Influence of rapid heat treatment on the photocatalytic activity of alkaline earth metal titanates

Doctoral (Ph.D.) Theses

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1. Introduction

Water pollution has become a pressing global concern, fueled by the widespread release of harmful contaminants into aquatic environments. Among these, the uncontrolled use of pesticides, pharmaceuticals, and other persistent organic pollutants poses a particularly serious threat to both environmental and public health. Conventional treatment methods often fall short in completely eliminating such compounds, especially at trace concentrations.

In response, researchers have increasingly turned to advanced oxidation processes (AOPs), which are capable of degrading recalcitrant pollutants through the generation of highly reactive species, such as hydroxyl radicals. Among the various AOPs, photocatalysis stands out as a particularly promising approach. It harnesses light energy to activate specific materials that drive oxidative reactions, ultimately breaking down pollutants into harmless byproducts. However, the success of photocatalysis largely depends on the choice of photocatalyst. With countless options available, the challenge lies in choosing a material that meets three essential requirements: efficiency, cost-effectiveness, and stability. Alkaline earth metal titanates are promising photocatalysts with a special crystal structure known as perovskite. They are chemically stable, relatively inexpensive, and environmentally friendly, making them good candidates for photocatalytic applications. Despite their potential, these materials have not been studied as much as others like titanium dioxide (TiO_2). Like other photocatalysts, titanates have some limitations. Due to their relatively wide band gaps, these materials are less responsive to visible light, limiting their efficiency under natural sunlight. This makes it essential to carefully design and optimize their synthesis to achieve desirable structural and functional properties.

This thesis focuses on the synthesis, characterization, and photocatalytic evaluation of alkaline earth metal titanates for the degradation of pollutants, such as phenol, chlorophenol, and oxalic acid, under UV light. It also explores their ability to disinfect water by inactivating harmful microorganisms. By optimizing synthesis conditions and investigating structure-activity relationships, this work aims to contribute to the development of efficient and sustainable photocatalysts for environmental applications.

2. Objectives

The primary goal of the research carried out during the PhD period was to **synthesize alkaline earth metal (Sr, Ca, Ba) titanates using various synthesis methods** and evaluate their performance in the degradation of pollutants. Based on the results of these measurements, I aim to reveal **the causal relationship between the morpho-structural properties** and **photocatalytic activity.**

This thesis explores and clarifies the topics outlined above, highlighting the novelty of employing the **rapid heating** as an innovative approach for calcination, and presents the following primary and additional objectives:

1. Employ sol-gel-derived materials and apply rapid heat treatment.
2. In-depth characterization of photocatalysts to study morpho-structural properties:
   i. Crystalline composition and primary crystallite size
   ii. Optical properties of the obtained materials
   iii. Surface species and chemical composition
3. Assess photocatalytic efficiency under UV light using various model pollutants with different functional groups:
   i. Hydroxyl group (-OH), associated with phenol
   ii. Halide group (-Cl), associated with chlorophenol
   iii. Carboxyl group (-COOH), associated with oxalic acid
4. Establish the relationship between morpho-structural properties and photocatalytic activity.
5. Evaluate the stability of the photocatalysts by conducting structural characterization after the degradation experiments.
6. Perform reusability tests to assess the recyclability of the photocatalysts by repeating the degradation process.
7. Conduct immobilization tests using phenol to assess the viability of the materials above laboratory scale.
8. Investigate the antimicrobial effects of hydrothermally synthesized samples.

3. Experimental methods

3.1. Synthesis of titanate samples

Strontium (STO), calcium (CTO), and barium (BTO) titanates were synthesized via sol-gel methods. Although hydrothermal and coprecipitation approaches were also explored in preliminary studies, the sol-gel route was ultimately chosen because the resulting catalysts proved to be overall the most effective. In this method, precursors were combined at a 1:1 molar ratio and vigorously stirred to form a homogeneous sol, which was then dried in a Memmert UNB500 oven to obtain a gel. The resulting xerogels were calcined using the rapid heating short exposure (RHSE) method [1].

All sol-gel samples were prepared following the same approach: components were mixed to achieve a stoichiometric Sr/Ca/Ba:Ti molar ratio of 1:1, followed by drying to form a gel and calcination of the xerogels to obtain crystalline materials. Calcination was conducted via the RHSE method with a constant air flow of 0.5 L/min. The temperature was increased in three stages (60, 20, and 10 °C/min) with the heating rate gradually reduced near the target temperature to prevent overheating. Once the target was reached, the temperature was held for 5 minutes. The calcination temperature for each catalyst was optimized based on the results of thermogravimetric (TG) analysis, ensuring the complete decomposition of residual organics and the formation of pure crystalline phases.

X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and diffuse reflectance spectroscopy (DRS) were used for the characterization of the materials.

3.2. Photocatalytic activity evaluation

Oxidation tests were conducted in a thermostated (25 °C) glass reactor illuminated by six UV-A lamps (λ_{max} = 365 nm). Pollutants included phenol (0.1 mM), chlorophenol (0.1 mM), and oxalic acid (5-10 mM). Suspensions were stirred in the dark to reach adsorption-desorption equilibrium before illumination. Degradation was monitored via HPLC using methanol/water or H_2SO_4 eluents, depending on the analyte.

CO_2 reduction by BTO was evaluated in a UV-illuminated quartz microreactor using a CO_2:H_2 (1:2) gas mixture. Catalysts were immobilized on a glass cylinder and pretreated with Ar, O_2, and H_2. Products were analyzed using gas chromatography with TCD and FID detectors.

Disinfection studies were carried out using hydrothermally synthesized titanates against *E. coli* and *B. licheniformis*, prepared following Bodor et al. [2]. Photocatalyst suspensions in 0.9 wt% NaCl were irradiated in a glass reactor surrounded by UV lamps. Colony counts were determined post-incubation. Hydroxyl radical generation was assessed via coumarin degradation to 7-hydroxycoumarin [3].

3.3. Catalyst immobilization

The top-performing STO sample was immobilized on ceramic paper using titanium isopropoxide as an adhesive. After UV curing, STO suspension was spray-coated and re-dried. The immobilized photocatalyst was tested for phenol degradation under UV light (λ_{max} = 355 nm, 40 W) with HPLC monitoring.

4. Perspective Novel Findings

T1: The samples prepared via the RHSE method showed comparable photocatalytic activity relative to conventional calcination, while being more cost-efficient.

The RHSE method was successfully integrated into the sol-gel synthesis of alkaline earth metal titanates (STO, CTO, and BTO), replacing conventional calcination. This substitution resulted in comparable or even superior photocatalytic activity for the prepared titanate catalysts (the differences were within ~10% in degradation yields in all cases). From an economic standpoint, the RHSE method offers a more cost-efficient alternative by reducing power consumption across all synthesis types (STO: 1742 to 1120 kW, CTO: 1920 to 1260 kW, and BTO: 1870 to 1320 kW) along with a shorter treatment time of 5 minutes. These advantages make rapid calcination a plausible method not only in terms of photocatalytic activity, but also a financially and environmentally attractive alternative.

T2: The catalysts prepared via the RHSE method exhibited high stability against non-acidic functional group-containing pollutants.

The alkaline earth metal titanate catalysts demonstrated overall good structural stability during the photocatalytic degradation processes. When used for the degradation of phenol and chlorophenol (compounds containing hydroxyl and halide groups, respectively), only minor structural changes were observed: primarily, the formation of alkaline earth metal carbonates. These changes did not significantly affect photocatalytic performance. However, in the case of

oxalic acid (containing carboxylic groups), structural changes were observed (Ca-oxalate for CTO, and $Sr(OH)_2$ for STO). Importantly, the stability of RHSE-synthesized STO was further investigated by comparing their activity in suspended and immobilized setups: the photocatalytic efficiency observed in suspension was largely maintained (the yield observed was only lower by ~2.5%) when the catalysts were immobilized on a ceramic paper.

T3: The RHSE synthesis yielded titanium dioxide species alongside $CaTiO_3$. The amount and type of titania were dependent on the calcination temperature.

During the sol-gel synthesis of calcium titanate, 10-20 wt.% of titanium dioxide phases were also formed. The type of titania present on the surface of the CTO depended on the applied calcination temperature, with anatase and brookite phases forming at lower temperatures, and rutile at higher temperatures. The presence of anatase and brookite titania phases significantly enhanced the overall photocatalytic activity of the composite material compared to the commercial CTO reference, primarily attributed to improved charge separation facilitated by these heterojunctions. In contrast, higher calcination temperatures reduced the specific surface area and favored rutile formation, resulting in lower photocatalytic activity.

T4: Barium titanate is more active in photocatalytic CO_2 reduction than in the photocatalytic oxidation of different pollutants.

BTO samples prepared using the RHSE method exhibited relatively limited activity in the oxidative degradation of pollutants such as phenol, chlorophenol, and oxalic acid. In contrast, they demonstrated remarkable performance in photocatalytic CO_2 reduction. All exhibited CO selectivity greater than 99.95%, with conversion rates strongly correlating with specific surface area. A larger surface area provides more active sites for photocatalytic reactions, thereby enhancing interactions with reactants and promoting higher CO formation rates. This contrast underscores the potential of BTO materials for selective CO_2 conversion to CO.

T5: Environmental Safety of Alkaline Earth Metal Titanates

Toxicological assessment of alkaline earth metal titanates revealed that their presence either does not enhance or outright decreases their inactivation efficiency against Gram-negative *E. coli* and Gram-positive *B. licheniformis* bacteria under UV light. Based on PL results, disinfection efficiency correlated with hydroxyl radical generation. It was ascertained that

alkaline earth metal titanates are unlikely to cause harm to microorganisms in surface or groundwater bodies without undergoing further changes.

5. Scientific Activities

Hungarian Scientific Bibliography (MTMT) identifier: 10081650

Research Articles – related to the dissertation

1. **Mahsa Abedi**, Ákos Szamosvölgyi, András Sápi, Ákos Kukovecz, Zoltán Kónya, Tamás Gyulavári, and Zsolt Pap

Influence of rapid heat treatment on the photocatalytic activity and stability of strontium titanates against a broad range of pollutants." *Catalysts* 13, no. 2 (2023): 219.

https://doi.org/10.3390/catal13020219

SJR indicator: Q2 **Impact factor**$_{2024}$: 4.0

Independent citations: 4

2. **Mahsa Abedi**, Zsejke-Réka Tóth, Milica Todea, Áron Ágoston, Ákos Kukovecz, Zoltán Kónya, Zsolt Pap, and Tamás Gyulavári.

Influence of rapid heat treatment on the photocatalytic activity and stability of calcium titanates against a broad range of pollutants." *Heliyon* 10, no. 14 (2024).

https://doi.org/10.1016/j.heliyon.2024.e34938

SJR indicator: Q1 **Impact factor**$_{2023}$: 3.4

Independent citations: 1

3. **Mahsa Abedi**, Haythem S. Basheer, Laura Lakatos, Ákos Kukovecz, Zoltán Kónya, Tamás Gyulavári, and Zsolt Pap.

Influence of Rapid Heat Treatment on the Photocatalytic Activity and Stability of Barium Titanates Against a Broad Range of Pollutants." *Molecules* 29, no. 22 (2024): 5350.

https://doi.org/10.3390/molecules29225350

SJR indicator: Q1 **Impact factor**$_{2024}$: 4.6

Independent citations: 0

4. Tamás Gyulavári, **Mahsa Abedi**, Sarolta Tóth, Áron Ágoston, Gábor Veréb, Attila Bodor, Ákos Kukovecz, Zoltán Kónya, Katalin Perei, Zsolt Pap.

Intrinsic and photocatalytic disinfection properties of $CaTiO_3$, $SrTiO_3$, and $BaTiO_3$ alkaline earth metal titanate perovskites." *Ceramics International*, ().

https://doi.org/10.1016/j.ceramint.2025.07.286

SJR indicator: Q1 **Impact factor**$_{2025}$: 5.6

Independent citations: 0

Research Articles – unrelated to dissertation

1. Tamás Gyulavári, Daniella Dusnoki, Viktória Márta, Mohit Yadav, **Mahsa Abedi**, András Sápi, Ákos Kukovecz, Zoltán Kónya, Zsolt Pap.

Dependence of photocatalytic activity on the morphology of strontium titanates." *Catalysts*, *12*(5), 523.

https://doi.org/10.3390/catal12050523

SJR indicator: Q2 **Impact factor**$_{2024}$**:** 4

Independent citations: 8

1. Áron Ágoston, Eszter Kanász, Lilla Balassa, Mahsa Abedi, Karolina Solymos, Csaba Bús, Ágota Deák, Ákos Kukovecz, Zoltán Kónya, Zsolt Pap.

Effect of silver deposition on the material characteristics and photocatalytic activity of barium titanates. " *Heliyon*, (**Submitted**).

SJR indicator: Q1 **Impact factor**$_{2023}$**:** 3.4

Independent citations: 0

Summary

Σ publications: 5	Of which related to Dissertation: 4
Σ independent citations: 13	Of which related to Dissertation: 5
Σ impact factor: 16	Of which related to Dissertation: 12

Conference Participation – related to dissertation

1. **Abedi, M**., A., Kukovecz, Á., Kónya, Z., Gyulavári, T., & Pap, Z.; Characterization and evaluation of photocatalytic activity of strontium titanate photocatalyst prepared by different synthesis methods; YOURHETCAT; Szeged (Hungary); 2022. (**Oral presentation**)

2. **Abedi, M**., Gyulavári, T., & Pap, Z.; Characterization and evaluation of photocatalytic activity of strontium titanate photocatalyst prepared by different synthesis methods; Chemistry conference; Oradea (Romania); 2022. (**Poster presentation**)

3. **Abedi, M**., Szamosvölgyi, Á., Sápi, A., Kukovecz, Á., Kónya, Z., Gyulavári, T., Pap, Z.; Influence of rapid heat treatment on the photocatalytic activity and stability of strontium titanates against a broad range of pollutants; 8th International Conference on Semiconductor Photochemistry (SP 8); Strasburg (France). (**Poster presentation**)

4. **Abedi, M**., A., Kukovecz, Á., Kónya, Z., Gyulavári, T., & Pap, Z.; Influence of rapid heat treatment on the photocatalytic activity and stability of calcium titanates against a broad range of pollutants, 8th International Conference on Semiconductor Photochemistry (SP 8); Strasburg (France). (**Poster presentation**)

5. **Abedi, M**., Gyulavári, T., Pap, Z.; Influence of rapid heat treatment on the photocatalytic activity and stability of strontium titanates against a broad range of pollutants; 28th International Symposium on Analytical and Environmental Problems; Szeged (Hungary); 2023. (**Oral presentation**)

6. Gyulavári, T., **Abedi, M**., Tóth, Z., Todea, M., Kukovecz, Á., Kónya, Z., Pap, Z.; Influence of rapid heat treatment on the photocatalytic activity and stability of calcium titanates against a broad range of pollutants; Belfast (Ireland); 2024. (**Poster presentation**)

7. **Abedi, M**., Basheer, H. S., A., Kukovecz, Á., Kónya, Z., Gyulavári, T., & Pap, Z.; Influence of rapid heat treatment on the photocatalytic activity of barium titanates; Cluj-Napoca (Romania); 2024. (**Poster presentation**)

<u>Conference Participation – unrelated to dissertation</u>

1. **Abedi, M.**, Márta, V., Yadav, M., Kedves, Z., Gyulavári, T., Sápi, A., Kónya, Z., Kukovecz, Á., Pap, Z.; Strontium Titanate-Based Nanostructures for CO_2 Conversion: A Step Towards a Carbon-free Environment; Turin (Italy); 2022. (**Poster presentation**)

6. References

1. Pap, Z., et al., *Dynamic changes on the surface during the calcination of rapid heat treated TiO_2 photocatalysts.* Applied Catalysis B: Environmental, 2012. **111**: p. 595-604.
2. Bodor, A., et al., *Exploitation of extracellular organic matter from Micrococcus luteus to enhance ex situ bioremediation of soils polluted with used lubricants.* Journal of Hazardous Materials, 2021. **417**: p. 125996.
3. Czili, H. and A. Horváth, *Applicability of coumarin for detecting and measuring hydroxyl radicals generated by photoexcitation of TiO_2 nanoparticles.* Applied Catalysis B: Environmental, 2008. **81**(3-4): p. 295-302.

DECLARATION

I declare that the contribution of Mahsa Shah Abedi was significant in the publication: "Intrinsic and photocatalytic disinfection properties of $CaTiO_3$, $SrTiO_3$, and $BaTiO_3$ alkaline earth metal titanate perovskites" which appeared in the Ceramics International journal in July 2025. The results reported in this article and in the Ph.D. dissertation of Mahsa Shah Abedi have not been used to acquire any PhD degree previously and will not be used in the future for the purpose of acquiring an academic degree or title.

Szeged, November 24, 2025

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