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PHOTOCATALYTIC ACTIVITY OF TiO_2/ZnAl LDH BASED COATING IN RELATION TO MECHANICAL TREATMENT OF THE POWDER

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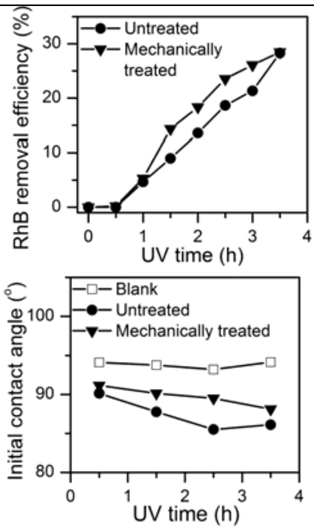
The photocatalytic activity of TiO_2-ZnAl layered double hydroxide based coating deposited on the ceramic tile was studied in relation to mechanical treatment of photocatalytic powder and in relation to suspension preparation. The coating prepared with the filtered suspension showed better photo-induced properties (photocatalytic Rhodamine B removal efficiency and surface hydrophilicity) and better stability towards rinsing with water compared to the decanted suspension. Considering the similar nature of the photocatalytic active sites for both decanted and filtered suspension, the narrow monomodal particle size distribution in the case of the filtered suspension was identified as responsible for better performances of the coating. The mechanical treatment of the photocatalytic powder generally did not show positive effect on the photo-induced properties of the coatings. The improvements regarding the particle size distribution obtained by the mechanical treatment were overruled by the mechanochemical reactions, leading to the formation of less photocatalytic active phases.



INTRODUCTION

Large building surfaces are exposed to severe outside conditions leading to both chemical and physical deterioration. One of the solutions for the protection could be the development of multifunctional self-cleaning coatings, possessing photocatalytic activity and surface hydrophilicity or hydrophobicity. Considering that the deterioration of building materials starts at the material surface and penetrates gradually into the material, the application of a coating could improve surface properties and prolong the material durability. The photocatalytic coatings are attractive because their photocatalytic activity is initiated by solar light enabling the decomposition of various organic, inorganic and biological pollutants, while on the other hand photo-induced surface hydrophilicity facilitates the washing of the residues and dust by rainwater.[1] This is the reason that the self-cleaning function is of great importance from both economic (money spent on cleaning maintenance) and environmental point of view (decomposition of pollutants). Although the photo-induced hydrophilicity and photocatalytic degradation of the contaminants are different processes, they occur simultaneously and it is difficult to distinguish which mechanism is more important for the self-cleaning.[1-3] The photocatalytic activity of the semiconductor occurs when the light

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irradiation causes the excitation of supra-bandgap photons leading to the migration of electron–hole pairs to the surface, initiating the hydroxyl radical formation reaction with adsorbed H_2O and OH^-. This results with the highly active oxidizing sites which can degrade a variety of organic and inorganic polutants to harmless inorganic anions, H_2O and CO_2.[4] In the case of hydrophilicity effect, the produced electrons and holes tend to reduce the Ti^{4+} cations to the Ti^{3+} state, while the produced holes oxidize the O_2 anions creating oxygen vacancies. Water molecules from outside atmosphere can easily occupy the created oxygen vacancies, adsorbing OH^- groups, which tend to produce surface with high hydrophilic properties.[1,2] For these applications, nano-sized TiO_2 is one of the most studied and used photocatalytic material.[5-7] The photocatalyst based on layered double hydroxides (LDHs) associated to TiO_2 were developed to prevent nano-particle aggregation, provide adequate porosity and improve photocatalytic activity and compatibility with the mineral substrate, since they belong to a class of synthetic two-dimensional nanostructured anionic clays. Due to their favorable textural, acid–base and redox properties, the LDHs have been intensively studied recently as photocatalysts or photocatalyst supports.[8-10] The TiO_2/Zn–Al nanocomposite powder with tested photocatalytic properties[11] was used for the preparation of the suspensions. In our previous research, this nanocomposite photocatalyst revealed the synergy of both composite components (TiO_2 and Zn–Al LDH) showing that the Zn–Al LDH alone has much lower activity under the same reaction conditions than TiO_2/Zn–Al nanocomposite powder.[11] The TiO_2 amount of 3 mass% was chosen taking into account the results of our previous research with photocatalytic powders containing different amounts of TiO_2 impregnated onto the Zn–Al LDH.[11,12] The particle size distribution of the photocatalyst in suspension is very important for the stability of the suspension and consequently the stability and aesthetic appearance of the deposited coating. One of the ways to reduce particle size is the mechanical treatment. Besides paricle size reduction, the mechanical treatment by milling initiates different physico-chemical changes in material and can be described as mechanochemical treatment or mechanical activation.[13-16] Mechanical activation of solid material in mills generates different structural defects, increases defects in the crystalline lattices; reduces particle size, increases surface energy and initiates chemical processes due to the physical changes during this process.[17-19] Mechanochemical activation is very interesting techniques for the synthesis of catalysts from an industrial point of view, because it is one of the least sophisticated and inexpensive technologies, especially in the case of nanosized catalyst preparation.[20] Mechanical activation changes the overall reactivity of solids, chemical nature and structure of a solid as well as the catalytically active sites. During mechanical activation solid catalyst accumulates excess potential energy, elastic and plastic deformations as well as a great variety of defects, which usually leads to an increase in its reactivity and formation of active metastable non-equilibrium catalytic systems.[20] For all these reasons the mechanical treatment of the photocatalytic powder was performed, with the aim to investigate the influence of the mechanical treatment of the powder on the particle size distribution, the generation of active sites in photocatalyst and photocatalytic activity of coating deposited on ceramic tile. Additionaly, since the suspensions prepared with the as synthesized and mechanically treated powder were not stabile and sedimentation of a considerable amount of photocatalytic powder occured, for the preparation of the coatings, suspension was decanted or filtered in order to eliminate the presence of large particles and stabilize the suspension. Photocatalytic and surface properties (liquid-solid contact angle, surface roughnes) of all deposited coatings were studied. As the coatings should provide stable photocatalytic activity in changing conditions of real environment, durability towards water rinsing was studied as one of the important coating properties.

EXPERIMENTAL

Materials and methods

Synthesis of the photocatalytic powder

Layer double hydroxides ZnAl-LDH were synthesized by low supersaturation coprecipitation method at constant pH (9–9.5).[11] The chosen zinc and aluminum precursors, $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were continuously (4ml min^{-1}) added together with 0.67M Na_2CO_3 and 2.25M NaOH solution in order to maintain a constant pH value. The precipitates were aged for 18h, washed with demineralized water until pH ≈ 7, dried at 100°C/24h and calcined at 500°C/5h. In order to obtain the TiO_2/ZnAl-LDH nanocomposite powder, the wet impregnation process was carried out by introducing 3 mass% TiO_2 suspensions (VP Disp.W 2730 X Evonik) onto calcined ZnAl-LDH powder. The denotation of the studied samples is given in Table 1.

Table 1

The denotation of the studied samples

	Sample denotation	Explanation
Powders	P	Powder – as synthesized
	P-MA	Powder – mechanically activated
Suspensions	S-D	Decanted suspension prepared with as synthesized powder
	S-D-MA	Decanted suspension prepared with mechanically activated powder
	S-F	Filtered suspension prepared with as synthesized powder
	S-F-MA	Filtered suspension prepared with mechanically activated powder
Coatings	C-D	Coating on ceramic tile prepared with suspension S-D
	C-D-MA	Coating on ceramic tile prepared with suspension S-D-MA
	C-F	Coating on ceramic tile prepared with suspension S-F
	C-F-MA	Coating on ceramic tile prepared with suspension S-F-MA
Coatings after durability testing	D-C-D	Coating C-D after durability testing
	D-C-D-MA	Coating C-D-MA after durability testing
	D-C-F	Coating C-F after durability testing
	D-C-F-MA	Coating C-F-MA after durability testing
Referent sample	Blank	Ceramic tile without coating

Mechanical activation of powder

Milling was performed in a planetary ball mill Fritsch Pulverisette 4. A tungsten carbide vial (250 cm^3 volume) filled with 14 tungsten carbide balls (10 mm in diameter) was used. The mass of the powder was 5 g. Milling was performed in air atmosphere for 1 h. The angular velocity of the supporting disc and vial were 400 and 800 rpm, respectively, with the relative ratio -2.

Preparation of suspensions

The obtained TiO_2/ZnAl-LDH nanocomposite powder (1 g) was then suspended into 100 ml demineralized water with the dispersing agent and stirred (300 rpm/h). Ultrasonic bathing was used for 30 min to prevent possible agglomeration of the prepared TiO_2/ZnAl-LDH nanocomposite suspension.

Decantation and the filtering procedures of the prepared suspensions were performed. Filtration was carried out as follows: first, using a medical syringe a considerable amount of liquid from the primary (parent) suspension was taken, and then passed through a filter ring (AllPure PTFE, the fineness of filtrate paper was 0.45 µm).

The obtained suspensions were deposited by spray technique (pressure was 6.5 bar, nozzle diameter was 0.6 mm, three layers of the coating were deposited) on the surface of the chosen materials. The specimens were afterwards dried at room temperature for 24 h with no additional thermal treatment. The amount of photocatalytic active powder in prepared decanted and filtered suspensions was estimated by measuring the dry weight of the residue.

Characterization of powders

The phase composition of the as synthesized and mechanically activated powders was determined by X-ray powder-diffraction (XRPD) analysis (Philips PW1710 device) under the following experimental conditions: monochromatic CuKα radiation with 1.5418 Å wavelengths in the 10–60° of 2θ range, scan rate 0.02°, 0.5 s per step. The crystallite size (*D*) of powders before and after milling were calculated by means of Scherrer equation[21] using XRPD data as:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where λ is the X-ray wavelength in nanometer, θ is the Bragg angle of the considered X-ray diffraction peaks. β represents the full width at half maxima of diffraction peak in radians. *K* is a constant related to crystallite shape, for spherical crystallites usually taken as 0.9.

Characterization of suspensions

The particle size distribution measurment of the prepared TiO_2/ZnAl-LDH suspensions was performed with a Malvern Instruments, zeta-nanoseries, NanoZS under the following conditions: refraction index of the investigated suspension, $n = 1.55$, light absorption, $a = 0.3$ and pH ≈ 9.

Characterization of the coatings

The contact angle between the experimental fluid (water) and the surfaces of the reference (non coated samples) and coated samples was measured using Surface Energy Evaluation System, Advex Instruments, (Brno, Czech Republic). The liquid droplets (5 µl in volume) were gently deposited on the substrate using a micro syringe. All measurements of the initial contact angle (θ_{ci}) at room temperature were performed at five different points for each of three specimens of the prepared samples. Each droplet deposited onto surface was measured five times.

The surface roughness measurements were performed using Surtronic 25, Taylor Hobson precision device according to the ISO 4287 standard. The surface roughness was evaluated based on R_a parameter which represents average roughness value obtained with a 4 mm linear probe length.

Evaluation of photocatalytic activity

The photocatalytic behavior of the coated samples was investigated by monitoring the Rhodamine B (RhB) concentration change under UV/VIS irradiation.[22] Preabsorption test with RhB solution (10 ppm dm^{-3}, during 24h) was carried out in order to saturate the investigated samples. After the preabsorption, RhB solution was replaced with a fresh one. The samples were then irradiated for 30, 90, 150 and 210 min (EVERSUN lamp, intensity of UV-A and Visible light spectra were 0.8 mW cm^{-2} and 0.3 Wm^{-2}, respectively). UV/VIS spectrophotometer *(EVOLUTION 600 spectrophotometer)* was used to carry out the monitoring of the removal efficiency of RhB at major absorption peak (λ = 554 nm). The photocatalytic activity was evaluated based on the removal efficiency of RhB, E_R, at the given absorption peak and expressed by the following equation:

$$E_R(\%) = [(C_0 - C)/C_0] \cdot 100 \quad (2)$$

where C_0 is the RhB concentration of the sample in the dark at defined time and C is the RhB concentration of the sample under UV/VIS light at defined time.

Coatings durability testing

In order to assess the durability properties of the coated surfaces by simulating severe outside conditions (rinsing rain), a device was designed in accordance with the literature reference.[23] The water rinsing was simulated with the equipment which provides constant tap water flow (250 mL min^{-1}) through a pipe system (nozzle diameter of 0.90 mm). The formed water streams fell on the coated samples for 30 min per sample. The samples were denoted D-C-D-MA and D-C-F-MA after the durability testing. These samples were analyzed by measuring the most important functional properties of the deposited coatings (photocatalytic activity, contact angle, surface roughness and micro-hardness) before and after the rinsing test.

RESULTS AND DISCUSSION

Characterization of the photocatalytic powders

The reflections in diffraction pattern of compound before mechanical treatment (Fig. 1) were indexed in a hexagonal lattice with an $R\overline{3}m$ rhombohedral symmetry, space group no. 116. Layered double hydroxides (LDH) with hydrotalcite crystal structure crystallize in the mentioned $R\overline{3}m$ space group. The mechanical treatment of the photocatalytic powder was performed, with the aim to investigate its influence on the particle size distribution, as well as on the photocatalytic activity of coating deposited on ceramic tile. The diffraction peaks present on the diffractogram after the mechanical treatment (Fig. 1) were indexed in hexagonal wurtzite structure (space group no. 186). Thus, XRPD analysis showed that during mechanical treatment mechanochemical reactions occurred. Impact-induced local heating and high pressures during mechanical treatment process relax in the form of lattice defects, fresh surface creation, lattice vibrations and very often by a formation of new phases.[24-26] Mechanosynthesis of complex oxides by using starting materials either with H_2O or OH-groups has extensively studied by Avvakumov *et al.*[27,28] There are reports of formation of nanocrystalline ZnO powders by mechanochemical treatment of zinc hydroxide.[29,30]

The obtained value of the crystallite size for powder before mechanical treatment, calculated for the strongest (1 0 1) reflections, was 4 nm. The strongest reflection (0 0 3) on diffractogram after mechanical treatment was also used for crystallite size calculation. Obtained value was 7 nm. Scherrer formula gives an estimate, calculated values for crystallite size before and after mechanochemical treatment were the same order of magnitude. Difference was observed concerning particle size distribution. Larger crystallite size after mechanical treatment could be explained by impact-induced local heating and high pressures which favored crystalline growth.

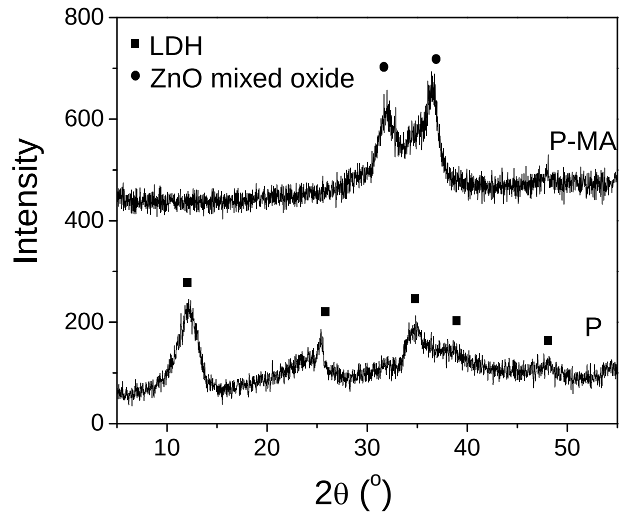

Fig. 1 – XRPD pattern of the as synthesized powder (P) and the mechanicaly treated powder (P-MA).

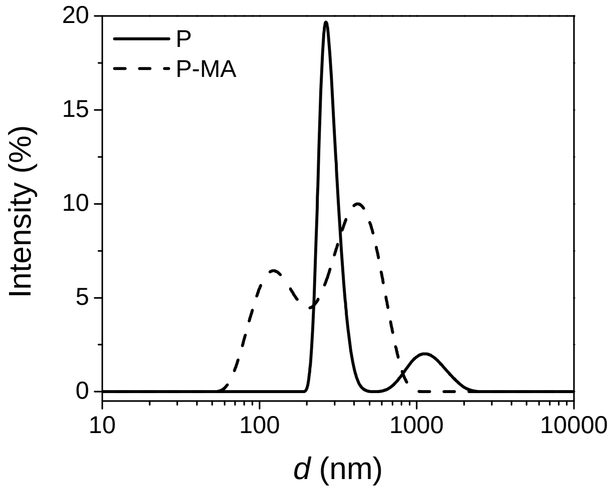

Fig. 2 – Particle size distribution of the as synthesized powder (P) and of the mechanically treated powder (P-MA).

The particle size distribution of the as synthesized powder (P) and of the mechanically treated powder (P-MA) is presented in Fig. 2. The as synthesized powder has one sharp and intensive peak with average particle diameter of 300 nm and a second wide, low intensity peak with average diameters of 1200 nm. After the mechanical treatment of the powder the particle size distribution changes and decreases leading to the formation of the two, wide, overlapping fractions of similar intensity with average particle diameters of 100 nm and 400 nm.

Characterization of the photocatalytic suspensions

The suspensions prepared with the as synthesized and mechanically treated powder were not stabile and the sedimentation of a considerable amount of photocatalytic powder was observed. The deposition of this suspension with large particles leaded to the formation of aesthetically unacceptable coating on the surface of the ceramic tile. For that reason, the suspension was decanted or filtered in order to eliminate the presence of large particles and stabilize the suspension.

The amount of photocatalytic active powder in the prepared decanted and filtered suspensions was estimated by measuring the dry weight of the residue. After the preparation of both decanted suspensions (S-D and S-D-MA) about 22% of the starting powder remains in suspension and in case of filtered suspensions (S-F and S-F-MA) about 10% of the starting powder. Prepared decanted suspension has 0.22 mass% of powder and filtered suspension 0.10 mas% of photocatalytic active powder.

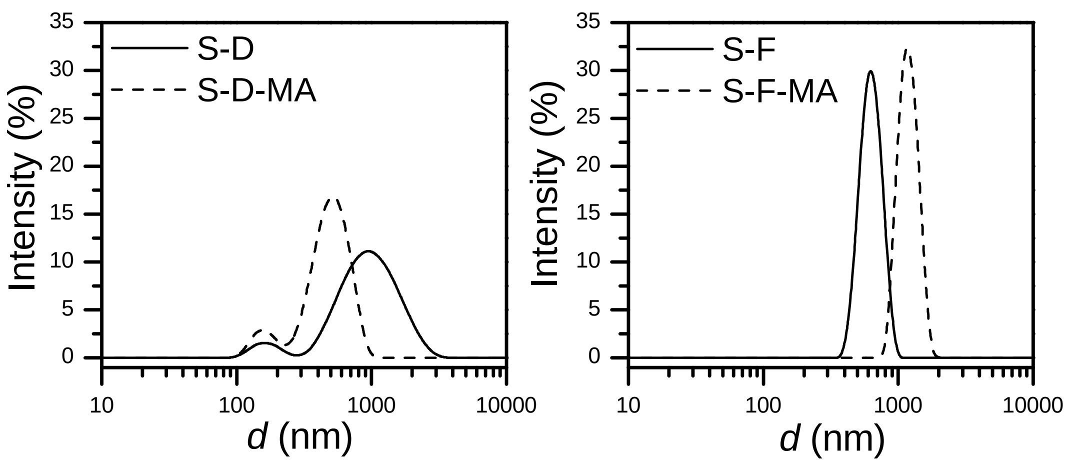

Fig. 3 – Particle size distribution of the designed suspensions prepared with untreated powder (S-D and S-F) and with mechanicaly treated powder (S-D-MA and S-F-MA).

The particle size distribution of all studied suspensions is presented in Fig. 3. When comparing the particle size distribution of two suspensions prepared with the as synthesized powder it can be concluded that the preparation of filtered suspension leads to the formation of the suspension with narrow monomodal particle size having average diameter of 600 nm. The decanted suspension has a wide bimodal particle size distribution with a larger fraction of particles with average diameter of 1000 nm and a very small fraction of particles with average diameter of 160 nm. The mechanical treatment of the powder has a positive effect in case of the decanted suspension regarding the decrease of suspension particle size lowering the size of the larger particles to 500 nm. Nevertheless, the mechanical treatment increases the particle size of the filtered suspension to 1200 nm. All of the studied suspensions can be characterized as micro-sized, which could present some difficulties regarding the stability. However, since the aim of this study was to develop coating that has appropriate compatibility with a ceramic tile chemical and surface properties, the micro-size of the particles in the suspension does not have to be a dissadvantage considering the pore size of ceramic tile within 1-2 μm range.[31]

Characterization of the photocatalytic coatings

The results of the evaluation of photocatalytic activity based on the RhB removal efficiency are presented in Fig. 4. All of the studied coatings showed photocatalytic activity towards the photo degradation of RhB. The highest removal efficiency among studied series after 3.5 h of UV irradiation exhibited the coating prepared with the decanted suspension (C-D). Discussing the influence of the suspension preparation, it could be concluded that the coating prepared with the decanted suspension has higher removal efficiency than coating prepared with filtered suspension because of the higher amount of photocatalytic powder present in the coating. Nevertheless, the removal efficiency of the coating prepared with the decanted suspension is not twice higher that the removal efficiency of the coating prepared with the filtered suspension, although the amount of photocatalytic material is twice higher in the decanted suspension. Taking this fact into account, the removal efficiency of C-F sample can be declared as very good, considering the presence of very small amount of the photocatalyst.

The removal efficiency of coating prepared with the mechanicall activated decanted suspension drastically lowered (17.5% after 3.5 h of UV irradiation) in comparison to coating prepared with the decanted suspension and no mechanical activation of powder (30.5% after 3.5 h of UV irradiation). It could be concluded that the mechanical activation of powder had a negative effect on the decanted suspension. On the contrary, the mechanical activation of the powder had a slight positive effect on the photocatalytic activity of coatings prepared with filtered suspensions.

The results of the average initial contact angle of the referent sample and of all studied coatings as the function of the UV irradiation time are presented in Fig. 5. The surface of the referent ceramic tile without coating is hydrophobic (94°) and does not change with the exposure to the UV light. After the deposition of the coating the contact angle decreases in the case of coating prepared with filtered suspension (90°) and slightly increases for the coating prepared with the decanted suspension (95°). For both coatings prepared with the as synthesized powder (C-D and C-F) a decrease in average initial contact angle is observed as the function of UV irradiation time, confirming the photo-induced hydrophilicity of the coatings. Comparing these results with the photocatalytic RhB removal efficiency and considering the amount of photocatalytic powder present in both coatings, it could be concluded that generally the coating prepared with the filtered suspension has better photo-induced properties. The mechanical treatment of the powder again has a negative effect on both coatings increasing slightly the average initial contact angle in the case of coating prepared with filtration, and significantly for the coating prepared with the decanted suspension.

It could be observed that mechanical treatment of the photocatalytic powder does not generally have a positive effect on the photo-induced properties of the coatings (RhB removal efficiency and initial contact angle). The improvements regarding the particle size distribution obtained by the mechanical treatment are overruled by the mechanochemical reactions, leading to the formation of the less photocatalytic active phases.

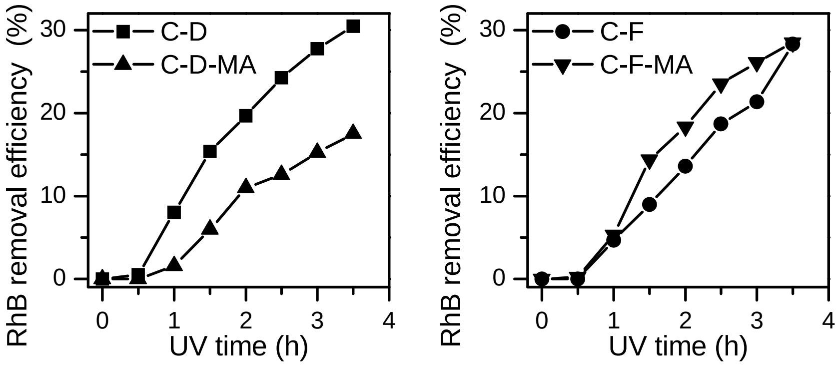

Fig. 4 – RhB removal efficiency of the studied coatings.

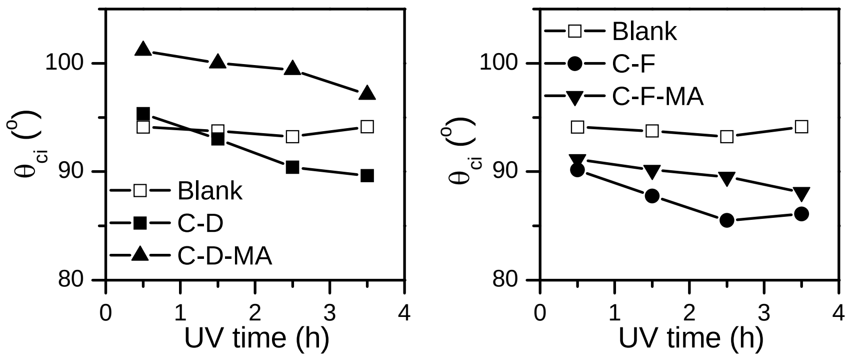

Fig. 5 – Average initial contact angle of all studied coatings as function of the UV irradiation time.

Table 2

Measurements of R_a parameter values for the coated ceramic tiles and coated ceramic tiles after the durability testing

Before durability testing	R_a (μm)	After durability testing	R_a (μm)
C-D	2.48	D-C-D	2.35
C-D-MA	2.21	D-C-D-MA	2.28
C-F	2.21	D-C-F	2.45
C-F-MA	2.11	D-C-F-MA	2.15

The results of the surface roughness measurements, evaluated based on R_a parameter, are presented in Table 2. Since the R_a parameter value of the referent sample (ceramic tile without coating) is 2.24 μm and very similar to the R_a parameter values of all studied samples, it could be concluded that the deposition of photocatalytic coating onto the ceramic tile surface does not change the surface roughness significantly.

Durability testing of photocatalytic coatings

The RhB removal efficiency of studied coatings before and after durability testing is presented in Fig. 6. The removal efficiency decreased significantly after the durability testing for the coatings prepared with both decanted suspension without and with mechanical treatment of powder, pointing out that these coatings have a very low resistance towards rinsing with water. On the contrary, the coating prepared with the filtered suspension showed no change in removal efficiency after durability tests, whereas, the coating prepared with mechanically treated powder and filtered suspension showed a small decrease in removal efficiency. Considering these results, it can be concluded that both coatings prepared with filtered suspension exhibited better resistance towards rinsing with water when compared with the coatings prepared with decanted suspension.

The results of the average initial contact angle measurement of all the studied samples as the function of the UV irradiation time before and after the durability testing is presented in Fig. 7. A significant increase in average initial contact angle is observed for both coatings prepared with the untreated powder suggesting a very low resistance towards rinsing with water. On the contrary, both coatings prepared with the mechanically treated powder exhibited better resistance towards rinsing with water. Based on these observations it can be concluded that mechanical treatment of powder has a positive effect on the stability of coatings regarding the photo-induced hydrophilicity.

The results of the surface roughness after durability testing method (Table 2) showed no significant differences in roughness before and after durability testing for all studied samples suggesting a good compatibility of coatings with ceramic tile and a stability of coatings towards the rinsing with water.

Taking all of the results into consideration, it could be concluded that mechanical treatment of photocatalytic powder does not have a positive effect on the photocatalytic behavior of the deposited coatings. The preparation of the photocatalytic suspension by filtration results with the formation of better photocatalytic properties of deposited coatings since, although having much smaller amount of photocatalytic powder, it shows similar removal efficiency, better photo-induced hydrophilicity and better stability towards rinsing with water.

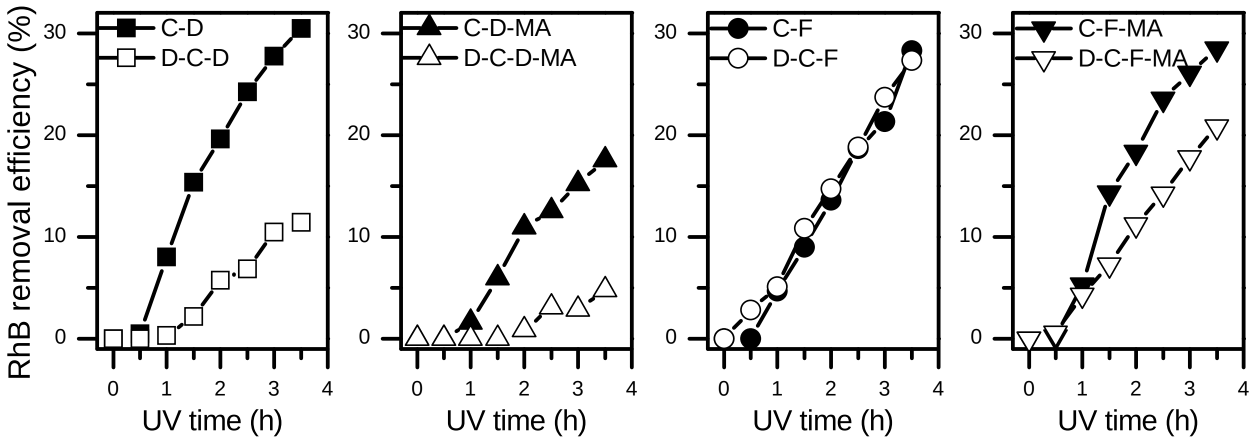

Fig. 6 – RhB removal efficiency of studied coatings before and after durability testing.

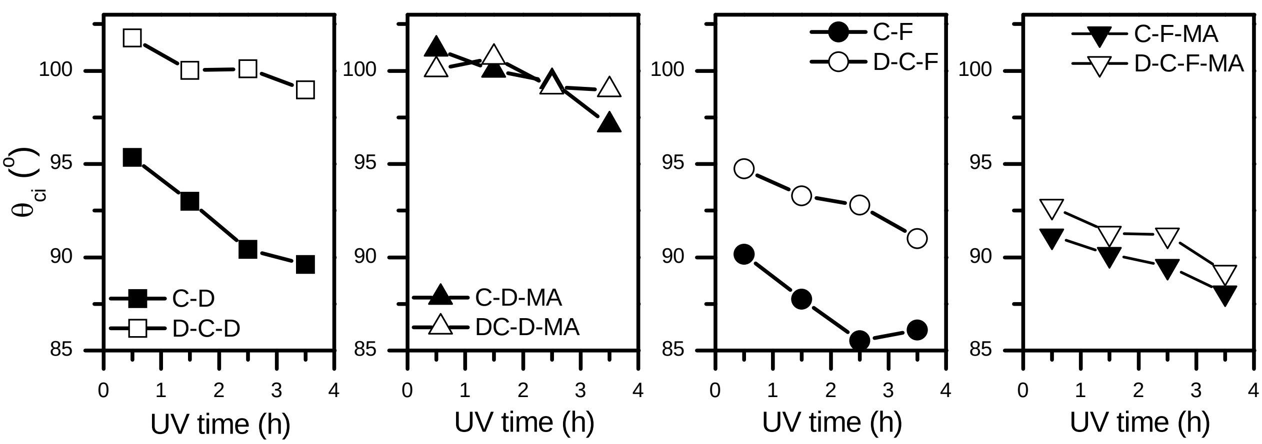

Fig. 7 – Average initial contact angle of studied coatings as function of the UV irradiation time before and after durability testing.

CONCLUSIONS

In this study the mechanical treatment of the TiO_2-ZnAl layered double hydroxide based photocatalytic powder was performed. It was observed that during the mechanical treatment, mechanosynthesis of complex oxides occurs leading to the thermal decomposition of layered double hydroxides and formation of mixed oxides. The suspensions prepared with the as synthesized and mechanically treated powder were not stabile and sedimentation of a considerable amount of photocatalytic powder was observed. In order to eliminate the presence of large particles and stabilize the suspension, the suspension was decanted or filtered. The preparation of filtered suspension leads to the formation of the suspension with narrow monomodal particle size, whereas the decanted suspension has a wide bimodal particle size distribution. The amount of remaining photocatalytic material is twice higher in decanted suspension. Considering the amount of photocatalytic powder present in both coatings, it could be concluded that generally the coating prepared with the filtered suspension has better photo-induced properties (photocatalytic RhB removal efficiency and surface hydrophilicity) and better stability towards rinsing with water. These results suggest that since the nature of photocatalytic active sites is similar for both decanted and filtered suspension, the narrow monomodal particle size distribution in filtered suspension is responsible for better performances of coating. It could also be observed that mechanical treatment of photocatalytic powder does not generally have a positive effect on the photo-induced properties of the coatings (RhB removal efficiency and initial contact angle). The improvements regarding the particle size distribution obtained by the mechanical treatment are overruled by the mechanochemical reactions, leading to the formation of the less photocatalytic active phases.

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