% of that in the case of NaNO<sub>2</sub> (1 M) light filtration. With this reduced light intensity, three photocatalysts (which sterilized the treated water after 1 h of irradiation in the case of NaNO<sub>2</sub> light filtration) lost their disinfection effect, and in the case of two other titanium dioxides (which sterilized the treated water after 20 min of irradiation in the case of NaNO<sub>2</sub> light filtration) the disinfection efficiency was also significantly reduced with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> light filtration [2]. These results clearly showed that the light intensity (in the wavelength range between 400 and 420 nm) of the applied light sources is crucial for indoor air/surface cleaning processes.

**6. In solar light-based, photocatalytic water treatment processes, the utilization of non-doped, anatase-phase titanium dioxides should be preferred [12].**

The photocatalytic decomposition of phenol was additionally investigated in the case of solar irradiation, and it was concluded that the three non-doped, mainly anatase-phase titanium dioxides (which have low, if any activity under visible light irradiation), give significantly higher photocatalytic performances than those of highly visible light-active titanium dioxides.

For the explanation of these results, the wavelength dependence of the photocatalytic efficiency of the titanium dioxides was investigated (**Figure 2**).



**Figure 2.**

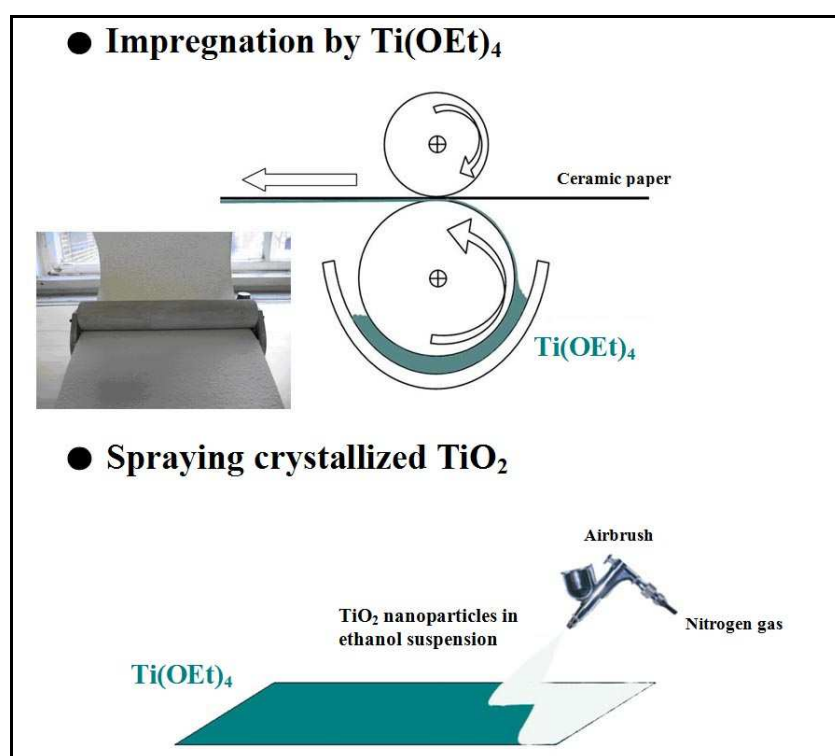
*Wavelength dependence of the photocatalytic efficiency of titanium dioxide samples*

In the case of UV irradiation, the non-doped, mainly anatase-phase titanium dioxides (TiO<sub>2</sub>-LH, Aeroxide P25 and Aldrich anatase) revealed significantly higher photocatalytic performances than those of doped and/or rutile-phase titanium dioxides. Under visible light irradiation, the doped or rutile-phase titanium dioxides displayed better performances. This is clearly seen in the case of

violet irradiation, but at longer wavelengths only the commercial (KRONOS) TiO<sub>2</sub>-VLP7000 photocatalyst exhibited significant photocatalytic efficiency. Although this latter photocatalyst can be activated by photons throughout the whole visible light range, the apparent quantum yields in most of the visible light range are two orders of magnitude smaller, than the apparent quantum yields of non-doped, mainly anatase-phase titanium dioxides under UV irradiation.

**7. Crystallized titanium dioxide nanoparticles can be immobilized into an amorphous titanium oxide-hydroxide layer, while the photocatalysts maintain their photocatalytic property. The photocatalytically active surface produced is not sensitive to UV irradiation or to the oxidative effect of activated titanium dioxide nanoparticles [13].**

A sheet of ceramic paper was perfused with ethanol, and was then impregnated with titanium(IV) ethoxide. After this step, precrystallized photocatalysts were immediately sprayed in suspension (ethanol) form with a handheld airbrush onto the surface (**Figure 3**).



**Figure 3.**

*Schematic figure of the method of immobilization of titanium dioxide nanoparticles*

The impregnated ceramic sheets were dried in air at room temperature for 24 h. During this step, the titanium(IV) ethoxide was hydrolyzed by the air humidity, and the amorphous Ti(IV) oxide-hydroxide formed fixed the photocatalytically active particles onto the surface. After the drying step, the impregnated ceramic sheets were washed with distilled water to eliminate non-

immobilized nanoparticles, and were finally cleaned from possible organic surface contaminants by irradiation with UV-A light for 24 h.

The photocatalytic performance of the prepared photocatalytically active surface was well reproduced. The differences in photocatalytic efficiency of three different immobilized titanium dioxide-coated ceramic papers were < 1%. The durability was confirmed in photocatalytic experiments in which the rate of phenol decomposition remained constant throughout five 2-h cycles on the same titanium dioxide-coated ceramic paper. Outdoor solar experiments were carried out to demonstrate that organic contaminants can be decomposed by solar light with the immobilized titanium dioxide, and we produced a pilot-scale photoreactor which requires only solar light for the purification of contaminated water.

## REFERENCES

- [1] G. Veréb, Z. Ambrus, Z. Pap, Á. Kmetykó, A. Dombi, V. Danciu, A. Cheesman, K. Mogyorósi, *Applied Catalysis A: General* 417-418 (2012) 26-36.
- [2] G. Veréb, L. Manczinger, G. Bozsó, A. Sienkiewicz, L. Forró, K. Mogyorósi, K. Hernádi, A. Dombi, *Appl. Catal.*, B 129 (2013) 566-574.
- [3] E. Szabo-Bardos, H. Czili, A. Horvath, *J Photoch Photobio A* 154 (2003) 195-201.
- [4] G. Veréb, L. Manczinger, A. Oszkó, A. Sienkiewicz, L. Forró, K. Mogyorósi, A. Dombi, K. Hernádi, *Appl. Catal.*, B 129 (2013) 194-201.
- [5] X. Hong, Z. Wang, W. Cai, F. Lu, J. Zhang, Y. Yang, N. Ma, Y. Liu, *Chem Mater* 17 (2005) 1548-1552.
- [6] G. Veréb, T. Gyulavári, Z. Pap, L. Baia, T. Radu, K. Mogyorósi, A. Dombi, K. Hernádi, Under preparation.
- [7] Z. Tang, J. Zhang, Z. Cheng, Z. Zhang, *Mater. Chem. Phys.* 77 (2002) 314-317.
- [8] V. Etacheri, M. K. Seery, S. J. Hinder, S. C. Pillai, *Adv. Funct. Mater.* 21 (2011) 3744-3752.
- [9] M. R. Ayers, A. J. Hunt, *Mater. Lett.* 34 (1998) 290-293.
- [10] Z. Pap, E. Karacsonyi, Z. Cegléd, A. Dombi, V. Danciu, I. C. Popescu, L. Baia, A. Oszko, K. Mogyorosi, *Appl. Catal.*, B 111 (2012) 595-604.
- [11] Z. Pap, V. Danciu, Z. Cegléd, Á. Kukovecz, A. Oszkó, A. Dombi, K. Mogyorósi, *Appl. Catal.*, B 101 (2011) 461-470.
- [12] G. Veréb, O. Virág, T. Alapi, K. Mogyorósi, A. Dombi, K. Hernádi, Under preparation.
- [13] G. Veréb, Z. Ambrus, Z. Pap, K. Mogyorósi, A. Dombi, K. Hernádi, Reaction kinetics, mechanisms and catalysis, Published online: 10 June 2014, DOI 10.1007/s11144-014-0734-y.

## SCIENTIFIC ACTIVITY (MTMT identifier: 10034558)

<b>Published papers:</b>	7 (Cumulative impact factor: 19,315)
Papers related to the Thesis:	4 (Cumulative impact factor: 16,164)
<b>References:</b>	45 (independent: 39)
<b>Conferences:</b>	35
as speaker:	21
as co-author:	14
<b>Book chapters:</b>	7

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### Published papers, related to the Thesis:

**G. Veréb, Z. Ambrus, Zs. Pap, Á. Kmetykó, A. Dombi, V. Danciu, A. Cheesman, K. Mogyorósi**  
*Comparative study on UV and visible light sensitive bare and doped titanium dioxide photocatalysts for the decomposition of environmental pollutants in water*  
Applied Catalysis A: General, Volumes 417–418, 29 February 2012, Pages 26-36  
**Reference: 10 (9)      Impact factor: 3,410**

**G. Veréb, L. Manczinger, A. Oszkó, A. Sienkiewicz, L. Forró, A. Dombi, K. Hernádi, K. Mogyorósi**  
*Highly efficient bacteria inactivation and phenol degradation by visible light irradiated iodine doped TiO<sub>2</sub>*  
Applied Catalysis B: Environmental, Volume 129, 17 January 2013, Pages 194-201  
**Reference: 6 (6)      Impact factor: 5.825**

**G. Veréb, L. Manczinger, G. Bozsó, A. Sienkiewicz, L. Forró, A. Dombi, K. Mogyorósi, K. Hernádi**  
*Comparison of the photocatalytic efficiencies of bare and doped rutile and anatase TiO<sub>2</sub> photocatalysts under visible light for phenol degradation and E.coli inactivation*  
Applied Catalysis B: Environmental, Volume 129, 17 January 2013, Pages 566-574  
**Reference: 8 (8)      Impact factor: 5.825**

**G. Veréb, Z. Ambrus, Zs. Pap, K. Mogyorósi, A. Dombi, K. Hernádi**  
*Immobilization of crystallized photocatalysts on ceramic paper by titanium(IV) ethoxide and photocatalytic decomposition of phenol*  
Reaction Kinetics, Mechanisms and Catalysis, Published online: 10 June 2014  
**Reference: 0      Impact factor: 1,104**

### Papers related to the Thesis (under preparation):

**G. Veréb, T. Gyulavári, Zs. Pap, L. Baia, T. Radu, K. Mogyorósi, A. Dombi, K. Hernádi**  
*Photocatalytic water treatment under visible light irradiation with particle size-tuned rutile titanium dioxides*  
Under preparation

**G. Veréb, O. Virág, T. Alapi, K. Mogyorósi, A. Dombi, K. Hernádi**  
*Wavelength dependent photocatalytic performance of UV and visible light active TiO<sub>2</sub> photocatalysts*  
Under preparation

### Published papers not related to the Thesis:

**K. Mogyorósi, A. Kmetykó, N. Czirbus, G. Vereb, A. Dombi, P. Sipos**  
*Comparison of the substrate dependent performance of Pt-, Au- and Ag-doped TiO<sub>2</sub> photocatalysts in H<sub>2</sub>-production and in decomposition of various organics*  
Reaction Kinetics and Catalysis Letters, Volume 98, 03 September 2009, Pages 215-225  
**Reference: 16 (12)      Impact factor: 0,557**

**E. Szabó, K. Vajda, G. Veréb, A. Dombi, K. Mogyorósi, I. Ábrahám, M. Májer**  
*Removal of organic pollutants in model water and thermal wastewater using clay minerals*  
Journal of Environmental Science and Health: Part A, Volume 46, 2011, Pages 1346-1356

**Reference: 5 (4)      Impact factor: 1,190**

**Zs. Pap, K. Mogyorósi, G. Veréb, A. Dombi, K. Hernádi, V. Danciu, L. Baia**  
*Commercial and home-made nitrogen modified titanias. A short reflection about the advantageous/disadvantageous properties of nitrogen doping in the frame of their applicability*  
Journal of Molecular Structure, Volume 1073, September 2014, Pages 157-163

**Reference: 0      Impact factor: 1,404**

### **Conferences (as speaker):**

#### **SZTE-TTIK-Környezettudományi Diákköri Konferencia**

Szeged, 2008. február 4.

**Veréb Gábor**, Mogyorósi Károly, Dombi András

*Kerámiapapír hordozón rögzített titán-dioxid fotokatalizátorok alkalmazása víztisztítási eljárásokban*

#### **XI. Országos Felsőoktatási Környezettudományi Diákkonferencia**

Nyíregyháza, 2008. 03. 25-26.

**Veréb Gábor**, Dr. Dombi András, Dr. Mogyorósi Károly

*Kerámiapapír hordozón rögzített titán-dioxid fotokatalizátorok alkalmazása víztisztítási eljárásokban*

#### **SZTE-TTIK-Tudományos Diákköri Konferencia**

Szeged, 2008. november 28.

**Veréb Gábor**, Dr. Dombi András, Dr. Mogyorósi Károly

*Kerámiapapíron rögzített titán-dioxid fotokatalizátor alkalmazása víztisztításra*

#### **XXIX. Országos Tudományos Diákköri Konferencia**

Debrecen, 2009. 04. 6-8.

**Veréb Gábor**, Dr. Dombi András, Dr. Mogyorósi Károly

*Kerámiapapíron rögzített titán-dioxid fotokatalizátor alkalmazása víztisztításra*

**First Prize**

#### **16<sup>th</sup> Symposium on Analytical and Environmental Problems**

Szeged, 2009. 09. 28.

**Veréb Gábor**, Ambrus Zoltán, Dombi András, Mogyorósi Károly

*Különböző titán-dioxid alapú fotokatalizátorok összehasonlítása áramlásos reaktorokban*

**Conference Proceedings: ISBN 978-963-482-975-1**

#### **IX. Környezetvédelmi és Analitikai Technológiai Konferencia**

Sopron, 2009. 10. 7-9

**Veréb Gábor**, Ambrus Zoltán, Pap Zsolt, Kmetykó Ákos, Dombi András, Mogyorósi Károly

*Vízkezelés kerámiapapíron rögzített titán-dioxid fotokatalizátorokkal*

**Conference Proceedings: ISBN 978-963-9970-00-7**

#### **A Magyar Tudomány Hete konferenciasorozat**

Dunaújváros, 2009. november 9-13.

**Veréb Gábor**, Ambrus Zoltán, Gácsi Attila, Dombi András, Mogyorósi Károly

*Szerves szennyező anyagok fotokatalitikus ártalmatlanítása áramlásos reaktorban*

**Conference Proceedings: ISSN 1586-8567**

#### **XII. Országos Felsőoktatási Környezettudományi Diákkonferencia**

Sopron, 2010. 04. 6-7.

**Veréb Gábor**, Dr. Dombi András, Dr. Mogyorósi Károly

*Kerámiapapíron rögzített titán-dioxid fotokatalizátor alkalmazása víztisztításra*

**Second Prize**

### **SP3 - Third International Conference on Semiconductor Photochemistry**

Glasgow, Scotland, 2010. 04. 12-16.

**G. Veréb**, L. Manczinger, A. Gácsi, Zs. Pap, Á. Kmetykó, A. Dombi and K. Mogyorósi

*Water purification and disinfection on UV and visible light irradiated doped titanium dioxide photocatalysts immobilized on ceramic papers (POSTER PRESENTATION)*

### **XXXIII. Kémiai Előadói Napok**

Szeged, 2010. 10. 25-27.

**Veréb Gábor**, Dr. Dombi András, Dr. Mogyorósi Károly

*Uv- és látható fényre aktív fotokatalizátorok alkalmazása víztisztításra szuszpenzióban és felületen rögzítve*

**Conference Proceedings: ISBN 978-963-315-020-7**

### **Természettudományi Doktori Iskolák Tudományos Fóruma**

Szeged, 2010. 11. 10.

**Veréb Gábor**, Dr. Dombi András, Dr. Mogyorósi Károly

*Szennyezők bontása napsugárzással gerjesztett fotokatalizátorral*

### **CEST 2011 - 12th International Conference on Environmental Science and Technology**

Rhodes, Greece; 2011. 09. 08.

**Gábor Veréb**, László Manczinger, András Dombi, Károly Mogyorósi

*Comparative study of disinfection and phenol degradation on different bare and doped titanium dioxide photocatalysts using visible light irradiation*

**Conference Proceedings: ISSN: 1106-5516; ISBN 978-960-7475-49-7**

### **X. Környezetvédelmi Analitikai és Technológiai Konferencia**

Sümege, 2011. 10. 5-7.

**Veréb Gábor**, Manczinger László, Dombi András, Mogyorósi Károly

*Fertőtlenítés és szennyezőanyag lebontás látható fényrel gerjesztett fotokatalizátorokkal*

**Conference Proceedings: ISBN 978-963-9970-17-5**

### **IPA-HU-SRB Workshop**

Szeged, 2011. december 1-2.

**Gábor Veréb**, László Manczinger, Andrzej Sienkiewicz, László Forró, András Dombi, Károly Mogyorósi, Monica Ilios, Dimitrie Botau, Florica Manea

*Decomposition of organic compounds and disinfection processes by heterogeneous photocatalysis*

### **I. Környezetkémiai Szimpózium**

Mátraháza, 2012. október 11-12.

**Veréb Gábor**, Pap Zsolt, Réti Balázs Vajda Krisztina, Mogyorósi Károly, Hernádi Klára, Dombi András

*Fotokatalizátorok hatékonyságának növelése, gyakorlati alkalmazások*

### **SIWAN5 - 5th Szeged International Workshop on Advances in Nanoscience**

Szeged, Hungary, 2012. október 24-27.

**G. Veréb**, L. Manczinger, A. Sienkiewicz, L. Forró, A. Dombi, K. Hernádi, K. Mogyorósi

*Purification of phenol and E.coli contaminated water by visible light activated titanias (POSTER PRESENTATION)*

**Conference Proceedings: ISBN 978-963-05-9305-2**

### **SP4 - 4th International Conference on Semiconductor Photochemistry**

Prága, Csehország, 2013. június 23-27.

**Gábor Veréb**, László Manczinger, Tamás Gyulavári, Károly Mogyorósi, András Dombi, Klára Hernádi

*Photocatalytic water treatment by various rutile phase TiO<sub>2</sub> photocatalysts under visible light irradiation (POSTER PRESENTATION)*

**Conference Proceedings: ISBN 978-80-7080-854-2**

**PAOT-2 - The 2nd International Conference on Photocatalytic and Advanced Oxidation Technologies**  
for Treatment of Water, Air, Soil and Surfaces  
Gdansk, Lengyelország, 2013. szeptember 9-12.  
**Gábor Veréb**, Orsolya Virág, Károly Mogyorósi, András Dombi, Klára Hernádi  
*Wavelength dependence of phenol degradation on different titanium dioxide based photocatalysts (POSTER PRESENTATION)*

**TÁMOP-4.2.2.A-11/1/KONV-2012-0047 Workshop**

Szeged, 2013. október 03.

**Veréb Gábor**, Alapi Tünde, Simon Gergő

*Reaktortervezés és reaktorépítés*

**KEN-2013 – XXXVI. Kémiai Előadói Napok**

Szeged, 2013. október 28-30.

**Veréb Gábor**, Virág Orsolya, Mogyorósi Károly, Dombi András, Hernádi Klára

*Napfény hasznosítása a víztisztításban UV és látható fényre aktív fotokatalizátorokkal*

**Conference Proceedings: ISBN 978-963-315-145-7**

**TÁMOP-4.2.2.A-11/1/KONV-2012-0047 Workshop**

Szeged, 2014. május 15.

**Gábor Veréb**, Alapi Tünde, Simon Gergő

*Reaktortervezés és reaktorépítés*

**Conferences (as co-author):**

**REUSE09 - 7th IWA World Congress on Water Reclamation and Reuse**

Brisbane, Australia, 21-25 September, 2009.

J. Szanyi, T. Medgyes, B. Kóbor, **G. Veréb**, Zs. Pap, K. Mogyorósi, A. Dombi, B. Kovács

*Maintaining Sustainability and Minimizing Impact: Developing the Know-how of Injecting Thermal Water into Porous Reservoirs and Removing Phenol from Aqueous Solution by Photocatalytic Processes Using Artificial UV-visible Light Sources and Solar Irradiation (POSTER PRESENTATION)*

**IX. Környezetvédelmi és Analitikai Technológiai Konferencia**

Sopron, 2009. 10. 7-9

Mogyorósi Károly, Kmetykó Ákos, **Veréb Gábor**, Sipos Pál, Dombi András

*Hidrogénfejlesztés és szerves vegyületek lebontása nemesfémekkel módosított TiO<sub>2</sub> fotokatalizátorokon*

**Conference Proceedings: ISBN 978-963-9970-00-7**

**A Magyar Tudomány Hete konferenciasorozat**

Dunaújváros, 2009. november 9-13.

Szabó Emese, **Veréb Gábor**, Kmetykó Ákos, Mogyorósi Károly, Dombi András

*Szerves szennyezők eltávolítása ipari és termálvizekből adszorpciós módszerekkel*

**Conference Proceedings: ISSN 1586-8567**

**SP3 - Third International Conference on Semiconductor Photochemistry**

12-16. April, Glasgow, Scotland, 2010

K. Mogyorósi, **G. Veréb**, Z. Ambrus, Zs. Pap, Á. Kmetykó, A. Dombi

*Comparative study on different synthesis pathways for obtaining UV and visible light active bare and doped titanium dioxide photocatalysts*

**ISEAC 36**

Rome, Italy, 5-9. October 2010

I. Ábrahám, A. Dombi, M. Májer, K. Mogyorósi, E. Szabó, K. Vajda, **G. Veréb**

*Removal and analysis of organic pollutants in industrial wastewater and thermal water (POSTER PRESENTATION)*

### **ISEAC 36**

Rome, Italy, 5-9. October 2010

I. Ábrahám, A. Dombi, M. Májer, K. Mogyorósi, K. Gajda-Schranz, E. Szabó, K. Vajda, **G. Veréb**

*Removal of organic pollutants from thermal water by adsorption-coagulation methods and advanced oxidation processes (POSTER PRESENTATION)*

### **Tudomány Hete a Dunaújvárosi Főiskolán,**

Dunaújváros, 2010. november 6-12.

Gácsi Attila, **Veréb Gábor**, Pap Zsolt, Dombi András, Mogyorósi Károly

*Titán-dioxid alapú fotokatalizátorokkal kezelt kerámiapapír alkalmazása gázfázisú acetaldehid ártalmatlanítására*

### **XXX. Országos Tudományos Diákköri Konferencia**

Pécs, 2011. 04. 27-29.

Gácsi Attila, **Veréb Gábor**, Mogyorósi Károly

*Gázfázisú illékony szerves vegyületek lebontása UV és látható fényvel megvilágított, rögzített titán-dioxid alapú fotokatalizátorokon*

### **International Conference on Photocatalytic and Advanced Oxidation Technologies for the Treatment of Water, Air, Solid and Surfaces**

Gdansk, Poland, 4-8. July 2011

**Gábor Veréb**, László Manczinger, András Dombi, Károly Mogyorósi

*Photocatalytic performance of different bare, metal and non-metal doped and noble metal deposited photocatalysts for phenol degradation and bacteria deactivation under visible light irradiation*

### **X. Környezetvédelmi Analitikai és Technológiai Konferencia**

Sümege, 2011. 10. 5-7.

Dombi András, Kmetykó Ákos, Mogyorósi Károly, Pap Zsolt, Vajda Krisztina, **Veréb Gábor**

*Titán-dioxid nanorészecskék fotokatalitikus alkalmazása vízkezelési eljárásokban*

**Conference Proceedings: ISBN 978-963-9970-17-5**

### **IPA-HU-SRB Workshop**

Szeged, 2011. december 1-2.

**Gábor Veréb**, Zsolt Pap, Ákos Kmetykó, Krisztina Vajda, Klára Hernádi, András Dombi, Károly Mogyorósi, Monica Ilios, Dimitrie Botau, Florica Manea

*Different photocatalytic approaches for water purification with suspended and fixed titanium dioxide particles*

### **IPA-HU-SRB Workshop**

Szeged, 2011. december 1-2.

Biljana Abramović, Tünde Alapi, Eszter Arany, Sándor Beszédes, Luka Bjelica, Milena Dalmacija, Vesna Despotović, András Dombi, János Farkas, Krisztina Gajda-Schranz, Valéria Guzsány, Erzsébet Illés, Szabolcs Kertész, Sonja Kler, Ákos Kmetykó, László Kredics, Zsuzsanna László, László Manczinger, Patrick Mazellier, Károly Mogyorósi, Dejan Orčić, Zsolt Pap, Ljiljana Rajić, Emese Szabó, Rita Szabó, Daniela Šojić, Csaba Vágvölgyi, Krisztina Vajda, **Gábor Veréb**

*Optimization of Cost Effective and Environmentally Friendly Procedures for Treatment of Regional Water Resources - HU-SRB IPA Cross-border Co-operation Programme*

### **I. Környezetkémiai Szimpózium**

Mátraháza, 2012. október 11-12.

Dombi András, Arany Eszter, Illés Erzsébet, Farkas János, Karácsonyi Éva, Kmetykó Ákos, Pap Zsolt, Szabó Emese, Vajda Krisztina, **Veréb Gábor**, Alapi Tünde, Schranz Krisztina, Hernádi Klára, Takács Erzsébet, Wojnárovits László

*Nagyhatékonyságú oxidációs eljárások biológiai és kémiai szennyezők eltávolítására*



## **SIWAN5 - 5th Szeged International Workshop on Advances in Nanoscience**

Szeged, Hungary, 2012. october 24-27.

Zs. Pap, Z. Ambrus, **G. Veréb**, Á. Kmetykó, A. Dombi, K. Hernádi, K. Mogyorósi

*Different synthesis approaches improving the photocatalytic performance of titanium dioxide photocatalyst nanoparticles for water purification and hydrogen production*

**Conference Proceedings: ISBN 978-963-05-9305-2**

### **Book chapters:**

#### **1. Veréb Gábor**

***Kerámiapíron rögzített titan-dioxid fotokatalizátor alkalmazása víztisztításra***

Vizek szerves szennyezőinek eltávolítása nagyhatékonyságú oxidációs módszerekkel, Removal of Organic Contaminants of Waters by Advanced Oxidation Processes

InnoGeo Kft., Szeged, 2010. Pages: 55-102. ISBN 978-963-06-9621-0

#### **2. Szabó Emese, Veréb Gábor, Kmetykó Ákos, Mogyorósi Károly, Dombi András:**

***Szerves szennyezők eltávolítása ipari és termálvizekből adszorpciós módszerekkel***

Vizek szerves szennyezőinek eltávolítása nagyhatékonyságú oxidációs módszerekkel, Removal of Organic Contaminants of Waters by Advanced Oxidation Processes

InnoGeo Kft., Szeged, 2010. Pages: 103-115. ISBN 978-963-06-9621-0

#### **3. Gábor Veréb, Zoltán Ambrus, Attila Gácsi, András Dombi, Károly Mogyorósi:**

***Removal of organic pollutants in water by photocatalysis in flow reactor***

Vizek szerves szennyezőinek eltávolítása nagyhatékonyságú oxidációs módszerekkel Removal of Organic Contaminants of Waters by Advanced Oxidation Processes

InnoGeo Kft., Szeged, 2010. Pages: 161-171. ISBN 978-963-06-9621-0

#### **4. Klara Hernadi, Andras Dombi, Gabor Vereb, Zsolt Pap, Akos Kmetyko,**

Hossam El Nazer, Károly Mogyorósi

***Photocatalytic Water Treatment with TiO<sub>2</sub> Nanoparticle***

NANOTECHNOLOGY FOR WATER PURIFICATION

BrownWalker Press, Boca Raton, Florida, USA, 2012. Pages: 125-178 ISBN-01: 1-33216-916-1

ISBN-31: 879-1-33216-916-0

#### **5. Emese Szabó, Krisztina Vajda, Gábor Veréb, András Dombi, Károly Mogyorósi, Imre Ábrahám, Marcell Májér**

***Removal of organic pollutants in model water and thermal wastewater using clay minerals***

Sustainable Use of Geothermal Energy: Research into Injection and Water Treatment

InnoGeo Kft., Szeged, 2012. Pages: 123-148. ISBN 978-963-89689-0-6

#### **6. G. Veréb, Z. Ambrus, Zs. Pap, Á. Kmetykó, A. Dombi, V. Danciu, A. Cheesman, K. Mogyorósi**

***Comparative study on UV and visible light sensitive bare and doped titanium dioxide photocatalysts for the decomposition of environmental pollutants in water***

Sustainable Use of Geothermal Energy: Research into Injection and Water Treatment

InnoGeo Kft., Szeged, 2012. Pages: 149-178. ISBN 978-963-89689-0-6

#### **7. Gábor Veréb, László Manczinger, Károly Mogyorósi, András Dombi, Klára Hernádi**

***Comparative study of disinfection and phenol degradation on different bare and doped titanium dioxide photocatalysts using visible light irradiation***

Sustainable Use of Geothermal Energy: Research into Injection and Water Treatment

InnoGeo Kft., Szeged, 2012. Pages: 191-220. ISBN 978-963-89689-0-6