Comparison of the functional properties of ilite clay/ TiO_2 and kaolinite clay/TiO_2 coatings

Poređenje funkcionalnih svojstava premaza od ilit gline/TiO_2 i kaolinit gline/TiO_2

Vojo Jovanov[1,*], Snežana Vučetić[2], Biljana Angjusheva[1], Jonjaua Ranogajec[2], Emilija Fidanchevski[1]

[1] *Ss. Cyril and Methodius University in Skopje, Faculty of Technology and Metallurgy, Ruger Bosković 16, 1000 Skopje, Republic of N. Macedonia*

[2] *University of Novi Sad, Faculty of Technology, bul. Cara Lazara 1, 21000 Novi Sad, Serbia*

https://doi.org/10.65614/uisk_yucorr.2025.26.ch31

*vojo@tmf.ukim.edu.mk

Abstract

Ilite/ TiO_2 and kaolinite/TiO_2 coatings, impregnated with 10 wt.% nano TiO_2 using mild conditions, was applied to and investigated on three types of substrates: porous (clay roofing tiles), highly porous (clay-fly ash composite), and non-porous (window glass). The coatings were analyzed for their capillary water absorption and surface properties, including roughness, micro-hardness, and hydrophilicity. The functional properties of self-cleaning and photocatalytic activity were evaluated by measuring the initial contact angle and the photodegradation of the model pollutant Rhodamine B, which was assessed during UV/VIS irradiation.
The study suggests that the applied synthesis by mechanical activation methodology resulted in a homogenous distribution of TiO_2 as an active component in the photocatalytic coating, leading to better surface and functional properties. Novel natural clay/TiO_2-based coatings are advantageous due to their low cost and simple preparation, ensuring high photo-degradation efficiency.
Keywords: *nano-TiO_2; kaolinite clay; illite clay; mechanical activation; photocatalytic coating*

Izvod

Premazi ilit/TiO_2 i kaolinit/TiO_2, impregnirani sa 10 tež.% TiO_2 korišćenjem nove metode pod blagim uslovima, naneti su i ispitani na tri vrste podloga: poroznim (glineni crepovi), visoko poroznim (kompozit gline i pepela) i neporoznim (prozorsko staklo). Premazi su analizirani na osnovu njihove kapilarne apsorpcije vode i površinskih svojstava, uključujući hrapavost, mikrotvrdoću i hidrofilnost. Funkcionalna svojstva samočišćenja i fotokatalitičke aktivnosti procenjena su merenjem početnog kontaktnog ugla i fotodegradacije modelnog zagađivača rodamina B, koja je procenjena tokom UV/Vis zračenja.
Studija sugeriše da je primenjena sinteza metodologijom mehaničke aktivacije rezultirala homogenom raspodelom TiO_2 kao aktivne komponente u fotokatalitičkom premazu, što je dovelo do boljih površinskih i funkcionalnih svojstava. Novi premazi na bazi prirodne gline/TiO_2 su predni zbog svoje niske cene i jednostavne pripreme, obezbeđujući visoku efikasnost fotodegradacije.
Ključne reči: *nano-TiO_2; kaolinitna glina; ilitna glina; mehanička aktivacija; fotokatalitički premaz*

Introduction

The surfaces of exposed building materials, such as ceramic tiles, roofing tiles, glass, and facades, are exposed to environmental conditions that can result in the deposition of pollutants onto them, so that cleaning, which is connected to a high consumption of energy, labor, and detergents, is needed, resulting in high maintenance costs. To reduce costs and enhance the long-term aesthetic appearance of the exposed surfaces of building materials, photocatalytic and self-cleaning coatings can be applied

[1,2]. Among various semiconductor catalysts, titanium dioxide (TiO_2) has garnered significant attention for this application due to its efficient photocatalytic activity, high stability, low cost, and non-toxicity [3]. One of the possibilities to increase its photocatalytic activity is the impregnation of TiO_2 nanoparticles into the clay mineral structure [8,9]. Clay minerals have unique layered structures, a large specific surface area, and high adsorption capacity [10,11]. The incorporation of TiO_2 into their structure enhances photocatalytic efficiency by providing a durable support structure and improving adsorption characteristics [12,13,14].
Many studies indicate that incorporating TiO_2 into clay minerals through mechanical activation offers several benefits. These include a uniform distribution of TiO_2 as an active component, increased reactivity due to reduced particle size, and a larger surface area, which improves absorption properties
This study aimed to develop photocatalitically active coatings based on kaolinite and illite clays serving as supports for the incorporation of 10 wt.% nano-TiO_2. The impregnation was carried out through mechanical activation using an attritor and a planetary mill under controlled conditions. The effects of the coatings on three types of substrates with varying porosities were evaluated in terms of capillary water absorption, surface properties (roughness, microhardness, and hydrophilicity), and functional properties (self-cleaning and photocatalytic activity).

Experimental

Materials

Illite and kaolinite clay were used in this study. Illite caly originates from the eastern part of Republic of North Macedonia, while kaolinite was commercial refractory clay from Republic of Poland.
The nano TiO2, sourced from the Degussa company in Germany, acted as the photocatalytic precursor. The suspension consisted of 30.0 ± 1.0 wt.% dry matter, primarily comprising 80 wt.% anatase and 20 wt.% rutile, with particle sizes under 100 nm and a neutral pH of 7.

Preparation of illite clay/nano TiO_2 coating

The impregnation of nano TiO_2 in content of 10 wt.% into the illite clay was performed using mechanical activation in an attritor mill for 90 minutes at a speed of 1500 rpm. The impregnation in kaolinite clay was performed in two ways: in an attritor mill under the same conditions as those for illite clay, and as a second way in a planetary mill during 180 minutes at a speed of 200 rpm. The material-to-ball ratio was set at 1:5, and the pH value was maintained between 9 and 9.5. This pH level was adjusted using $NaCO_3$ solution with a concentration of 0.67 mol/dm^3. The resulting powders were then dried at 105°C for 24 hours. The coatings were prepared by diluting 0.5 g of the synthesized powder in 100 mL of demineralized water, followed by the stabilization procedure procedure [10, 14]. This coating suspensions were then applied using a spray technique onto three different types of model substrates: porous, highly porous and non-porous. Industrial clay roofing tile (CRT) was used for the porous substrate, a composite of fly ash and clay (CFA) was employed as the highly porous substrate and window glass (WG) served as the non-porous substrate. The capillary water absorption coefficients for these substrates were as follows, [kg/m² min$^{1/2}$]: CRT - 8.22, CFA - 1.04 x 10^{-6} and WG - 0.73[10]. The coding system for the samples used in this investigation is as follows: uncoated reference substrates are marked with the suffix "R" (e.g., CRT-R, CFA-R, WG-R). Substrates coated with an Ilite clay/TiO_2 suspension are labeled with the suffix "H2A" (e.g., CRT-H2A, CFA-H2A, WG-H2A). Those coated with a kaolinite clay/TiO_2 suspension are designated with the suffix "E2A" (e.g., CRT-E2A, CFA-E2A, WG-E2A) when impregnated in an attritor mill, or "E2P" (e.g., CRT-E2P, CFA-E2P, WG-E2P) when processed in a planetary mill.

Characterization methods

The capillary water absorption of the reference and coated substrates was evaluated according to the standard SRPS U. M8.300, 1985 – EN [15].
Surface roughness (Surtronic 25, Taylor Hobson) of the coatings was evaluated based on the Ra parameter. The obtained data were calculated according to the standard cited in ISO 4287.
Vickers micro-hardness for the reference and coated samples was measured using the Vickers micro-hardness technique (Micro hardness tester model HVS 1000A, ZZV Precision Tool Supply) with a load of 0.3 kg.
To assess self-cleaning efficiency, the initial contact angle was measured using the Surface Energy Evaluation System (Advex Instruments, Brno, Czech Republic), following the procedure described in [10].
The photocatalytic activity of the coatings was assessed following the procedure described by Jovanov et al. [7], and the values were measured using UV/VIS spectroscopy (EVOLUTION 600 spectrophotometer).

Results and discussions

Characterization of reference and illite clay/TiO_2 and kaolinite clay/TiO_2 coated substrates

The capillary water absorption coefficients (A) of the three reference substrates, as well as those coated with illite/nano-TiO_2 and kaolinite/nano-TiO_2, are presented in Table 1. All coated substrates exhibited a decrease in the capillary water absorption coefficient compared to their respective references, regardless of the clay type or impregnation method used. The greatest reduction in the coefficient (A) for all three substrates was achieved with the illite/nano-TiO_2 coating prepared by mechanical activation in the attritor mill. The extent of reduction was strongly influenced by substrate porosity. Namely, it was the most pronounced for the highly porous CFA substrate, moderate for CRT, and negligible for the non-porous WG, consistent with previous findings [7]. Overall, the comparison of capillary water absorption coefficients suggests that the coatings successfully reduce water absorption in the mineral substrates.

Table 1. Capillary water absorption coefficients (A) of the reference – R substrate and substrates with illite/nano TiO_2 and kaolinite/nano TiO_2 coating

Mineral substrate	A, [$kg/m^2min^{1/2}$]
CRT-R	0.73
CRT-H2A	0.54
CRT-E2A	0.59
CRT-E2P	0.63
CFA-R	8.22
CFA-H2A	5.72
CFA-E2A	6.22
CFA-E2P	6.43
WG-R	1.04×10^{-6}
WG-H2A	1.02×10^{-6}
WG-E2A	1.03×10^{-6}

WG-E2P	$1.03x10^{-6}$

The surface properties, including surface roughness and Vickers microhardness of the reference substrates and substrates with illite/nano TiO_2 and kaolinite/nano TiO_2 coating, are presented in Tables 2 and 3, respectively.
The surface roughness (Ra parameter), Table 2, for the coated substrates exhibits an increase in the WG substrate, a negligible increase in the CRT substrate, and a slight decrease in the CFA substrate, after the deposition of all three different coatings. The minor changes in roughness for CRT and CFA are due to these substrates already being rough because of their porosity [14]. Therefore, the coatings did not significantly affect the surface roughness of the two porous substrates. In contrast, when the coating was applied to the WG substrate, the Ra value increased, with the most pronounced effect observed for the E2P coating.

Table 2. Surface roughness (Ra parameter) of the reference -R and substrates with illite/nano TiO_2 and kaolinite/nano TiO_2 coating

Mineral substrate	Ra [μm]
CRT-R	2.45
CRT-H2A	2.53
CRT-E2A	2.50
CRT-E2P	2.55
CFA-R	12.31
CFA-H2A	12.25
CFA-E2A	12.24
CFA-E2P	12.26
WG-R	0.09
WG-H2A	0.20
WG-E2A	0.21
WG-E2P	0.27

The Vickers micro-hardness (HV), results, Table 3, indicate that the hardness of the substrates increased only negligibly after coating with all three different coatings, most likely due to the presence of additional crystalline particles on the surface [16].
Regarding the type of clay used as a coating carrier and the conditions of mechanical impregnation of the active component, the E2A coating, made of kaolin clay impregnated with 10% TiO_2 in an attritor mill, shows better values for Vickers microhardness, compared to the H2A and E2P coatings, when applied to all three types of substrates.

Table 3. Vickers micro-hardness (HV) values of the reference -R and coated substrates

Mineral substrate	Vickers micro-hardness (HV) values
CRT-R	45.0
CRT-H2A	46.4

CRT-E2A	45.8
CRT-E2P	45.5
CFA-R	13.3
CFA-H2A	13.6
CFA-E2A	13.7
CFA-E2P	13.4
WG-R	453.0
WG-H2A	455.5
WG-E2A	456.3
WG-E2P	455.7

The average initial contact angles (θci) for both the reference and coated substrates are shown in Table 4. The θci values for the reference substrates were below 90°, indicating that the substrates used were hydrophilic. After coating, the θci values decreased further, indicating improved hydrophilicity. The most pronounced reduction was observed for the E2A coating, with the θci decrease of nearly 60% on the WG substrate.

Table 4. Average values of initial contact angles (θci) of the reference -R and coated substrates

Mineral substrate	Average initial contact angle values θci, (°)
CRT-R	54.7
CRT-H2A	43.24
CRT-E2A	36.99
CRT-E2P	38.97
CFA-R	52.56
CFA-H2A	38.35
CFA-E2A	35.29
CFA-E2P	37.92
WG-R	67.02
WG-H2A	28.13
WG-E2A	27.40
WG-E2P	28.73

Self-cleaning and photocatalytic properties of the coated substrates

The self-cleaning capabilities of the coated substrates were assessed by measuring θci after 24 hours of UV/VIS irradiation, as shown in Figure 1. All three different types of substrates, coated with three types of coatings demonstrated a reduction in θci during UV/VIS exposure. The most significant decrease occurred within the first four hours, after which the contact angles of the substrates continued to decline at a slower pace. This pattern reinforces the coating's effectiveness in promoting self-cleaning properties across the different substrate types (highly porous, porous, and non-porous).

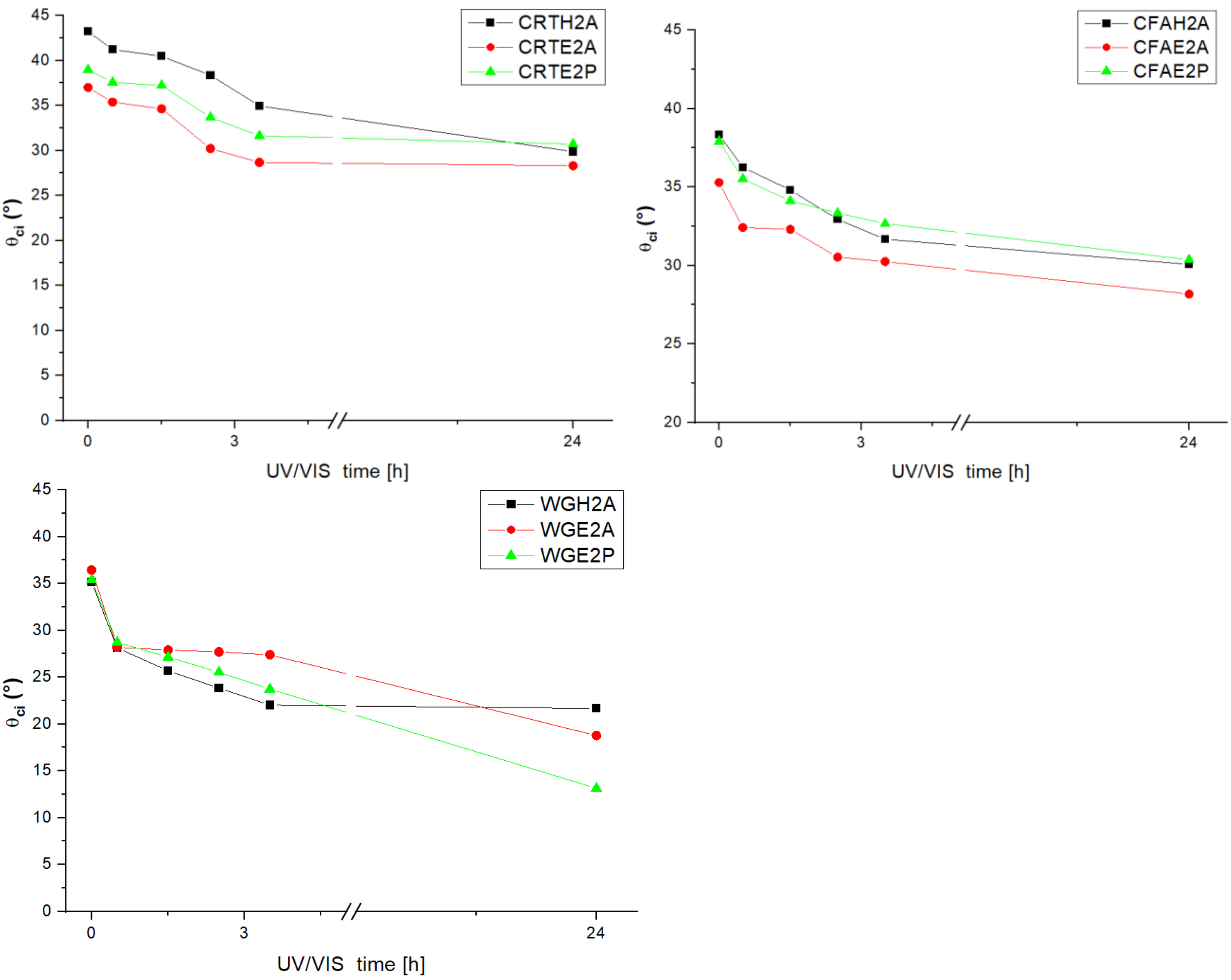

Figure 1. *Initial contact angle (θci) of coated substrates (CRT, CFA and WG) as a function of UV/VIS radiation time.*

The photocatalytic effectiveness was evaluated by measuring the degradation rate of rhodamine B (RhB) after 24 hours of UV/VIS light exposure, illustrated in Figure 2. The CRT substrate achieved around 43% photocatalytic effectiveness with the E2A coating and roughly 26% with the H2A and E2P coatings. In comparison, the CFA-coated substrate showed minimal activity across all three coatings. Conversely, the WG-coated substrate samples displayed remarkable photocatalytic performance, reaching a 90% degradation rate after 24 hours when treated with all three coatings.
The differences in photocatalytic performance can be linked to the varying surface characteristics and porosity of the substrates, as explained presented in Tables 1, 2, and 3. The CFA substrate, characterized by high porosity and significant capillary water absorption, allowed the active suspensions to penetrate deeper into the material, limiting their availability on the surface for light activation. Consequently, only a small amount of the suspension remained on the surface, which restricted the photocatalytic reaction.

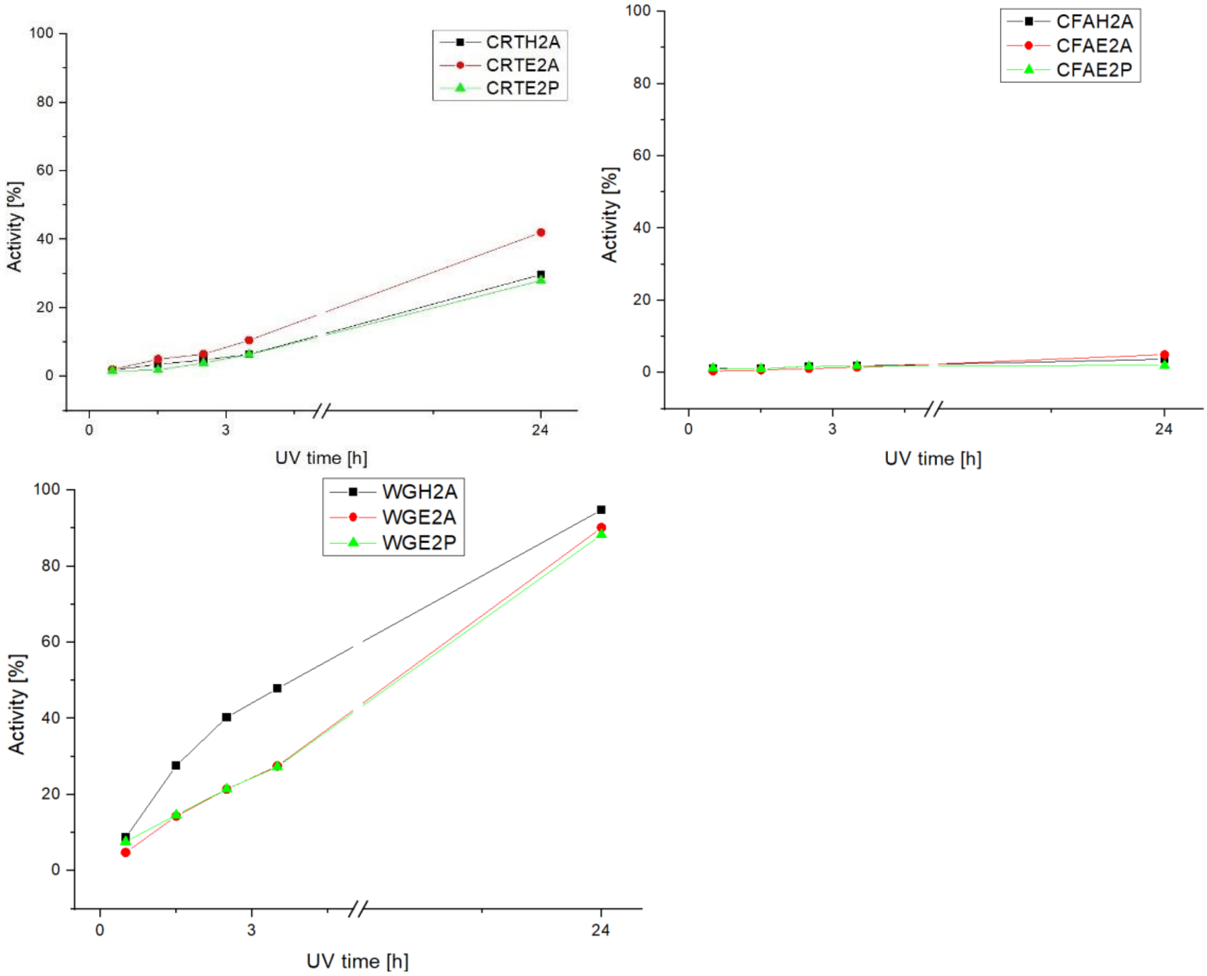

***Figure 2.** Photocatalytic activity of coated substrates (CRT, CFA, and WG) as a function of UV/VIS radiation time.*

Conclusion

The study presents the potential of applying two types of clay, illite and kaolinite, as support for impregnation 10wt. % nano TiO_2 to create coatings with self-cleaning and photocatalytic properties. Nano TiO_2 was successfully impregrated on both clays by mechanical activation. The effect of coatings was studied on three different substrates (porous, highly porous, and non-porous) and the coatings have potencial to be applied on porous and non-porous substrate based on the results obtined for capillary water absorption and surface properties (roughness, micro-hardness, and hydrophilicity), as well as functional properties (self-cleaning and photocatalytic) were followed on the applied illite/TiO_2 and kaolinite/TiO_2 coating. Kaolinite/TiO_2 coatings obtained by atrittor mill showed favorable properties. The study shows the potential of using low-cost natural clays as supports for TiO_2 impregnation to create composite photocatalyst coatings, and it offers valuable insights for guiding future research efforts.

Acknowledgement

This research was supported by the Ministry of Education and Science of the Republic of North Macedonia, Grant no. 15-6171/34.

References

1. Rabajczyk A, Zielecka M, Klapsa W, et al. Self-Cleaning Coatings and Surfaces of Modern Building Materials for the Removal of Some Air Pollutants. *Materials* 2020; 14(9), 2161. https://doi.org/10.3390/ma14092161
2. Ranogajec J, Vučetić S, Milan J, et al. Photocatalytic Protection of Building Materials in Real Environmental Conditions. *Microscopy and Microanalysis* 2018; *24*(S1), 1698-1699. https://doi.org/10.1017/S1431927618008978
3. Manzoor Q, Sajid A, Ali Z, et al. Toxicity spectrum and detrimental effects of titanium dioxide nanoparticles as an emerging pollutant: A review. *Desalination and Water Treatment* 2023; *317*, 100025. https://doi.org/10.1016/j.dwt.2024.100025
4. Du X, Men K, Xu Y, et al. Enhanced capacitance performance of Al2O3–TiO_2 composite thin film via sol–gel using double chelators. *Journal of Colloid and Interface Science* 2015;*443*, 170-176. https://doi.org/10.1016/j.jcis.2014.11.038
5. 5. Mishra A, Mehta A, Basu S. Clay supported TiO_2 nanoparticles for photocatalytic degradation of environmental pollutants: A review. *Journal of Environmental Chemical Engineering* 2018; *6*(5), 6088-6107. https://doi.org/10.1016/j.jece.2018.09.029
6. Ozawa M, Matui H, Setsuhara Y. Microstructure and surface/interface characterization of TiO_2-pillared mica for photocatalytic acetaldehyde degradation. Hybrid Advances 2025; 10, 100435 https://doi.org/10.1016/j.hybadv.2025.100435
7. Jovanov V, Rudic O, Ranogajec J, et al. Synthesis of nanocompositecoating based on TiO_2/ ZnAl layer double hydroxides, Materiales de Construcción 2017; 67, 112–120. https://doi.org/10.3989/mc.2017.07215
8. Cardona Y, Korili SA, Gil A. Use of clays and pillared clays in the catalytic photodegradation of organic compounds in aqueous solutions. *Catalysis Reviews* 2023; *66*(5), 2063–2110 https://doi.org/10.1080/01614940.2023.2178736
9. Szczepanik B. Photocatalytic degradation of organic contaminants over clay-TiO_2 nanocomposites: A review. *Applied Clay Science* 2017; 141, 227-239. https://doi.org/10.1016/j.clay.2017.02.029
10. Jovanov V, Zečević V, Vulić T, et al. Preparation and characterization of protective self-cleaning TiO_2/kaolin composite coating, *Materiales de Construcción* 2018; 68, 163 https://doi.org/10.3989/mc.2018.08517
11. Qi Y, Zhao S, Shen Y, et al. A Critical Review of Clay Mineral-Based Photocatalysts for Wastewater Treatment. *Catalysts* 2024; *14*(9), 575. https://doi.org/10.3390/catal14090575
12. Tole I, Delogu F, Qoku E, et al. Enhancement of the pozzolanic activity of natural clays by mechanochemical activation. *Constr. Build. Mater.* 2022; 352, 128739. https://doi.org/10.1016/j.conbuildmat.2022.128739
13. Baláž P. Mechanochemistry in nanoscience and minerals engineering, *Springer Berlin Heidelberg* 2008; pp. 257-296
14. Jovanov V, Vučetić S, Ranogajec J, et al. Photocatalytic illite clay/TiO_2 composite powder synthesized by mechanical activation, GREEN CIRC 2025 PROCEEDINGS https://congress.sctm.mk/event/6/book-of-abstracts.pdf
15. SRPS U.M8.300:1985, Determination of the Capillary Water Absorption of Building Material and Coatings, 1985.
16. Rudic O, Ranogajec J, Vulic T, et al. Photo-induced properties of TiO_2/ZnAl layer double hydroxide coating onto porous mineral substrates, *Ceramic International* 2014; 40(7) 9445-9455. https://doi.org/10.1016/j.ceramint.2014.02.017