The behavior and environmental impact of metal oxide nanoparticles in soil solutions

Ph.D. theses

Karolina Solymos

Supervisor:

Dr. Zsolt Pap

co-supervisor:

Prof. Dr. Andrea Farsang †

Doctoral School of Geosciences

Faculty of Science and Informatics

University of Szeged

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1. PROBLEM STATEMENT AND RESEARCH OBJECTIVES

Nowadays, nanomaterials (NMs) can be found everywhere, including industrial applications and daily facilities. Their wide range of applications means that they can be released into the environment, where their main receiving medium is soil. In soil, however, they can undergo several changes that can affect their mobility, dispersibility, and bioavailability, which can be strongly influenced by the soil type and chemistry. To the best of our knowledge, existing studies mainly focus on the relationships between the soil solid phase and nanomaterials (e.g., mobility, dispersion). In contrast, there is little information available from studies with soil solutions. The latter is often referred as the "living" medium between soil pores, where chemical reactions and various dissolution and dispersion processes take place. The properties of soil solutions, such as ionic content, pH, and organic matter content, can all influence how nanomaterials aggregate, what their surface chemistry will be, and how this could potentially affect their applicability (e.g. photocatalytic activity). The previously mentioned aspects are currently poorly understood, although this raises important questions both for the optimization of nanoparticles (NPs) formation and for soil health.

Therefore, the possible changes of ZnO and TiO_2 NPs in three artificial soil solutions with different properties were investigated. The soil solutions were prepared from three different soil types, namely, Regosol, Chernozem, and Solonetz. The two different crystal forms of TiO_2, anatase and rutile, and one of the most popular catalysts used in industry, Evonik Aeroxide P25 (containing 89 wt.% anatase and 11 wt.% rutile), and commercially available ZnO with a wurtzite structure were used as test materials.

Hence, the main objectives of the dissertation can be summarized in the following points:

I. Since both TiO_2 and ZnO NMs are intensively used as photocatalysts, our first and one of our main goals was to investigate the photocatalytic activity of TiO_2 nanoparticles in different chemical conditions via artificial soil solutions.

II. A further aim was to investigate the possible surface and structural change of the nanoparticles after interaction with different soil solutions. This was achieved by following parameters such as the surface charge of the materials, the adsorption of different organic substances and ions on the surface, the band gap, the crystal structure, and the primary crystallite size and morphology.

III. Determination of the stability and aggregation behavior of nanoparticles in soil solutions with different chemistry and composition based on the above-mentioned parameters.

IV. Investigation of the time-dependent changes of Aldrich Anatase, Aldrich Rutile, and Evonik Aeroxide P25 during interaction with short- and long-term in various soil solutions.

2. EXPERIMENTAL SECTION

Soil sampling involved collecting 10 Regosol, 10 Chernozem, and 10 Solonetz topsoil samples from three different locations. MQ water was used for soil solution preparation, and the solid-to-solution ratio was 1:2.5. After 17 hours of rotation, the mixtures were centrifuged at 4400 rpm for 10 minutes and filtered through a 13-μm pore-size paper filter in the case of Solonetz samplesIn the case of Regosol and Chernozem soil extracts, it was a 0.45-μm pore-size cellulose nitrate membrane. Subsequently, the following parameters were determined in the soil solutions: pH, ionic strength, total organic carbon, chemical oxygen demand, major elements (Na, K, Ca, Mg, Al, Fe, Mn and S), trace elements (Cu, Zn, Ni, Co and As), and various ions such as NO_3^-, NO_2^-, PO_4^{3-}, F^-, Cl^-, SO_4^{2-}, HCO_3^-, and NH_4^+.

Each soil solution was prepared by combining the 10 samples we took from their (Chernozem, Regosol, or Solonetz) corresponding sites. As a result, we obtained a single homogeneous representative sample for each soil solution type. Stock suspensions containing the ZnO and TiO_2 concentration in the soil solutions was adjusted to 1 $g \cdot L^{-1}$ (in the case of *Chapter 5*, we also applied a concentration of 500 $mg \cdot L^{-1}$; however, we did not observe significant changes in the properties of the NMs compared to those at 1 $g \cdot L^{-1}$). Following the addition of the NM-containing stock suspension to the soil solution, the resulting mixture was stirred using a magnetic stirrer, which was protected from light. After different times of interaction (*Chapter 2 and 4*—4 hours; *Chapter 3*—1, 4, and 24 hours; *Chapter 5*—4 and 168 hours) between the NMs and the soil solutions, the suspensions were centrifuged at 3700 rpm for 10 minutes.

X-ray diffraction (XRD) patterns were recorded using a Rigaku Miniflex II diffractometer with a Cu-Kα radiation ($\lambda = 1.5406$ Å). Data points were taken in the $2\theta = 20$–$80°$ range at a scan speed of 1 min^{-1}. Primary crystallite sizes were calculated using the Scherrer equation.

The morphology was examined using a Hitachi S-4700 Type II scanning electron microscope (SEM) after coating the samples with gold NPs (<10 nm).

Surface changes were investigated using an infrared spectroscopy (Bruker Equinox 55), which were recorded with a resolution of 2 cm^{-1}.

Diffuse reflectance spectra (DRS) were recorded with a JASCO-V650 spectrophotometer using $BaSO_4$ as a reference, and the bandgap energy was calculated based on the Kubelka-Munk method.

Data for the X-ray photoelectron spectroscopy (XPS) was collected using a Specs XPS equipment, which was outfitted with an Phoibos 150 hemispherical electron analyzer and an XR50 dual anode X-ray source. 150 W was the operating power of the Al Kα source.

The ζ potential of the NPs was assessed using a Horiba SZ-100 Nanoparticle Analyzer, within a carbon electrode cell. The ζ potential values were obtained employing the Smoluchowski model, with a measured dispersion concentration of 0.001 w/v%.

The hydrodynamic diameter (HD) of ZnO NPs was determined via dynamic light scattering (DLS) using the same analyzer and concentration.

A suspension of ZnO and TiO_2 NPs at a concentration of 1 $g \cdot L^{-1}$ was combined with a phenol solution with an initial concentration (c_0) of 0.1 mM. Subsequently, the suspension was transferred into a double-walled glass vessel with a volume of 100 mL, which was surrounded by six fluorescent UV tubes (λ_{max} = 365 nm; Vilber-Lourmat T-6L UV-A, 6W). To achieve adsorption–desorption equilibrium, the suspension was stirred in the dark for 10 minutes before switching on the lamps. The concentration of phenol was monitored using high pressure liquid chromatography (HPLC), (Merck Hitachi L-4250) The flow rate was set to 0.7 $cm^3 \cdot min^{-1}$, and the detection wavelength was 210 nm. The eluent used was a 70:30 (v/v) mixture of methanol and water.

In the case of *Chapter 2*, photocurrent measurements were conducted using a Metrohm Autolab PGSTAT302n potentiostat/galvanostat in an aqueous medium with a classical three-electrode system. Photocurrents were measured following the linear sweep voltammetry (LSV) method within the potential range of –1 V to 0.3 V at a sweeping rate of 2 $mV \cdot s^{-1}$.

3. DISSERTATION OUTLINE

Chapters 2-6 of the dissertation contain articles already published in peer-reviewed journals. The various chapters outlined and discussed below summarize the objectives, main conclusions, and results of the study.

Chapter 1. This chapter begins with a presentation of the literature background of the dissertation, highlighting the current relevance of the research. It also includes a description of the methodological approach and a detailed description of the chosen methods and sample areas. The chapter also sets out the objectives and main questions of the dissertation and summarizes the content of the following chapters.

Chapter 2. This chapter investigates the behavior of the two crystal phases of TiO_2, anatase and rutile. An artificial soil solution of the Chernozem type, considered one of the world's best agricultural soils, was used as the experimental medium. In this section, the surface chemical, structural, and photocatalytic properties of the materials after interaction with the soil solution were analyzed. The results showed that although the activity of the TiO_2 adsorbed on the surface by various organic substances and ions was degraded compared to the reference samples, they recovered their original efficiency after three hours.

Chapter 3. In this chapter, one of the most widely used and efficient commercially available photocatalysts, Evonik Aeroxide P25 (89% anatase: 11% rutile), was investigated after interaction with various artificial soil solutions. The main objective of this section was to investigate the effect of different chemical compositions of soil solutions (one being Chernozem with a slightly alkaline pH, low organic matter and ionic content, and the other Regosol with an acidic pH, high organic matter, and low ionic content) on the behavior of P25. The results show that the nature of the medium has a strong influence on photocatalytic activity and aggregation of the material and, consequently, on its environmental stability.

Chapter 4. This study investigates the stability and photocatalytic activity of commercially available ZnO nanoparticles with wurtzite crystal structure. The experiments were carried out in three artificial soil solutions with different chemical compositions: the above-mentioned Chernozem and Regosol soil types and the highly alkaline Solonetz solution with high organic matter and ion content. The results show that the chemical properties of the medium are a very influential factor in the case of ZnO behavior. In acidic media (Regosol), the hydrodynamic diameter of the material decreased, while in alkaline media (Chernozem, Solonetz), it remained unchanged compared to the reference sample. However, the photocatalytic activity was also strongly influenced by the nature of the soil, but for all three soil-solution interactions, ZnO completely degraded the model contaminant (total degradation achieved after 270 min).

Chapter 5. This section discusses how the anatase and rutile nanoparticles change their properties during short (4 hours) and longer (168 hours) interaction times in two different (Regosol and Solonetz) soil solutions. The results showed that during shorter times, surface chemistry changes (adsorbed organic matter and ions) occurred, which negatively affected the catalytic activity. However, longer-term Solonetz (high ionic and highly alkaline chemistry) interaction induced a size decrease in the case of rutile, which could also enhance mobility in soil and bioavailability.

Chapter 6. The chapter summarizes the main results of the dissertation and discusses its applicability, limitations, and conclusions.

4. NEW SCIENTIFIC RESULTS

T.1. Acidic (Regosol) and alkaline environments (Solonetz, Chernozem) decreases the primary crystallite size of ZnO nanoparticles.

The hydrodynamic diameter of the ZnO nanoparticles decreased in acidic environments but remained unchanged in alkaline conditions (using distilled water as a reference). In acidic environments, Zn^{2+} leaching was detected, whereas in alkaline environments, this was not the case, suggesting that an amorphous hydroxyl layer formed in alkaline conditions. This can be attributed to the formation of water-soluble Zn^{2+} complexes on the surface of the nanoparticles. Subsequently, the formation of an amorphous layer on the surface of the nanoparticles occurs due to the constant equilibrium between the surface of the particles and a liquid medium. If an amorphous layer is present on the surface of ZnO, it could not be detected by XRD; however, its presence can still be inferred from the hydrodynamic diameter results. This suggests that the amorphous layer stabilizes the particles in the alkaline medium, as its presence in alkaline conditions can prevent further dissolution or aggregation of the particles.

T.2. After interaction with soil solutions (Chernozem, Regosol, Solonetz), the photocatalytic activity of both TiO_2 and ZnO nanoparticles decreased compared to the pure reference samples. However, their overall efficiency was retained.

This phenomenon can be attributed to organic materials adsorbed on the surface of the nanoparticles from the soil solutions. According to infrared spectroscopy results, these organic materials contain functional groups such as –COOH, –OH, and C=O, as well as C=C bonds. Additionally, based on the XPS results, various anions and cations (e.g., Na^{+}, K^{+}, Ca^{2+}, Al^{3+}, Fe^{3+}, S^{2-}, and Cl^{-}) also contributed to this effect. These species occupy the active sites on the surface of TiO_2 and ZnO, thereby reducing their photocatalytic activity. However, all types of materials were able to completely degrade the phenol model pollutant within 270 minutes at the latest. This demonstrates that during photocatalytic degradation, the materials can continuously "self-clean" their surfaces.

T.3. The type of soil and the chemical composition of the soil solution impacts differently the photocatalytic activity of TiO_2 and ZnO nanoparticles.
Photocatalytic degradation results consistently showed that the lowest activity was observed after interaction with the Solonetz soil solution, which showed a high ionic strength (~12 mmol·L^{-1}), while being strongly alkaline (pH ~9.4). This was followed by the Regosol soil solution, which instead showed a low ionic strength but a high organic matter content (TOC ~91 mg·L^{-1}) and an acidic pH (~4.9). The activity was preserved in the Chernozem soil solution, which was slightly alkaline (pH ~7.7), and possessed a low ionic strength (~4.3 mmol·L^{-1}), while containing a moderate amount of organic matter (TOC ~43 mg·L^{-1}). These results suggest that high ionic strength negatively affects photocatalytic activity, possibly by altering the surface charge of the catalyst, while organic matter may also play a role by occupying active sites on the catalyst surface.

T.4. After interaction with soil solutions, no significant changes were observed in the semiconductive properties and bulk structural properties of ZnO and TiO_2 nanoparticles. Although the color of the materials changed after exposure to soil solutions, this did not alter their light absorption properties or band gap energy. This suggests that the observed color change is due to surface interactions rather than to a fundamental change in optoelectronic structure and semiconductor properties. Furthermore, the structure of the bulk phase remained unchanged, as confirmed by the XRD results. Compared to the pure reference samples, the diffractograms of the soil-treated materials indicated that their structural integrity was preserved. This stability suggests that the nanoparticles can retain their photocatalytic properties even under extreme environmental conditions, potentially leading to long-term environmental exposure and associated risks.

T.5. TiO_2 nanoparticles retained their photocatalytic activity even after prolonged interaction (1 week) with soil solutions.

Both Aldrich Anatase and Aldrich Rutile suffered a decrease in photocatalytic activity after longer-term interaction with soil solutions. However, despite this decrease, the activity did not completely disappear, indicating that TiO_2 NMs are still functional in the environment in the longer term. This longer-term stability also indicates that over time they can persist to influence the chemical composition of the topsoil.

5. APPLICABILITY OF THE SCIENTIFIC RESULTS

The results of this thesis show that ZnO and TiO_2 NMs remain stable and retain their semiconducting properties even in matrices with differentiated chemistry (e.g., Solonetz soil solution, which is highly alkaline and of high ionic strength). This information is essential for the longer-term applicability of these materials. However, it also means that they are persistent, potentially accumulating in soil and groundwater.

The results show that the investigated NMs can adsorb various organic substances and ions from the soil onto their surface and still remain photocatalytically active. Consequently, they may also alter the natural chemical composition of the soil, which may have a direct negative impact on the composition of the soil micro- and macrofauna. In addition, through surface adsorption, foreign ions and toxic heavy metals can be transported with NMs into deeper soil layers or even into groundwater. As the production of these compounds has been growing rapidly in recent years, their concentration in the environment is likely to be higher in the future. It is therefore imperative that wastewater treatment plants and waste operators are adequately prepared to deal with nanoparticulate materials. Furthermore, regular environmental monitoring of nanomaterials that have been shown to have adverse effects on living organisms would be necessary. The key to this is the establishment of an appropriate regulatory framework, the precise development and standardization of tests for this purpose, and the inclusion of permissible concentrations in regulations.

The use of nanotechnology and NPs will make our everyday lives much easier, but sustainability and environmental protection must be a priority. This is the reason for the crucial importance of studying the behavior of new types of substances in the environment and their effects on living organisms.

6. LIMITATIONS, RECOMMENDATIONS AND FUTURE RESEARCH

While this thesis presents an innovative approach to understanding the behavior of commercial nanomaterials in the environment, it is also essential to acknowledge its limitations.

First and foremost, it is important to note that since the experiments were conducted under laboratory conditions, they do not always reflect real environmental conditions. Factors such as soil texture and continuous changes caused by weather conditions, including temperature fluctuations, are not fully represented in this study.

Secondly, although the selection of soil types was guided by the aim of achieving chemical diversity, incorporating a broader range of soil types would allow for a more comprehensive understanding of how nanomaterials behave under natural conditions.

Thirdly, while this study examined longer-term interactions (one week) in the case of TiO_2, it did not extend to observations over several months or years.

To obtain a more comprehensive picture of the environmental behavior of nanomaterials, future research should aim to address these limitations. A holistic approach is crucial in studies of this nature, requiring consideration of multiple external environmental factors (e.g., weather conditions and duration), as well as the properties of both the investigated material and the surrounding medium (e.g., in the case of soil, its structure and chemical composition, which may influence mobility). Additionally, microbiological activity and composition should also be taken into account.

In the future, it may also be worthwhile to investigate other commercially available (e.g., CdS, CuO, Ag) and intensively researched (e.g., $CsPbX_3$) nanoparticles, incorporating the extended considerations mentioned above.

7. ÖSSZEFOGLALÁS

A nanoanyagok széleskörű ipari és hétköznapi használata miatt egyre nagyobb mennyiségben jutnak a környezetbe, ahol fő befogadó közegük a talaj. A talajoldat kulcsszerepet játszik ezen anyagok viselkedésének szabályozásában, mivel itt zajlanak azok a kémiai reakciók és átalakulások, amelyek befolyásolják mobilitásukat, stabilitásukat és fotokatalitikus aktivitásukat.

Jelen kutatás célja a cink-oxid (ZnO) és titán-dioxid (TiO_2) nanorészecskék viselkedésének vizsgálata volt három különböző kémiai összetételű mesterséges talajoldatban (Regosol, Chernozem és Solonetz). A kísérletek során a TiO_2 két kristályformáját (anatáz és rutil), valamint az iparban széles körben alkalmazott Evonik Aeroxide P25 katalizátort és wurtzit szerkezetű ZnO-t használtuk.

Az eredmények alapján a nanorészecskék szerkezeti és felületi tulajdonságai jelentős mértékben függtek a talajoldatok összetételétől. A ZnO nanorészecskék primer krisztallit mérete savas közegben csökkent, míg lúgos közegben egy amorf hidroxidréteg képződött a felszínükön, amely stabilizálta őket és megakadályozta további oldódásukat.

A fotokatalitikus aktivitási mérések eredményei azt mutatták, hogy a talajoldatokkal való kölcsönhatás után mind a TiO_2, mind a ZnO aktivitása csökkent a tiszta referenciaanyagokhoz képest, de összességében megőrizték hatékonyságukat. A csökkenést főként a talajoldatokból adszorbeálódó szerves anyagok (pl. huminsavak) és ionok (pl. Na^+, K^+, Ca^{2+}, Fe^{3+}, S^{2-}, Cl^-) okozták, amelyek elfoglalták a katalizátorok aktív helyeit. A legnagyobb aktivitásbeli csökkenést a magas ionerősségű (~12 $mmol \cdot L^{-1}$) és lúgos (pH ~9,4) Solonetz talajoldat idézte elő, míg a legkevésbé a Cherznozem, amely mérsékelten lúgos (pH ~7,7) és alacsony ionerősségű (~4,3 $mmol \cdot L^{-1}$) volt.Bár a nanorészecskék színe megváltozott a talajoldatokkal való kölcsönhatás után, ez nem befolyásolta a tiltott sávszélességüket, ami arra utal, hogy a változás csak a felszíni kölcsönhatásokból eredt.

A röntgendiffrakciós (XRD) vizsgálatok megerősítették, hogy a nanorészecskék kristályszerkezete nem változott, így azok hosszú távon is megőrizhetik félvezető tulajdonságaikat.

A hosszabb távú (egyhetes) kísérletek azt mutatták, hogy a TiO_2 nanorészecskék csökkent aktivitás mellett, de továbbra is működőképesek maradtak, ami arra utal, hogy tartósan jelen lehetnek a környezetben és befolyásolhatják a talaj kémiai összetételét.

A kutatás eredményei arra világítanak rá, hogy ezek a nanorészecskék stabilak maradnak és megőrzik félvezető tulajdonságaikat eltérő kémiai összetételű talajoldatokban is, ami hosszú távú alkalmazhatóságuk szempontjából kedvező, de egyben a környezeti felhalmozódás és potenciális kockázatok veszélyére is felhívja a figyelmet.

Az adszorpciós képességük révén képesek különböző szerves anyagokat és ionokat megkötni, így közvetlenül befolyásolhatják a talaj mikro- és makrofaunáját, illetve elősegíthetik toxikus fémek mélyebb talajrétegekbe és akár a talajvízbe történő szállítását.

Mivel az ilyen típusú nanoméretű anyagok előállítása az utóbbi években rohamosan növekedett, várhatóan koncentrációjuk is növekedni fog a környezetben. Ezért kiemelten fontos a szennyvíztisztító rendszerek és hulladékkezelő létesítmények megfelelő felkészítése, valamint az olyan szabályozások kidolgozása, amelyek meghatározzák a környezetbe kerülő nanorészecskék megengedett mennyiségét.

A jövőbeli kutatások során érdemes lenne tovább vizsgálni más, széles körben alkalmazott nanorészecskéket (pl. CdS, CuO, Ag), valamint valós környezeti körülmények között elemezni azok hosszú távú hatásait. A nanotechnológia fejlődése számos előnnyel jár, de a fenntarthatóság és a környezetvédelem prioritást kell, hogy élvezzen a jövőbeni fejlesztések során.

8. SCIENTIFIC PUBLICATIONS

Hungarian Scientific Bibliography (MTMT) identifier: 10074621

Papers related to the theses:

(1) Solymos, Karolina; Babcsányi, Izabella; Ariya, Badam; Gyulavári, Tamás; Ágoston, Áron; Szamosvölgyi, Ákos; Kukovecz, Ákos; Kónya, Zoltán; Farsang, Andrea; Pap, Zsolt: *Photocatalytic and surface properties of titanium dioxide nanoparticles in soil solutions*. Environmental Science - Nano 11: 3 pp. 1204-1216., 13 p. (2024)
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(2) Solymos, Karolina; Babcsányi, Izabella; Ariya, Badam; Gyulavári, Tamás; Ágoston, Áron; Kukovecz, Ákos; Kónya, Zoltán; Pap, Zsolt: *Environmental significance of the interaction between titanium dioxides and soil solutions.* Environmental Sciences Europe 36: 1 Paper: 85, 14 p. (2024)
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(3) Solymos, Karolina; Kanász Eszter; Ágoston, Áron; Gyulavári, Tamás; Pálffy Benjámin; Szamosvölgyi, Ákos; Kukovecz, Ákos; Kónya, Zoltán; Pap, Zsolt: *Impact of Different Soil Solutions on the Stability and Photocatalytic Activity of Commercial Zinc Oxide Nanoparticles.* Environmental Science – Nano: 12:2 pp. 1328-1339., 12 p. (2024)
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(4) Solymos, Karolina; Ágoston, Áron; Gyulavári, Tamás; Szalma, Lilla; Todea, Milica; Kukovecz, Ákos; Kónya, Zoltán; Pap, Zsolt: *Environmental impacts on the photocatalytic activities of anatase and rutile.* Catalysts: 5:2 Paper: 190 (2025)
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CO-AUTHOR STATEMENT

I, ***Áron Ágoston***, hereby declare that the role of the doctoral candidate in the publication of

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was decisive in confirming that I have not used these publications to obtain a scientific degree and will not do so in the future.

Szeged, 31.03.2025.

....

Áron Ágoston

Co-author statement

I, ***Benjámin Pálffy***, hereby declare that the role of the doctoral candidate in the publication of

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Szeged, 31.03.2025.

Pálffy Benjámin

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Benjámin Pálffy

CO-AUTHOR STATEMENT

I, ***Dr. Tamás Gyulavári***, hereby declare that the role of the doctoral candidate in the publication of

SOLYMOS, KAROLINA; BABCSÁNYI, IZABELLA; ARIYA, BADAM; GYULAVÁRI, TAMÁS; ÁGOSTON, ÁRON; SZAMOSVÖLGYI, ÁKOS; KUKOVECZ, ÁKOS; KÓNYA, ZOLTÁN; FARSANG, ANDREA; PAP, ZSOLT: Photocatalytic and surface properties of titanium dioxide nanoparticles in soil solutions. Environmental Science - Nano 11: 3 pp. 1204-1216., 13 p. (2024). doi.org/10.1039/D3EN00622K

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Dr. Tamás Gyulavári

CO-AUTHOR STATEMENT

I, ***Prof. Dr. Ákos Kukovecz***, hereby declare that the role of the doctoral candidate in the publication of

SOLYMOS, KAROLINA; BABCSÁNYI, IZABELLA; ARIYA, BADAM; GYULAVÁRI, TAMÁS; ÁGOSTON, ÁRON; SZAMOSVÖLGYI, ÁKOS; KUKOVECZ, ÁKOS; KÓNYA, ZOLTÁN; FARSANG, ANDREA; PAP, ZSOLT: Photocatalytic and surface properties of titanium dioxide nanoparticles in soil solutions. Environmental Science - Nano 11: 3 pp. 1204-1216., 13 p. (2024). doi.org/10.1039/D3EN00622K

SOLYMOS, KAROLINA; BABCSÁNYI, IZABELLA; ARIYA, BADAM; GYULAVÁRI, TAMÁS; ÁGOSTON, ÁRON; KUKOVECZ, ÁKOS; KÓNYA, ZOLTÁN; PAP, ZSOLT: Environmental significance of the interaction between titanium dioxides and soil solutions. Environmental Sciences Europe 36: 1 Paper: 85, 14 p. (2024). doi.org/10.1186/s12302-024-00903-y

SOLYMOS, KAROLINA; KANÁSZ ESZTER; ÁGOSTON, ÁRON; GYULAVÁRI, TAMÁS; PÁLFFY BENJÁMIN; SZAMOSVÖLGYI, ÁKOS; KUKOVECZ, ÁKOS; KÓNYA, ZOLTÁN; PAP, ZSOLT: Impact of Different Soil Solutions on the Stability and Photocatalytic Activity of Commercial Zinc Oxide Nanoparticles. Environmental Science – Nano: 12:2 pp. 1328-1339., 12 p. (2024). doi.org/10.1039/D4EN00354C

SOLYMOS, KAROLINA; ÁGOSTON, ÁRON; GYULAVÁRI, TAMÁS; SZALMA, LILLA; TODEA, MILICA; KUKOVECZ, ÁKOS; KÓNYA, ZOLTÁN; PAP, ZSOLT: Environmental impacts on the photocatalytic activities of anatase and rutile. Catalysts: 5:2 Paper: 190 (2025). doi.org/10.3390/catal15020190

was decisive in confirming that I have not used these publications to obtain a scientific degree and will not do so in the future.

Szeged, 31.03.2025.

....

Prof. Dr. Ákos Kukovecz

CO-AUTHOR STATEMENT

I, ***Lilla Szalma***, hereby declare that the role of the doctoral candidate in the publication of

SOLYMOS, KAROLINA; ÁGOSTON, ÁRON; GYULAVÁRI, TAMÁS; SZALMA, LILLA; TODEA, MILICA; KUKOVECZ, ÁKOS; KÓNYA, ZOLTÁN; PAP, ZSOLT: Environmental impacts on the photocatalytic activities of anatase and rutile. Catalysts: 5:2 Paper: 190 (2025). doi.org/10.3390/catal15020190

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Szeged, 31.03.2025.

Szalma Lilla
…………………………………………….

Lilla Szalma

CO-AUTHOR STATEMENT

I, ***Milica Todea***, hereby declare that the role of the doctoral candidate in the publication of

SOLYMOS, KAROLINA; ÁGOSTON, ÁRON; GYULAVÁRI, TAMÁS; SZALMA, LILLA; TODEA, MILICA; KUKOVECZ, ÁKOS; KÓNYA, ZOLTÁN; PAP, ZSOLT: Environmental impacts on the photocatalytic activities of anatase and rutile. Catalysts: 5:2 Paper: 190 (2025). doi.org/10.3390/catal15020190

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Cluj-Napoca, 31.03.2025.

……………………………………………

Milica Todea

CO-AUTHOR STATEMENTS

I, ***Dr. Zsolt Pap***, hereby declare that the role of the doctoral candidate in the publication of

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Szeged, 31.03.2025.

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Dr. Zsolt Pap

CO-AUTHOR STATEMENT

I, ***Ákos Szamosvölgyi***, hereby declare that the role of the doctoral candidate in the publication of

SOLYMOS, KAROLINA; BABCSÁNYI, IZABELLA; ARIYA, BADAM; GYULAVÁRI, TAMÁS; ÁGOSTON, ÁRON; SZAMOSVÖLGYI, ÁKOS; KUKOVECZ, ÁKOS; KÓNYA, ZOLTÁN; FARSANG, ANDREA; PAP, ZSOLT: Photocatalytic and surface properties of titanium dioxide nanoparticles in soil solutions. Environmental Science - Nano 11: 3 pp. 1204-1216., 13 p. (2024). doi.org/10.1039/D3EN00622K

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Szeged, 31.03.2025.

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Ákos Szamosvölgyi

Co-author statement

I, ***Dr. Izabella Babcsányi***, hereby declare that the role of the doctoral candidate in the publication of

Solymos, Karolina; Babcsányi, Izabella; Ariya, Badam; Gyulavári, Tamás; Ágoston, Áron; Szamosvölgyi, Ákos; Kukovecz, Ákos; Kónya, Zoltán; Farsang, Andrea; Pap, Zsolt: Photocatalytic and surface properties of titanium dioxide nanoparticles in soil solutions. Environmental Science - Nano 11: 3 pp. 1204-1216., 13 p. (2024). doi.org/10.1039/D3EN00622K

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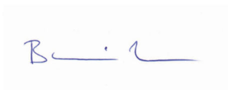

…………………………………………

Dr. Izabella Babcsányi

CO-AUTHOR STATEMENT

I, ***Badam Ariya***, hereby declare that the role of the doctoral candidate in the publication of

SOLYMOS, KAROLINA; BABCSÁNYI, IZABELLA; ARIYA, BADAM; GYULAVÁRI, TAMÁS; ÁGOSTON, ÁRON; SZAMOSVÖLGYI, ÁKOS; KUKOVECZ, ÁKOS; KÓNYA, ZOLTÁN; FARSANG, ANDREA; PAP, ZSOLT: Photocatalytic and surface properties of titanium dioxide nanoparticles in soil solutions. Environmental Science - Nano 11: 3 pp. 1204-1216., 13 p. (2024). doi.org/10.1039/D3EN00622K

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Badam Ariya

CO-AUTHOR STATEMENT

I, ***Prof. Dr. Zoltán Kónya***, hereby declare that the role of the doctoral candidate in the publication of

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Prof. Dr. Zoltán Kónya