Rev. LatinAm. Metal. Mat.

Artículo Regular

www.rlmm.org

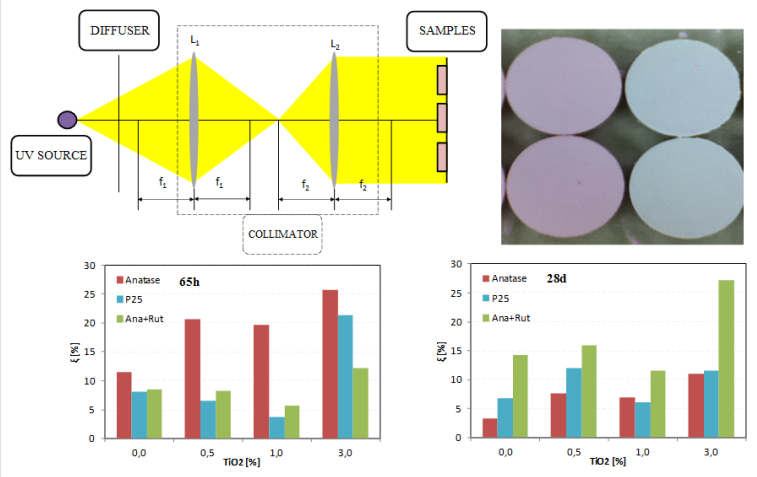
PHOTOCATALYTIC PROPERTIES EVALUATION OF PORTLAND WHITE CEMENT ADDED WITH TiO_2-NANOPARTICLES

Carolina Cárdenas[1], Jorge Tobón [2], Claudia García[1]*

1: Grupo de Cerámicos y Vítreos, Universidad Nacional de Colombia, Calle 59A # 63-20, Medellín, Colombia.

2: Grupo del Cemento y Materiales de Construcción, CEMATCO, Facultad de Minas, Universidad Nacional de Colombia, Calle 75 # 79A – 51, Medellín, Colombia.

**e-mail: ccardenr@unal.edu.co*



ABSTRACT

Photocatalytic activity of white Portland cement paste samples, added with 0.5, 1.0 and 3.0% wt of titanium dioxide nanoparticles, was evaluated trough the degradation of Rhodamine B. The degradation was measured by the change of the color coordinates CIE L*a*b* of samples exposed to a UV source and a photocatalytic efficiency coefficient, ξ, was calculated for two times of curing (65h and 28d). Three ratios of anatase:rutile were used (100:0, 85:15, 50,50) for each percentage of addition. Results showed that samples with the highest photocatalytic activity correspond to 3.0% of anatase at early ages, and 3.0% of anatase:rutile (50:50) at late ages.

Keywords: Photocatalysis, Nanoparticles of TiO_2, Portland Cement.

EVALUACIÓN DE LAS PROPIEDADES FOTOCATALÍTICAS DE CEMENTO PÓRTLAND BLANCO ADICIONADO CON NANOPARTÍCULAS DE DIÓXIDO DE TITANIO

RESUMEN

La actividad fotocatalítica de pastas de cemento Pórtland blanco, adicionadas con 0,5%, 1,0% y 3,0% en peso de nanopartículas de dióxido de titanio, fue evaluada a través de la degradación de Rodamina B. La degradación fue medida en función del cambio en las coordenadas de color CIE L*a*b* de las muestras expuestas a un fuente ultravioleta, UV, y un coeficiente fotocatalítico, ξ, fue calculado para dos edades de curado (65 horas y 28 días). Tres proporciones de anatasa:rutilo fueron empleadas (100:0, 85:15, 50:50) para cada porcentaje de adición. Los resultados mostraron que las muestras con la mayor actividad fotocatalítica correspondieron a un 3,0% de anatasa a edades tempranas y un 3,0% de anatasa:rutilo (50:50) a edades tardías.

Palabras Claves: Fotocatálisis, Nanopartículas de TiO_2, Cemento Pórtland.

Recibido: 20-02-2012 ; **Revisado:** 02-07-2012

Aceptado: 02-10-2012 ; **Publicado:** 12-11-2012

pISSN: 0255-6952 | eISSN: 2244-7113

Rev. LatinAm. Metal. Mat. 2013; **33** (2): 316-322

1. INTRODUCTION

Catalysis under radiation, called photocatalysis, is an area of great interest in basic science, with many environmental applications such as the reduction of harmful pollutants found in the air and in the water [1] and the self-cleaning applications useful in the construction industry. The air pollution (NOx, SOx, CO_2, VOCs) caused by road traffic and industry is one of the major problems in urban areas [2] that can be reduced using the photocatalytic phenomena occurring on the surface of some semiconductors such as TiO_2, ZnO, CdS, Fe_2O_3 and WO_3. A photocatalyst is characterized by its capability to adsorb simultaneously two reactants, which can be reduced and oxidized by a photonic activation through an efficient absorption ($h\nu \geq E_g$). The ability of a semiconductor to undergo photoinduced electron transfer to an adsorbed particle is determined by the band energy positions of the semiconductor and the redox potential of the adsorbates. The energy level at the bottom of conduction band is the reduction potential of photoelectrons. The energy level at the top of valence band determines the oxidizing ability of photoholes, and its value reflects the ability of the system to promote reductions and oxidations [3].

Worldwide, photocatalysts have been used in ceramic tiles [4], glass [5], concrete [6], gypsum, roofing tiles, sealers and blends of cements [7-9] to create composites with self-cleaning, decontaminating and anti-bacterial properties. In Colombia, the application of photocatalysts in industry has been poorly studied and, therefore, its investigation is needed.

Titanium dioxide appears to be the most suitable semiconducting material for use in photocatalysis due to its chemical stability, non-toxicity and, relatively low cost in comparison with other semiconductor metal oxides. In nature, the TiO_2 can be found in three crystalline forms named rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Their structures can be discussed in terms of (TiO_2^{6-}) octahedrals. The three crystal structures differ in the distortion of each octahedral and by the assembly patterns of the octahedral chains.

Anatase can be regarded to be built-up from octahedrals that are connected by their vertices, meanwhile in rutile, the edges are connected, and in brookite both vertices and edges are connected [3]. The differences in lattice structure of anatase and rutile cause different densities and electronic band structures leading to different band gaps, 3.20 eV for anatase and 3,02 eV for rutile; therefore, the absorption thresholds correspond to 388 nm and 411 nm of wavelength, respectively. According to this, it is necessary an UV-A light source to excite the electrons from the valence band to the conduction band and begin with the redox reactions. In presence of oxygen and water, the reactions taking place on the surface of the TiO_2 are:

$$TiO_2 + h\nu \leftrightarrow h^+_{BV} + e^-_{BC} \quad (1)$$

$$e^-_{BC} + O_2 \rightarrow \ ^{\cdot}O_2^- \quad (2)$$

$$h^+_{BV} + H_2O_{ads} \leftrightarrow H^+_{ads} + \ ^{\cdot}OH_{ads} \quad (3)$$

The holes mediate the oxidation of organic compounds by the formation of hydroxyl radicals, and the electrons mediate reduction and oxidation reactions by the formation of superoxide radicals [10].

Among the greatest difficulties in developing nano-TiO_2 cement materials is the lack of information about the variables that must be controlled, such as the percentage of addition of nanoparticles in cement, the optimum level of mineralogical phases present in the titanium dioxide, the form of dispersion in the substrate and the appropriate means to characterize the photocatalytic properties. The existing legislation is very recent, and is still under discussion by the scientific community.

This paper proposes a methodology for evaluating the photocatalytic properties of cement pastes, with 0.5, 1.0 and 3.0% of titanium dioxide nanoparticles, at different times of curing (65h and 28d) by the measure of color change that results from the degradation of the organic dye Rhodamine B under UV exposure.

2. EXPERIMENTAL PART

2.1 Materials

The cement paste samples were prepared using Colombian Portland white cement (Argos, Colombia). The dye that was used was Rhodamine B (Industria Química Andina S.A, Colombia) and three commercial titania samples were chosen: TiO_2 anatase (Nabond, China), TiO_2 rutile (Nabond, China) and Aeroxide P25 (Evonik-Degussa,

Germany). The content of anatase and rutile phases in TiO_2 powders were determined by X-ray diffraction spectroscopy (XRD, Philips, X'Pert).

The degradation process of dyes (methylene blue, rhodamine B, methyl green, acid orange) as a measure of photocatalytic efficiency of semiconducting materials is still a subject of discussion as these substances show, in some extent, a low resistance to UV light by themselves [14]; however, they are commonly used as model pollutants, partly because its change under UV exposure can be easily followed using spectrometry or spectrophotometry. Rhodamine B has been chosen because it is highly soluble in water, it has a low sensitivity to the alkalinity of cementicious materials [8] and its chemical structure is related to polycylic aromatic hydrocarbons, which are some of the pollutants agents found in urban environments.

Aqueous suspensions of titania were made using a dispersion agent, based on modified polycarboxylate polymer. In order to prove the stability and the degree of dispersion of the nanoparticles in the suspension, zeta potential measurements were carried out with a Zetasizer Nano (Malvern Instruments) as follows: 1 ml of the suspension, prepared as indicated in Section 2.2, was diluted in 80 ml of deionized water, then the measurement was performed at the given pH value (c.a 8); and a second measurement was performed at a higher pH value (c.a 12), simulating the alkaline media of the cement. The rise of the pH was achieved by the addition of a 3% wt solution of NaOH.

2.2 Preparation and evaluation of the samples

In Table 1, it is shown the experimental studied compositions used in this work. For each sample, 4 disc-shaped specimens of cement paste were made (2.8 cm in diameter and 0.5 cm thick), with a water /cement ratio of 0.5. The rhodamine B was incorporated into the mixing water (concentration of 0.5 g/l) and then the titanium dioxide and the dispersing agent (19% wt respect to TiO_2) were added to this solution. They were mixed in a Heidolph 900 Diax rotor-stator mixer for 4 minutes; this dispersion was added to the cement and manually mixed.

After being formed, the disc-shaped specimens were cured during 24 hours in a moist environment, and they were stored in dark until the age of measurement, 65 hours or 28 days. The used nomenclature will be: "Anatase" for the sample with 100% pure anatase, "P25" for the samples with a proportion 85:15, anatase:rutile; and "Ana+Rut" for the samples with a proportion 50:50, anatase:rutile.

A laboratory experimental setup was designed to evaluate the photocatalytic activity, as shown in Figure 1. The assembly consists of a UV lamp with a spectrum between 320nm and 410nm, which passes through a Fresnel lens collimator which collimates and filters the spectrum below 370nm. The intensity of the UV source in the position where the specimens are to be irradiated was 1.18 W/m^2. The use of this UV source corresponds to the facilities given in our laboratory; despite this irradiance is about 10 times lower than suggested in the standards.

Table 1. Studied compositions.

Sample	*% TiO_2**	*Anatase:rutile*
Reference	0	0:0
Anatase-1	0.5	100:0
Anatase-2	1.0	100:0
Anatase-3	3.0	100:0
P25-1	0.5	85:15
P25-2	1.0	85:15
P25-3	3.0	85:15
Ana+Rut-1	0.5	50:50
Ana+Rut-2	1.0	50:50
Ana+Rut-3	3.0	50:50

*Percentages of addition are considered with respect to cement weight

After 65 hours and 28 days, the samples were exposed to an UV source for 6 hours and the photocatalytic activity was determined by the degradation of rhodamine B with time which is evidenced by a change in color. Samples were light red at the beginning of the test, but after the UV exposure they showed a tendency to turn white, due to the photocatalytic degradation of the dye. Therefore, colorimetric measurements in the color space L*a*b* [11] given by CIE (Commission Internationale de l'Éclairage) were performed in a spectrophotometer Ocean Optics 2000.

Morphology of TiO_2 powders was examined by using a transmission electron microscope (TEM, FEI TECNAI 20 Twin), and the cement pastes with TiO_2 were examined with a field emission scanning electron microscope, (FE-SEM, HITACHI S-4800).

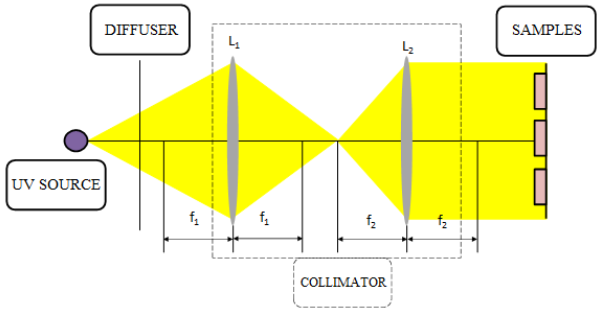


Figure 1. Morphology of TiO_2 powders was examined by using a transmission electron microscope (TEM, FEI TECNAI 20 Twin), and the cement pastes with TiO_2 were examined with a field emission scanning electron microscope, (FE-SEM, HITACHI S-4800).

3. RESULTS AND DISCUSION

The characteristics of the applied titanium dioxides are summarized in Table 2. The different particle characteristics are expected to give different photocatalytic efficiencies due to the size of the crystals and the synergism between the anatase and rutile phases [12]. However, the precise reasons for differing activities have not been elucidated in detail [13].

Table 2. Characteristics of the used titanium oxide

Titania sample	*Crystalline phases**	*Dv.50** [nm]*	*BET** [m^2/g]*
Aeroxide P25	85% Anatase 15% Rutile	21	50±15
TiO2 Anatase	99% Anatase	≤20	≥120
TiO2 Rutile	99% Rutile	≤80	≥30

*Estimated by XRD measurements
**According to manufacturers' specifications

The TEM images (Figure 2) showed pure rutile particles from about 40-60nm, hexagonally shaped; pure anatase particles from about 20nm, showed hexagonally rounded shaped and P25 particles seem to have two different sizes depending on the present phases, for anatase phase the particle size was about 20nm, while for rutile phase was about 60nm and the morphology of each phase in P25 particles was the same as for the pure phases indicated above.

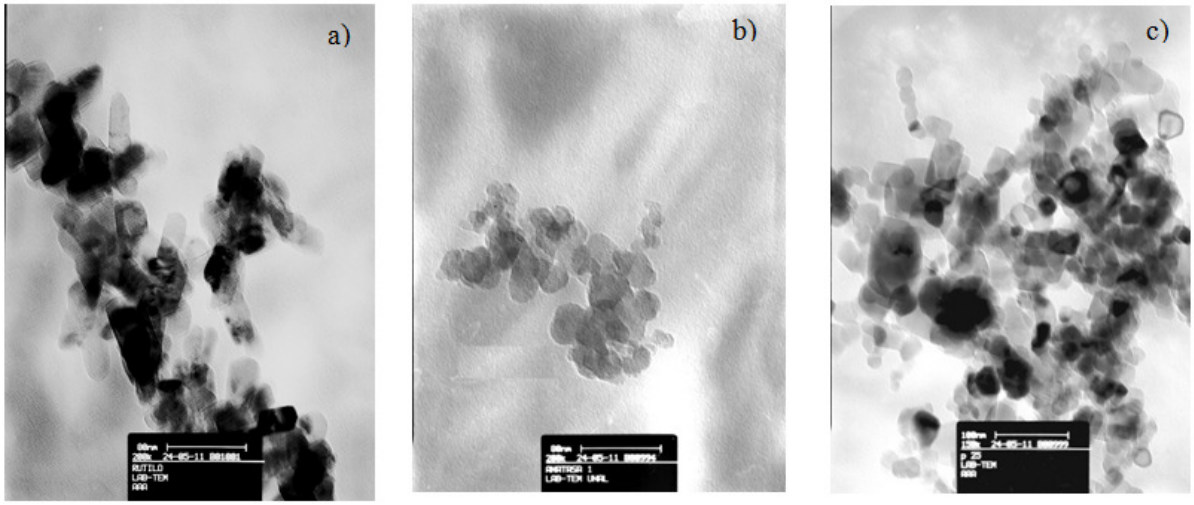


Figure 2. TEM images for TiO_2 powders: a) Rutile, b) Anatase, c) P25.

Zeta potential results are shown in Figure 3. The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If all particles in suspension have a large negative or positive zeta potential, then they will tend to repel each other and there is no tendency to flocculate. In general it is accepted that suspensions with values greater than 30mV o lower than -30mV are normally considered stable. From the results of these tests we can conclude that all of the TiO_2 suspensions were stable, even in alkaline cement-like pH. This implies that the nanoparticles were well dispersed throughout the cement paste, result that was confirmed with SEM and TEM images (figures do not showed).

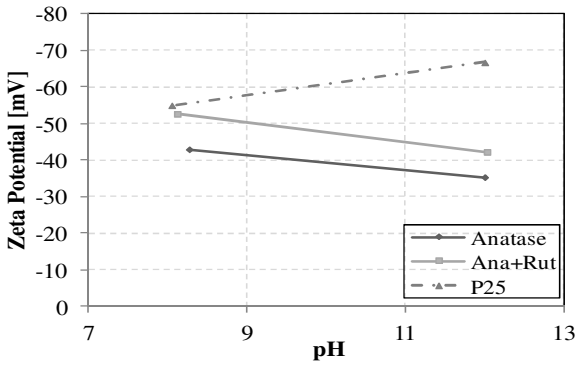


Figure 3. Zeta potential measurements at different pH for Anatase, P25 and Ana+Rut.

Figure 4 presents the changes in color for two ageing times: 65 hours and 28 days. Figure 4.a), 4.b) and 4.c) correspond to samples added with P25, Anatase and Ana+Rut, respectively. Only Δa * data will be presented since coordinate a* indicates the change in the red coloration, measured as the difference between two points, corresponding to the initial color of the sample at t=0 and the color at time t, as follows [11]:

$$\Delta a^* = a_0^* - a_t^* \quad (4)$$

Results are compared against a reference cement paste sample, TiO_2-free, in order to avoid misinterpretation of the analysis of the catalytic efficiency due to the extent of decomposition of rodhamine under UV. For samples measured at 65 hours and 28 days of fabrication, it can be observed that all of them suffer a drastic change in color during the first 50 minutes of UV exposure, even the reference sample; this could be explained by the fact that, after a while, the samples may be saturated with the decomposition products of the rodhamine and, since there is no presence of water or another vehicle for them to be evacuated, the products remain adsorbed and they slow down the photocatalytic degradation of the dye.

In Figure 4, positive Δa^* values imply that the red coloration at the initial time, t=0, was stronger than the red coloration at the final time of measurement. At 65h, samples containing 3,0% of TiO_2, except for the Ana+Rut, presented the greatest change in color compared with the other addition percentages. This was expected since there were a lot of more catalytic particles on the surface of the samples that increased rodhamine degradation. In the case of Ana+Rut samples, it seems that the change in a* was similar for all addition percentages.

In order to quantify the change in color, a photocatalytic efficiency coefficient, ξ, was calculated as follows:

$$\xi(a^*) = \frac{A(a_0^*) - A(a^*)}{A(a_0^*)} x100 \quad (5)$$

Being $A(a_0^*)$, Equation 6, the area of the rectangle having a length equal to t_f, time at the end of the UV exposure, and a height equal to a_0^*. This area can be considered as an ideal region where the sample undergoes no color change, since a* doesn't change with time. Also, we considered $A(a^*)$, Equation 7, the area under the real curve of a* as it changes with time.

$$A(a_0^*) = t_f \times a_0^* \quad (6)$$

$$A(a^*) = \int_{t_0}^{t_f} a^* dt \quad (7)$$

The photocatalytic efficiency coefficients for all samples are shown in Figure 5 at 65h and 28d.

According to these results, we can see that, at 65h, pure anatase seems to be the best catalyst when a 3,0% is incorporated into the cement matrix, followed by 3% of P25. At late ages, an interesting behavior arises from the coefficients of the Ana+Rut samples which showed an increment in the photocatalytic activity. This could be explained by the fact that there is a synergic effect between the anatase phase and the rutile phase of the titanium dioxide that leads to a slower recombination phenomenum of electron and holes in the semiconductor, allowing a more prolonged time to create the reactive radicals that finally will decompose the organic dye, or any organic compound adsorbed on the catalyst. The photocatalytic activity is being influenced by the ageing of the samples and a loss of catalytic activity is evidenced at 28 days for all sample measurements. Few authors [9] have studied the influence of ageing in the photocatalytic activity, concluding that carbonation of the TiO_2-modified cements leads to a very pronounced loss in catalytic efficiency during several months. The formation of calcite, formed from the environmental CO_2 and the cement calcium, which would cover and block much of the cement surface could result in a reduction of

specific surface area (smaller amount of active sites) and a decrease in the sample's adsorption (smaller amounts of organic compounds can be adsorbed by the cement). Nevertheless, it exists, in some extent, the degradation of organic compounds when the results are compared with the color parameters of the samples with no TiO_2. The presence of calcite or any other carbonate formed on the cement surface must be proved in future works.

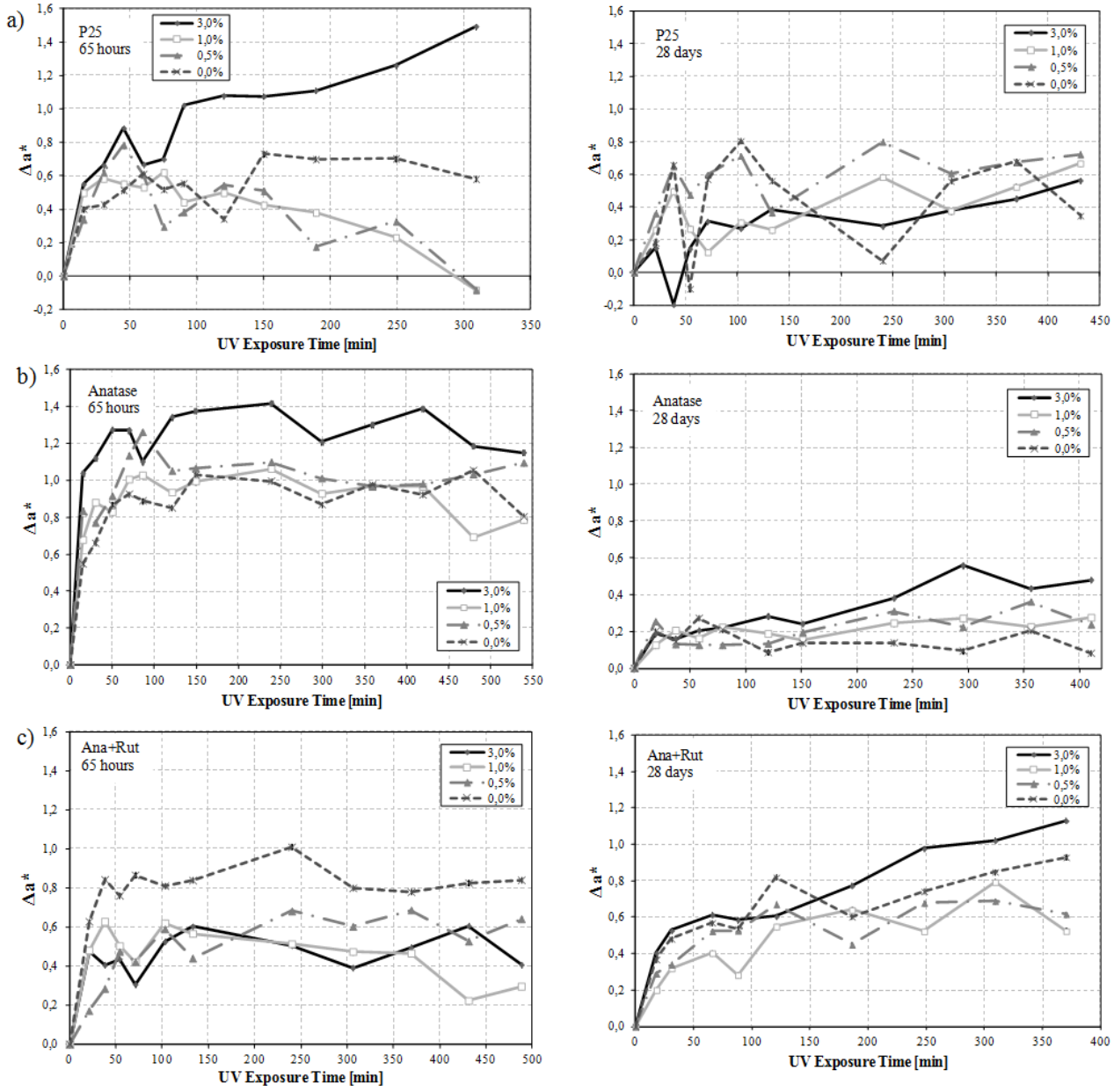


Figure 4. Change in coordinate a* during exposition to UV radiation for reference sample and samples containing 3,0%, 1,0%, 0,5% of **a)** P25, **b)** Anatase and **c)** Ana+Rut. Results are presented for two ageing times: 65 hours (left column) and 28 days (right column).

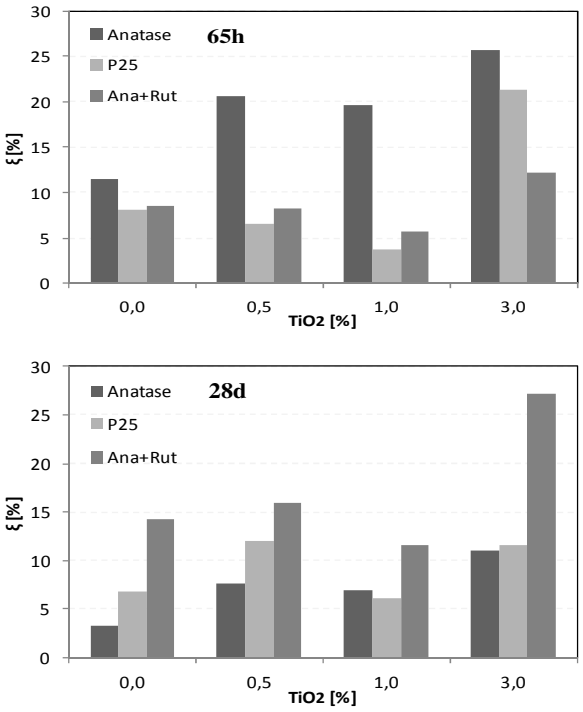


Figure 5. Photocatalytic efficiency coefficients at 65 hours and 28 days of curing.

4. CONCLUSIONS

The addition of titanium dioxide nanoparticles conferred to the cement pastes the property of degrade organic compounds, therefore, this photocatalyst-modified cements can be used to design construction materials friendly with the enviroment which break down pollutants.

The experimental set up used in this work seems to be a good choice to characterize the photocatalytic properties of any material that wanted to be measured.

In spite that the employed irradiancy was of low intensity (1.8W/m^2) compared which those used in the standard regulation (10-20W/m^2) it can be noticed a change in color of the cement paste samples due to photocatalysis. This implies that the photocatalysis reactions can be achieved even under low irradiance conditions.

At early ages, the more efficient addition in the degradation of rhodamine B was the anatase while for older ages, the 50:50 ratio of anatase:rutile presented the higher photocatalytic activity. This could be explained because the smaller particle size of anatase makes it more active than the rutile as long as no other phenomena occur like carbonation or cement hydration. When this happens, at older ages, the synergy between the two phases seems to be more efficient against those phenomena.

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