Research Regarding the Influence of TiO$_2$ Nanoparticles on the Performance of Cementitious Materials

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Abstract. Urban buildings are subject to deterioration and degradation due to the action of external factors, air pollutants, water, compounds resulting from fuel combustion used for heating and transportation, etc. Research on self-cleaning cementitious materials is developing at fast pace and contributes to the high interest in the industry in the decrease of environmental pollution, which is of real interest. The aim of this paper is to highlight the influence of the addition of TiO$_2$ nanoparticles on the self-cleaning ability of cementitious materials, under staining with an aqueous solution of a rodamina B, followed by exposures to the action of UV rays, followed by artificial rain cycles and to determine the physico-mechanical properties of the material, as well as the white degree of the samples and their self-cleaning. Based on experimental research results it can be said that the white degree of the samples increased with the increase of the TiO$_2$ amount in the mixtures. Several other factors such as the intensity of the UV light also affected the self-cleaning capacity of the samples, better results being recorded for higher UVA intensity. The TiO$_2$ amount in the mixtures also influences fresh and hardened state properties of the material such as setting time, apparent density, water absorption and porosity of the material. It can therefore be said that it is necessary to identify an optimal range of TiO$_2$ nanoparticles concentration in the cementitious matrix, in order to obtain the maximum cumulative benefits in terms of self-cleaning capacity, physico-mechanical properties and costs.

1. Introduction

Due to the action of external factors, pollutants from air, water, compounds resulting from the combustion of fuels used for heating and transport, urban constructions are subject to deterioration and degradation. Thus, research on self-cleaning materials and contributing to pollution reduction is of real interest. Currently, worldwide, the possibility of producing cementitious composite materials with self-cleaning properties is widely reported due to the photocatalytic capacity of titanium dioxide nanoparticles (TiO$_2$), used as an addition or as a substitute for a part of cement. It also raised awareness of the importance of building sustainability and thus the need for a material with self-cleaning properties mainly used in urban areas to ensure a cleaner environment and reduce maintenance costs.

Accidentally, in 1995 one of the most important properties was discovered, namely the superhydrophility effect of the surface of a composition of titanium dioxide-silicon dioxide, TiO$_2$-SiO$_2$, in the presence of UV rays. This effect occurs as a result of the oxido-reduction reaction of H$_2$O, forming OH$^-$ groups. Due to the multitude of OH$^-$ formed groups, the water that reaches the surface of the material containing TiO$_2$-SiO$_2$ forms more flattened, lamellar droplets, which take the impurities from the surface of the material. Unlike TiO$_2$ where the photocatalytic effect ceases in the absence of
UV radiation, in the case of TiO$_2$-SiO$_2$ mixtures, the photocatalytic effect continues for hours even after the removal of the source of UV radiation [1-3]. The first official publication regarding the production of cementitious materials with self-cleaning properties was registered in 1997 by Luigi Cassar [4-6]. Subsequently, it was proved that the self-cleaning effect is actually the sum of two mechanisms that occur simultaneously: increasing the hydrophilicity of the surface of cementitious composites containing TiO$_2$ nanoparticles, and catalysing redox reactions, under the action of UV radiation, which allow oxidation and decomposition of organic particles on the cementitious surface (particles that produce the effect of soiling) into smaller particles, molecules with simpler structure, which can either be easily taken over by rainwater), either continue to decompose until their final reduction according (Figure 1) [7-9]. This combination of mechanisms, which creates the self-cleaning property of cementitious composites containing TiO$_2$ nanoparticles is also schematically represented in Figure 2.

![Organic compound reduction mechanism](image1)

**Figure 1.** Organic compound reduction mechanism.

![Schematic representation of the self-cleaning capacity](image2)

**Figure 2.** Schematic representation of the self-cleaning capacity by the cumulation of the two mechanisms: the process of photocatalytic oxidation of organic substances (left) and easing the removal of foreign substances by increasing surface hydrophilicity [7].

To highlight the ability of self-cleaning, research in the literature indicates several test methods, among which the method of staining with rhodamine B is the most common. The principle of this method is relatively simple: the surface of the test specimen is stained with a generally aqueous solution of rhodamine B, after which it is exposed to the action of UV rays, by combining or not with additional actions, for example artificial rain. Measurable indicators expressing the degree of staining / cleaning of the surface are identified, which are compared [10-12]. UNI 11259 standard regulates this test indicating the amount of aqueous solution of Rhodamine B applied to the surface (0,05 g / dm$^2$), and as a measurable indicator, the measurement of the staining degree [12]. Literature reports that comply with this standard and reports of tests performed with some deviations from the standard especially regarding the concentration of the solution of Rhodamine B (0.5 g/l and 1 g/l, respectively) [12].

Literature experimental results led to several conclusions:

- The report of the Institute of Chemical Technology, Prague, indicates a 20% discoloration after 1 minute exposure and 75-95% after 4 hours exposure to UV rays [12];
The photocatalytic efficiency of TiO$_2$ nanoparticles is not altered by accelerated ageing cycles on cementitious composites [13];

Folli indicates the dependence of self-cleaning performance on the granulometric size and distribution of TiO$_2$ nanoparticles. At the same time this is indicated to achieve a significant effect after only 30 minutes of exposure to UV radiation of a cementitious composite sample characterized by water/cement ratio of 0.4 and TiO$_2$/cement ratio 3.5:96.5, stained with Rhodamine B 1g/l solution, exposed to UV radiation with wavelength in UVA II domain. On the other hand, the exposure of the samples to accelerated ageing cycles simulating a period of 5 years under climatic conditions typical of northern Denmark, a good odelling and durability of this property was observed [10, 14];

Khataee et al. Report the increase in self-cleaning performance with the increase in TiO$_2$ nanoparticles in the range 0%-5% [11];

Odedra et al. Report the existence of self-cleaning capacity in the case of an existing structure, Church “Dives in Misericordia”, Rome, made of concrete with a ratio of 3.5: 96.5, TiO$_2$: cement [15];

Bianchi et al. On the one hand, confirm the effect of the self-cleaning capacity of TiO$_2$ nanoparticles addition in the cementitious composites, and, on the other hand, shows the influence of the type of particle, the structure of the crystal size, particle size distribution, the ratio of the three structures (rutile – tetragonal crystalline structure, anatase peaks – tetragonal crystalline structure and brukit – odelling ic crystalline structure) in the performance of these materials [16];

Zhang et al. It indicate on one hand the reduction of the self-cleaning effect with the reduction of the time of action of UV rays, the long-term efficiency of this performance, for cementitious composites containing up to 6% TiO$_2$, however recommend keeping the dosage of TiO$_2$ to a maximum of 2%. The authors note a possible reduction in performance with increasing irradiation duration, performances that are subsequently recovered as soon as the specimen is subjected to the action of wet-dry cycles, artificial rain, so washing removal of reaction products from the surface [17].

Research in the literature has shown that adding TiO$_2$ nanoparticles also influences the odell-mechanical properties of cement paste, cement-based mortars and concrete. Thus, when introducing quantities of TiO$_2$ nanoparticles in the range 0.5% - 10% in the cementitious matrix, it was observed that the initial and final setting time decreases as the content of TiO$_2$ nanoparticles increases [18]. The decrease of the setting time as the amount of TiO$_2$ nanoparticles introduced into the cement paste increases, can be explained by the catalyst effect that nanoparticles have on the cement hydration reaction and by the fact that they can function as potential nuclei of accumulation of hydration products [11, 19, 20].

The literature indicates a reduction in porosity as the amount of nanoparticles in the cementitious mixture increases, the change in the size and orientation of the crystals of cement hydrating products and the formation of a greater amount of calcium hydroxilicate gel C-H-S [23-27].

As the amount of nanoparticles in the mixture increases, water absorption decreases, with 0.5% being the optimal amount of nanoparticles added if water absorption is assessed at the age of 28 days and 90 days, as reported by Rashad [18]. If water absorption is assessed 7 days after casting, the optimal amount of TiO$_2$ nanoparticles addition is 4% [18]. However, if water absorption is assessed at the age of 2 days after casting, the addition of TiO$_2$ nanoparticles increases this parameter [18].

The aim of this paper is to highlight the influence of the addition of TiO$_2$ nanoparticles on the self-cleaning capacity of cementitious composites, under staining with an aqueous solution of a Rhodamine B, followed by exposure to the action of UV rays (in 2 cases of UV radiation incidency on the surface of the composite material), followed by artificial rain cycles and to determine the odell-mechanical properties of the material, as well as the white degree of the samples and the end of the self-cleaning procedure.
2. Materials and methods

The analysis of the influence of the addition of TiO₂ nanoparticles on the performance of the cementitious matrix, has been achieved producing samples using white Portland cement CEM I 52,5 R, with the addition of Degussa P25 TiO₂ nanoparticles, while maintaining a constant ratio of water:dry mixture = 0,5, where the dry mix was considered to be the total amount of white Portland cement and TiO₂ nanoparticles. The amount of TiO₂ nanoparticles added in the preparation of cementitious composites was: 0% (control sample), 1%, 2%, 3%, 4% and 5% (percent relative to the amount of dry cement). Beginning and end of setting time was determined on the fresh mixtures, according to EN 196-3. At the same time, specimens with dimensions of 130x85x10mm were produced. The test specimens were conditioned for 24 hours in molds, at 20°C temperature and 90% relative humidity, without any light. After demolding, the specimens were completely immersed in water at a temperature of 20°C, without light, for 27 days. After maturation, apparent density of the test specimens was determined according to EN 12390-7, absolute density according to EN 1907-6, porosity (as ratio between absolute and apparent density difference and absolute density), water absorption (EN 1015-18), and the white degree by direct measurement with portable WSB-1 leuco meter, on samples exposed to natural light, under laboratory conditions, as absorbed fraction of light directed.

The measurement of the white degree was initially performed without exposure of the specimens to the action of UV radiation, after which they were exposed 24 hours to the action of UV rays and the measurement was repeated. Exposure to UV action was achieved in a closed enclosure with 4 UVA light bulbs with wavelength in the characteristic range of 315-400 nm, providing an intensity of 3.8mW/cm². A set of test specimens was exposed to a total luminous flux intensity of 860 lux, and the second set of test specimens, similar to the first, was exposed to a total luminous flux intensity of 405 lux. The modelling of the total luminous flux was measured at the exposed surface of the samples. The variance of this modelling of the luminous flux was achieved by exposing the specimens in the first case at a distance of 10 cm and in the second case at a distance of 20 cm from the UV bulbs.

Experimental research on the self-cleaning capacity of cementitious composites containing TiO₂ nanoparticles consisted of staining, by the method of dripping the surface of the specimens with aqueous solution of rhodamine B (1g/l), then subjecting them to UV rays cycles, artificial rain, respectively drying (Figure 3). After each step of the diagram the white degree (WD) was measured and at established intervals the surface of the specimen was microscopically analysed (MA) in the stained area. Exposure to artificial rain and drying were carried out in the absence of any light source.

![Figure 3. Test diagram.](image)

The efficiency of the addition of TiO₂ nanoparticles on the self-cleaning character of the cementitious composites was visually analyzed by means of two measurable parameters:
- The white degree of the sample, determined in the stained area;
- Cleaning degree-representing the variation of the white degree of the sample after the test diagram, in the stained area, relative to the white degree of the stained sample but not yet exposed to UV light activation, washing under the action of artificial rain or drying, as in equation (1).

\[
GC = \frac{GA_f - GA_0}{GA_0} \times 100 (\%)
\]
where:

$GC =$ cleaning degree

$G_{A_f} =$ white degree of the specimen in the tarnished area after the test diagram has been completed

$G_{A_0} =$ the degree of initial whiteness of the stained sample but not yet exposed to UV light activation, washing under the action of artificial rain or drying

3. Results and discussions

The main aim of this study was to analyze the influence of the presence of titanium dioxide nanoparticles ($\text{TiO}_2$) on the following characteristics of cementitious composites: setting time, apparent density, absolute density, porosity, water absorption, white degree and self-cleaning capacity.

From the point of view of the influence of $\text{TiO}_2$ nanoparticles on the setting time, it can be said that with the increase in the amount of $\text{TiO}_2$ nanoparticles in the cementitious mixture, the setting time, both initial and final, decreases. The same evolution of recorded setting times can be defined by grade 2 polynomial functions (Figure 4), with a sufficiently high coefficient of accuracy ($R^2 = 0.9789$, respectively $0.9774$) in order to be used for the assessment of the initial time, respectively the final setting time for cementitious mixtures made with another content of $\text{TiO}_2$ nanoparticles, contained in the range 0% - 5%, under the conditions of preservation of the previously presented preparation conditions.

On the other hand, it is noted that the greater the addition of nanoparticles, the smaller the difference between the beginning and the end of the setting time, which means a strong influence of $\text{TiO}_2$ nanoparticles on the setting of cementitious composites. The influence of the addition of nanoparticles on the setting times is consistent with some specifications in the literature [18] and it probably occurs as a result of the acceleration of hydration-hydrolysis processes and the operation of nanoparticles as nuclei of formation and growth of the network of hydration-hydrolysis products specific to the cement setting.

![Figure 4](image-url)

**Figure 4.** Identification of polynomial functions for modelling the evolution of the initial/final outlet time, in relation to the content of $\text{TiO}_2$ nanoparticles in the cementitious matrix.

As for the apparent density in the hardened state of cementitious composites, it is noted that it does not vary in proportion to the content of $\text{TiO}_2$ nanoparticles. However, a constant range of high values is recorded in the concentration range of nanoparticles (4% - 5%). In the concentration range of $\text{TiO}_2$ nanoparticles added to the cementitious matrix, 0% - 5% relative to the dry cement quantity, apparent density evolution in relation to this variable can be expressed mathematically by a polynomial function of order 4 (Figure 5).

Experimental results regarding the absolute density of cementitious composites with the addition of $\text{TiO}_2$ nanoparticles also indicates that this parameter does not vary in proportion to the content of
nanoparticles, nor has it been possible to identify with sufficient precision a representative mathematical function (Figure 6).

Figure 5. Polynomial function of evolution of apparent density in relation to the content of TiO$_2$ nanoparticles in the cementitious matrix.

Figure 6. Absolute density of cementitious composites with the addition of 0% - 5% TiO$_2$ nanoparticles.

Porosity was determined by calculation based on experimentally obtained values for apparent density and absolute density, for each mixture. Thus, it was observed that the lowest value of porosity was obtained for a content of TiO$_2$ nanoparticles of 4% relative to the quantity of cement. In the case of cementitious materials with content of 1%, 2%, 3% and 5%, an almost constant porosity was noted. These results cannot be considered relevant for an analysis of the evolution of the parameter, considering that additional tests are necessary, possibly for a series of composites to which the addition of nanoparticles varies by one step less than 1% and over a concentration range extending beyond 5% (Figure 7). A similar situation, inconclusive and also requiring the development of experimental research, was also recorded in terms of water absorption (Figure 8).

Regarding the white degree, it was observed that for the same cementitious mixtures with the addition of TiO$_2$ nanoparticles, comparing the white degree initially recorded with the one recorded after 24 hours UV rays exposure, increased for all analyzed cases (Figure 9). It was noted that a
maximum increase in white was recorded, both as difference between the initial and final values and as percentage change relative to the initial value, for the mixture containing 2% TiO$_2$.

Figure 7. Porosity of cementitious composites with the addition of 0% - 5% TiO$_2$.

Figure 8. Water absorption of cementous composites with the addition of 0% - 5% TiO$_2$ nanoparticles.

Mixtures with content 1%, 3% and 4% TiO$_2$ nanoparticles addition had increases in the white degree, with differences between the final values and the initial values in the range of 0.4 units, as opposed to the cementitious matrix with content of 5% nanoparticles, for which there was an increase in the parameter by only 0.31 units from the initial value. This increase can be considered a first image of the photoactivation activity, respectively, the mixtures with the greater difference in the white degree with and without UV exposure are activated more strongly. The percentage increase in the degree of white after exposure to UV radiation for 24 hours relative to the initial value can be considered a measure of the effectiveness of the addition of nanoparticles on this parameter (Figure 10). It can be seen that additions of 1 – 4% TiO$_2$ provide a minimum 50% increase in white degree by photoactivation, and larger additions of nanoparticles, not only are not more effective, but even are unfavorable to the evolution of this parameter. Therefore, it can be said that a large amount of nanoparticles in the cementitious matrix does not guarantee a higher white degree of hardened material and no better photoactivation activity. It is essential to identify the optimal concentration range of nanoparticles, so as to achieve an optimal benefit-cost ratio, namely maximum efficiency photoactivation, while maintaining the other physical-mechanical performances of the cementitious composite, at the same time with a reasonable cost in relation to the benefits. This conclusion is consistent with some specifications in the literature [24].
exposure to UV radiation for 24 hours relative to baseline can be mathematically described by a grade 3 polynomial function (Figure 11).

![Figure 9](image1.png)

**Figure 9.** White degree before and after exposure to UV 24h of cementitious composites with the addition of 0% - 5% TiO$_2$ nanoparticles

![Figure 10](image2.png)

**Figure 10.** Difference between white degree of recorded for cementitious composites with the addition of 0% - 5% TiO2 nanoparticles exposed and, respectively, not exposed to UV action.

![Figure 11](image3.png)

**Figure 11.** Polynomial function of determining the percentage increase in the white degree after exposure to UV 24h.

From the point of view of the self-cleaning capacity of cementitious composites, visual, microscopic analysis and assessment of the white degree of test specimens according to the test schedule presented in the test diagram indicated the following:
Immediately after staining, the white degree of test specimens is significantly reduced, as expected, from values in the range (73–82) to values in the range (53 – 67), for test specimens exposed at a distance of 10 cm from UVA bulbs (860 lux) (Fig. 11) and from values in the range (73–82) to values in the range (57 – 67), for specimens exposed at a distance of 20 cm from UVA bulbs (405 lux) (Figure 13);

After staining, the variation curve of the white degree of the specimens retains a trend similar to the variation curve of the white degree of the unpaired specimens, respectively, the higher the content of TiO₂ nanoparticles, the higher white degree;

By exposing the tarnished specimens to the photocatalysing action of UV, the degree of white increases constantly, at each assessment after the predetermined exposure ranges (0.5 h, 1h, 2h, 3h, 4h, 24h). Visual discoloration of the spots is observed, and microscopic analysis notes that there is a discoloration especially of the surface in the immediate vicinity of micro-cracks occurring during the maturation process. The exception is the blank specimen, made without the addition of TiO₂ nanoparticles, in which only a slight change in the degree of staining is observed. This behavior of the blank specimen can be attributed both to the degradation of a small amount of organic molecules of Rhodamine B under the effect of ultraviolet radiation, and to a low but existing content of titanium dioxide in the cement composition, characteristic especially of White Cement, which was activated in the presence of UVA radiation;

The tests carried out by the Rhodamine B staining method provide evidence of the self-cleaning capacity of cementitious matrices enriched with TiO₂ nanoparticles by photoactivation under the influence of UVA rays. However, the experimental results obtained cannot provide the basis for a documented selection of the optimal content of nanoparticles, so that the cost – benefit balance is the most favorable;

The degree of cleaning of the test specimens obtained after completing the test diagram indicates on the one hand the influence of the concentration of TiO₂ nanoparticles in the cementitious matrix, and on the other hand the influence of the intensity of the incident ultraviolet radiation on the surface, on the self-cleaning capacity.

As seen, at an incidence UVA intensity of 860 lux, additions of 1% - 3% TiO₂ nanoparticles (quantity related to cement quantity) provide cementitious composite matrices a better self-cleaning capacity, expressed by the quantifiable parameter “cleaning degree (CD)”, compared to samples in which the addition of nanoparticles was higher (4%, 5%). However, this is not the case when the UVA
light intensity is reduced (405 lux). In this situation, two phenomena were observed. On one hand, the degree of cleaning decreases with an increase in the percentage of TiO$_2$ used up to 3%, after which an increase was observed again for the test specimens produced with 4% and 5%, respectively.

**Figure 13.** White degree of cementitious composites exposed to a UVA radiation intensity of 405 lux.

On the other hand, comparing the cleaning degree obtained for the composite matrix with 5% TiO$_2$ nanoparticles, it is observed that the difference between the values of this parameter obtained for the situation of UVA intensity of 860 lux and UVA intensity of 405 lux was very small, unlike the cases of samples with lower TiO$_2$ content where this difference is much greater (Figure 14). It can therefore be said that, on a case-by-case basis, in terms of the degree of cleaning, it may be more advantageous to use a lower or higher amount of TiO$_2$ nanoparticles. In Figure 15 and Figure 16 illustrative and demonstrative, images taken at microscopic analysis of the stained surface in various situations are presented.

**Figure 14.** Degree of cleaning of cementous composites.
Figure 15a. UVA 860 lux intensity test control sample: (a) initial; (b) 24 h UVA exposure; (c) after completing the test diagram.

Figure 15b. UVA 860 lux intensity test 3% TiO₂: (a) initial; (b) 24 h UVA exposure; (c) after completing the test diagram.

Figure 15b. UVA 860 lux intensity test 5% TiO₂: (a) initial; (b) 24 h UVA exposure; (c) after completing the test diagram.

Figure 16a. UVA 405 lux intensity test control sample: (a) initial; (b) 24 h UVA exposure; (c) after completing the test diagram.

Figure 16b. UVA 405 lux intensity test 3% TiO₂: (a) initial; (b) 24 h UVA exposure; (c) after completing the test diagram.

Figure 16b. UVA 450 lux intensity test 5% TiO₂: (a) initial; (b) 24 h UVA exposure; (c) after completing the test diagram.
4. Conclusions
Based on experimental research it can be said that with increasing the amount of TiO$_2$ in the cementitious matrix, the white degree increases, but also the capacity of self-cleaning of test specimens. The self-cleaning capacity is also influenced by the intensity of UV light flux on the surface of the sample, better results being recorded for a higher UVA intensity. In terms of setting time, it decreases with increasing concentration of TiO$_2$ in the cementitious matrix, which we cannot say about the apparent density, absolute density, water absorption and porosity, whose values do not vary proportionally with the content of TiO$_2$ nanoparticles, for the last three parameters it is not possible to identify a function of modeling their evolution in relation to the TiO$_2$ content.

The experimental results showed the following:

- The setting time, both initial and final, decreased, with the increase in the amount of TiO$_2$ nanoparticles in the cementitious mixture, conclusion in accordance with the literature;
- Regarding the apparent density of cementitious composites in hardened state, it is noted that a constant interval of high values is recorded in the concentration range of nanoparticles (4% - 5%);
- The absolute density, porosity and water absorption of cementitious composites with added TiO$_2$ nanoparticles tested do not vary in proportion to the nanoparticle content and functions could not be identified to express the evolution of these parameters in relation to the TiO$_2$ content;
- The lowest porosity value was obtained for a 4% TiO$_2$ nanoparticle content relative to the cement quantity. In the case of cementitious matrices with content of 1%, 2%, 3% and 5%, an almost constant porosity was noted;
- Comparing the white degree recorded initially with that recorded after 24 hours exposure to UV rays, it increased for all analyzed cases;
- With the increase in the quantity of TiO$_2$ introduced into the cementitious matrix, the white degree increased, but also the self-cleaning capacity of the specimens.
- Tests carried out by the method of staining with rhodamine B provide evidence of the self-cleaning ability of cementitious matrices enriched with TiO$_2$ nanoparticles by photoactivation under the influence of UVA rays;
- The degree of cleaning analyzed as a measurable indicator of the self-cleaning capacity was higher at a lower exposure distance from the UV source. However, in the case of cementitious composition with 5% TiO$_2$ following exposure to a lower UVA intensity (405 lux), the degree of cleaning obtained is almost equal to that obtained for exposure to a higher UVA intensity (860 lux). This observation indicates the need for in-depth analysis to establish the optimal addition of TiO$_2$ nanoparticles, depending on several factors, among which very important, the degree of sunshine, the incident light intensity on the surface;
- Similarly, the analysis of the types of functions identified as representative for the evolution of settings times, density, white degree, being functions of order greater than 1, therefore nonlinear, indicates the influence of several factors on these performances, the factor representing the TiO$_2$ content being only one of them;
- Achievement of an optimum ratio between benefit and cost, respectively, of photoactivation with maximum efficiency, while maintaining the other properties, physical and mechanical properties of the cementitious materials, along with a reasonable cost in relation to benefits, it is essential that the necessary conclusion is that it is consistent with the literature from the literature.

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