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# Pilot Scale Production and Compatibility Criteria of New Self-Cleaning Materials

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***Abstract*—**The paper involves a chain of activities from synthesis, establishment of the methodology for characterization and testing of novel protective materials through the pilot production and application on model supports.

It summarizes the results regarding the development of the pilot production protocol for newly developed self-cleaning materials. The optimization of the production parameters was completed in order to improve the most important functional properties (mineralogy characteristics, particle size, self-cleaning properties and photocatalytic activity) of the newly designed nanocomposite material.

***Keywords*—**Cultural heritage**.** Materials compatibility. Pilot production. Self-cleaning.

## I. Introduction

DEGRADATION phenomenon of the porous building materials, especially in the field of the Cultural Heritage, presents a commonly acknowledged problem. Namely, a constant exposure to numerous environmental conditions, pollutants of inorganic and organic origins, significantly contributes to deterioration processes of the porous building materials [1]-[3]. Deterioration processes are irreversible, involving both chemical and physical changes of the material, always starting at the surface of the material and penetrating steadily into the bulk.

Regarding the known degradation and deterioration problems of the building materials, a part of research in the field of photocatalysis has been focused in the development of self-cleaning and photocatalytic active building materials [4]. The increasing interest in combining photocatalytic active materials with building materials has been widely recognized [5]–[9] as well as most of the attention and research activities were driven to the application of nano-sized $TiO_2$ semiconductor as photocatalytic active material [10], [11]. It is a known fact that $TiO_2$ based materials possess self-cleaning properties which include photocatalytic activity (promote decomposition of various organic and inorganic pollutants) and photo-induced surface hydrophilicity activated by UV-A light irradiation. The well-known synergy of the photocatalytic action and hydrophilicity effect is very important in sustaining the surface with self-cleaning property [12]. The deterioration, degradation and damage of the porous building materials could be avoided by their adequate surface protection. Based on these facts, the photocatalysts based on $TiO_2$ / nano-coatings could provide decomposition of the organic compounds and inhibit the attachment of the organic/inorganic substances on the coated surface [13].

The main aim of this paper was to present the established pilot production of the developed $TiO_2$/LDH coating precursors in order to be used for protection of the Cultural Heritage immovable objects. A newly developed coating precursor was produced by using the established pilot production line in the HEROMAT project [14]. The functional properties (*mineralogical characteristics, particle size distribution, suspension stability, photocatalytic activity and self-cleaning properties*) were evaluated.

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## II. Development and Optimization of the Pilot Production Line

The newly synthesized nanomaterials, based on the layered double hydroxides - LDH (e.g. anionic clays) and the photocatalytic active $TiO_2$, were developed in two step production:

- new materials ($TiO_2$/LDH) were synthesized by modified low super saturation co-precipitation method (with a constant pH value) – *synthesis protocol,*
- suspension stabilization process was performed by dilution procedure with adding an appropriate polyelectrolyte stabilizer. The amount of the newly synthesized nanomaterial was 1 wt.%.

The pilot scale production was optimized in order to satisfy the requirements of ***ISO 9001/2008, ISO 14001/2004*** standards. During construction and development of the production line (Fig. 1) it was realized that additional optimization of certain process parameters (raw materials flow, pH value range, stirring rates during synthesis and time for stabilization, etc.) was required in order to significantly decrease the cost of the pilot scale production. At the same time it was mandatory to keep the properties such as particle size distribution, self-cleaning efficiency and photocatalytic activity on the same level. The following processes parameters were optimized:

- raw material flow rate during the synthesis and stabilization,
- pH value range; during the synthesis step it was kept constant, while during the stabilization step it was slightly increased,
- stirring rate during stabilization was considerably

increased in order to decrease the stirring time (from 24 hours to 30 minutes).

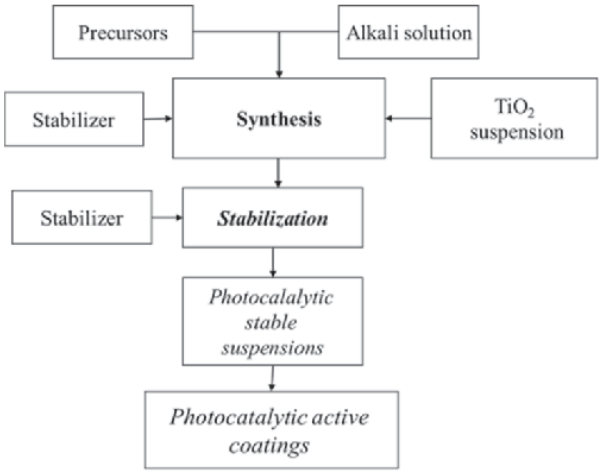



Fig. 1 Scheme of the pilot scale production

## III. Materials and Characterization Methods

For the development of protective coatings, inorganic-inorganic nano composites based on layered double hydroxides (LDH) associated with the photocatalytic active $TiO_2$ were synthesized. Commercially available precursors were continuously added together with the alkali solution in order to maintain a constant pH value during the synthesis (9.2 – 9.3). After the dilution of the synthesized material, stabilization procedure was performed resulting with a photocatalytic suspension [14].

The developed suspension was deposited by spray technique on the surface of the laboratory produced model substrates (Brick 1 and Render 2, dimensions 4x5x2 cm). These model substrates were prepared in accordance with the following characteristics of the historical materials sampled from the Bač Fortress, Serbia: chemical and mineralogical composition, mechanical, textural, surface and mechanical properties [14]. The quality control, regarding the phase composition of the synthesized nanocomposite, was performed by XRD analysis (*Philips PW1710 device*). The following experimental conditions were used: CuKα radiation with 1.5408 Å wavelengths in the 10 – 60° of 2θ range, scan rate 0.02°, 0.5s per step.

The particle size distribution (PSD) of the prepared stable suspensions was performed with *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. The results are presented in Fig. 2.

The photocatalytic behavior of the coated samples (Brick 1 and Render 2) was investigated by monitoring the change of Rhodamine B (RhB) concentration under UV/VIS irradiation. In order to saturate the samples before the photocatalytic assessment, a preabsorption test with RhB solution (10 ppm $dm^{-3}$, 24h) was carried out. After the preabsorption procedure, the RhB solution was replaced with a fresh solution and the samples were irradiated for 30, 90, 150 and 210 min (EVERSUN lamp, intensity of UV-A and Visible light spectra were 8 $Wm^{-2}$ and 0.3 $Wm^{-2}$, respectively). A UV/VIS spectrophotometer (*EVOLUTION 600 spectrophotometer*) was used to carry out the monitoring of the RhB concentration change at the major absorption peak (at $\lambda = 554$ nm). The photocatalytic activity was evaluated based on the efficiency of RhB degradation at the given absorption peak and expressed by the following equation:

$$Photocatalytic\ activity\ (\%) = [(C_0 \cdot C)/C_0] \cdot 100 \quad (1)$$

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

Contact angle measurements of the coated model substrates (Brick 1 and Render 2) were performed with *Surface Energy Evaluation System, Advex Instruments, (Brno, Czech Republic*) in order to evaluate the self-cleaning phenomenon (hydrophilicity effect) of the coated model substrates measuring the initial contact angle ($\theta_{ci}$). The experimental fluid was glycerol. The relevant data for the contact angle measurements were:

- Sample dimensions: 4 x 4 cm,
- Experimental fluid: glycerol
- Volume value of the glycerol drops: 5ml

## IV. Results and Discussion

### *A. Quality Control for the First Step of the Pilot Scale Production*

Four industrial tryouts were done (Table I) in order to test the implemented changes of the process parameters (pH value and temperature).

TABLE I
Experimental Conditions of the Industrial Tests

| Industrial test | pH value | Temperature (°C) |
|---|---|---|
| Test 1 | 9.25 | 33.9 |
| Test 2 | 8.11 | 34.2 |
| Test 3 | 9.31 | 33.7 |
| Test 4 | 9.45 | 34.0 |

The influence of the pH value and temperature (Table I) on the mineralogy and particle size distribution (PSD) was evaluated (Figs. 2 and 3). Namely, the main peaks of the LDH structure (marked with 0, Fig. 2) in the case of the Test 2 were not visible as in the case of the Tests 1, 3 and 4. The problem with the Test 2 was clearly related to the control of the pH value during the synthesis (Table I) which implies the importance of this parameter during the synthesis protocol. In the case of the Tests 1, 3 and 4, the XRD peaks for the LDH structure are sharp and with high intensities that suggests a well-defined crystal structure [15].

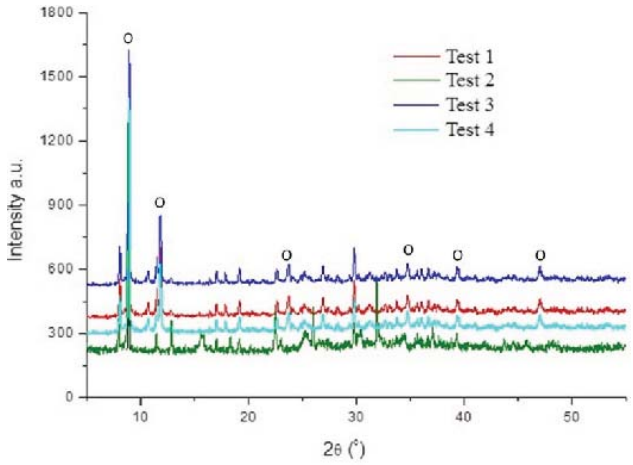



Fig. 2 XRD analyses of the sample synthesized in the industrial tests 1 – 4, 0 - LDH

The PSD analysis revealed difference between the Test 2 and the Tests 1, 3 and 4 (Fig. 3). It was observed that the mean diameter of the particles for the synthesized materials (Tests 1-4) were 256 nm, 548 nm, 289 nm and 298 nm, respectively. Evidently, there is a significant influence of the pH value, during the synthesis protocol, on the PSD of the designed photocatalytic suspension.

Due to inappropriate mineralogy and PSD characteristics of the synthesized nanoparticles, the *Test 2* was not considered for the further quality control of the synthesis protocol.

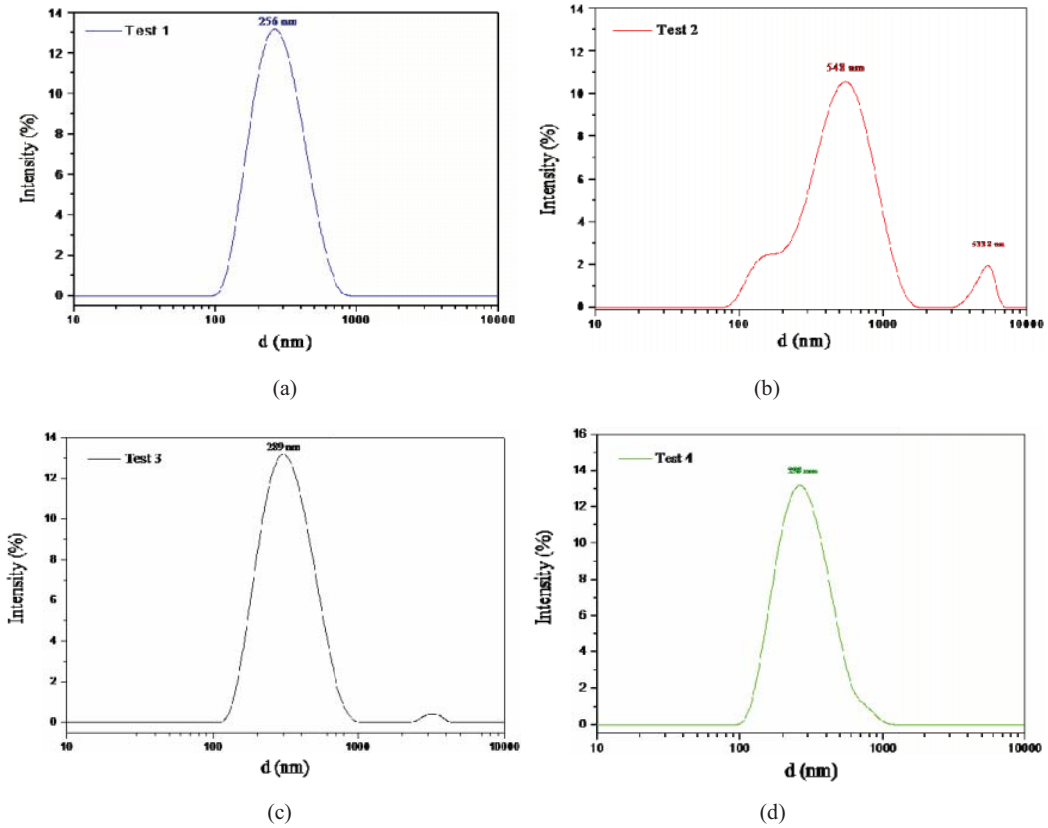



Fig. 3 Particle size distribution (PSD) of the prepared industrial suspensions (a) Test 1, (b) Test 2, (c) Test 3, (d) Test 4

The results of the photocatalytic effect assessment of the Tests 1, 3 and 4, by monitoring the Rhodamine B (RhB) degradation efficiency, with UV/VIS irradiation, are presented in Fig. 4. As a model substrate was used the Brick 1. The obtained results confirm the presence of the photocatalytic phenomenon for the suspensions of the Tests 1, 3 and 4 on the coated surface of the porous Brick 1. Namely, an increasing of the photocatalytic activity with UV/VIS irradiation for all synthesized test materials was observed: after 3.5h of UV/VIS irradiation, the photocatalytic activity was around 5 %, while with a prolonged irradiation, it was 17.27 %, 18.76 % and 19.64 % for Test 1, Test 4 and Test 3, respectively.

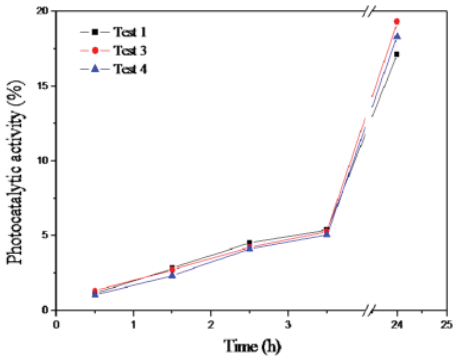



Fig. 4 Photocatalytic activity of the coatings obtained by deposition of the suspensions of the Tests 1, 3 and 4

Since the mineralogy and PSD properties were the same for the Tests 1, 3 and 4, the photocatalytic performance was the decisive parameter which singled out the ***Test 3*** and its process parameters during the synthesis (pH = 9.31 and = 33.9°C).

*B. Quality Control for the Second Step of the Pilot Scale Production of the Suspension Test 3*

In order to establish the quality control for the second step of the pilot scale production, several characterization techniques were used:

- PSD analysis and zeta potential assessment
- Self-cleaning properties – measuring the initial contact angle, $\theta_{\chi\iota}$
- Photocatalytic activity - (UV/VIS) spectrophotometry.

The most important functional properties (*self-cleaning effect, photocatalytic activity and particle size distribution*) of the chosen suspension Test 3 were measured immediately *after the stabilization* (fresh) and after *two months* of its storage (aged) in order to investigate its stability.

The results of the PSD and Zeta potential measurements of the industrial photocatalytic suspension related to the storage period are presented in Fig. 5 and Table II.

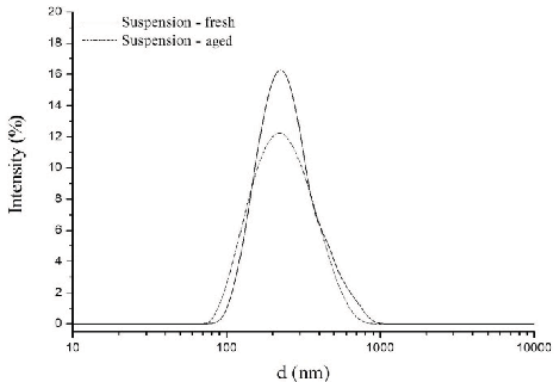



Fig. 5 Comparison of the PSD of the fresh and aged suspension of the Test 3

TABLE II
ZETA POTENTIAL MEASUREMENT

| Suspension Test 3 | Zeta potential (mV) |
|---|---|
| Fresh | - 42.5 |
| Aged | - 44.7 |

According to the results of the PSD analysis (Fig. 4), it was concluded that there are no differences noted after two months of storage. In addition to the observed stability, the value of zeta potential was unchanged (Table II) which implies that the produced photocatalytic suspension can be considered as stable in the defined period of time (2 months of storage).

The photocatalytic effect was evaluated by applying the two suspensions: fresh and aged on the Brick 1 and the Render 2. The presence of the photocatalytic phenomenon was noted on both cases due to increasing of the photocatalytic activity with UV/VIS irradiation. Namely, after 3.5h of UV/VIS irradiation, the photocatalytic activity was unchanged regardless the storage period (Fig. 6). The obtained results indicate the suitable stability of the designed photocatalytic suspension regarding its photocatalytic activity on the porous model substrates.

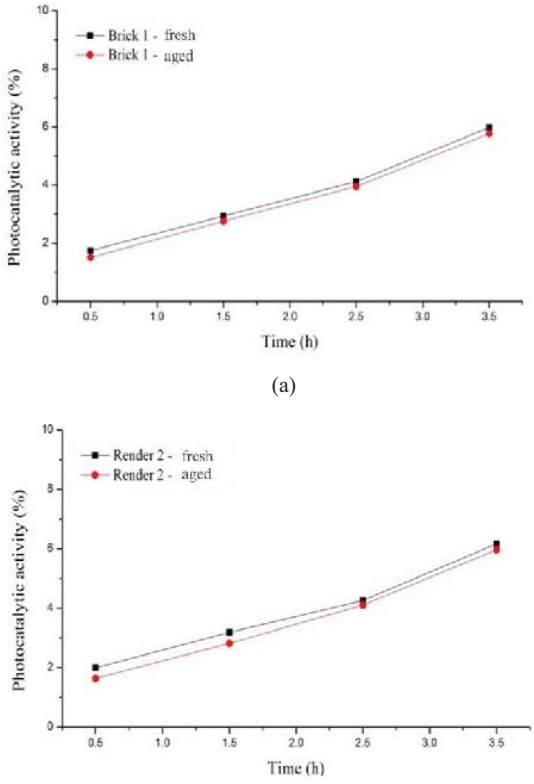
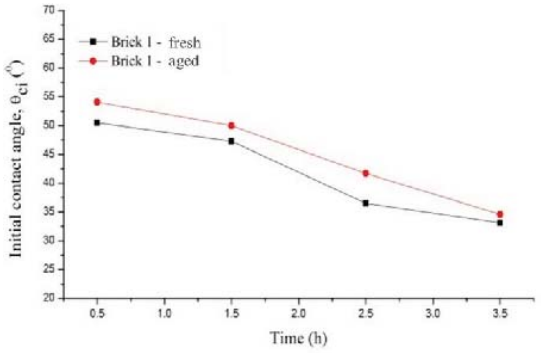
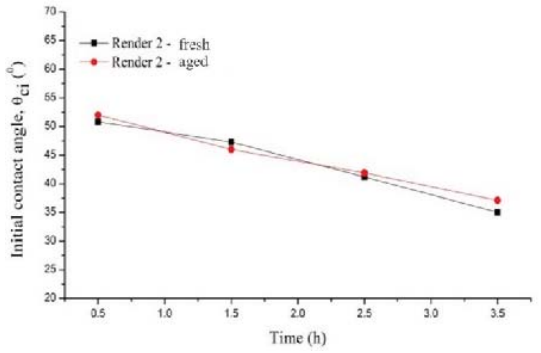



Fig. 6 Comparison of the photocatalytic activity of the fresh and aged suspensions deposited on (a) Brick 1 and (b) Render 2




(a)




(b)

Fig. 7 Comparison of the self-cleaning efficiency by measuring the initial contact angle ($\theta_{ci}$) of the fresh and aged suspensions deposited on (a) Brick 1 and (b) Render 2

The assessment of the self-cleaning properties of the designed photocatalytic coating was performed by measuring the initial contact angle, $\theta_{ci}$. The decreasing values of the initial contact angle indicate the existence of a notable self-cleaning phenomenon of the coated surface of the Brick 1 and Render 2 model substrates. Moreover, there were no noticeable differences between the coatings originated from the fresh and aged photocatalytic suspension (Fig. 7).

According to the obtained results and their analysis, the following quality testing procedures and methods were proposed to be applied in a regular control of the produced photocatalytic suspension:

- Particle size distribution and zeta potential assessment
- Self-cleaning properties – measuring the contact angle, $\theta_{ci}$,
- Photocatalytic activity - (UV/VIS) spectrophotometry

## V. Conclusions

The pilot scale production of the stabilized photocatalytic suspension was designed and established. During the development of the pilot production line the optimization of the production parameters was completed in order to improve the most important functional properties (*mineralogy characteristics, particle size, self-cleaning properties and photocatalytic activity*) of the newly designed nanocomposite materials.

Appropriate particle size distribution (no particles higher than 900 nm) and suspension stability (no significant change of the value of zeta potential) were achieved for the photocatalytic suspensions (tests 1, 3 and 4) produced according to the designed production protocol.

A very good stability of the produced photocatalytic suspension, Test 3, was confirmed since no changes of the particle size, self-cleaning properties and photocatalytic activity were noticed regardless of the storage period (two months).

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