

TiO₂/Zeolite Composite on Ceramic Tiles: Influence of the Amount of Photocatalyst on Adsorption and Photocatalytic Properties.

Giuseppe Sarno, Vincenzo Vaiano, Diana Sannino

Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano (SA), Italy;
 vvaiano@unisa.it

In this work, TiO₂-Ag-zeolite was supported on porous ceramic tiles to enhance the self-cleaning properties. The influence on adsorption and photocatalytic properties of the anchored composite with respect to a coating with only TiO₂ has been evaluated. Functionalized tiles were obtained through a method that involves a sol-gel preparation followed by calcination at 550 °C for 2 h and different samples at different titanium and silver surface loads were prepared. The verification of the self-cleaning properties was conducted through adsorption and photocatalytic tests realized using aqueous solutions containing methylene blue (MB). Characterization results evidenced that the deposition method induced the formation of TiO₂/Ag-zeolite layer, strongly adherent to the tile surface, in which TiO₂ is present in anatase phase. The photocatalytic performances are strongly influenced by the amount of TiO₂-Ag-zeolite composite deposited on the tile surface.

1. Introduction

Photocatalytic functionalization of surfaces involves the conferring of self-cleaning and antibacterial properties due to the spontaneous oxidizing power of semiconductors when they are irradiated by a light with a suitable range of wavelengths (Banerjee et al., 2015). Titanium dioxide is one of the most used semiconductor since it actually well known that under UV light irradiation it generates electron-hole pairs active for the degradation of a wide range of dangerous organic compounds in water (Sacco et al., 2015), air (Hajaghazadeh et al., 2014) and for the inactivation of different bacterial strains (Rizzo, 2009). TiO₂ has been also widely applied for the realization of multifunctional coatings (Ragesh et al., 2014); for this purpose, recently, composites have been deposited on the surface of ceramic tiles to attribute self-cleaning characteristics (Sarno et al., 2015). However, TiO₂ is rarely utilized in indoor environments as photocatalyst, due to the limited availability of light irradiation belonging to the UV region. Different approaches have been achieved for the modification of TiO₂ with various heteroatoms which allow to exploit, for photocatalytic reactions, both UV and visible light irradiation (Asahi et al., 2001). On the other hand, to improve the photocatalytic efficiencies, the combination of a specific photocatalyst with other materials such as clays or porous materials is an interesting opportunity for the design of a composite with specific functions (Durga Kumari et al., 2002).

Adsorption of organic pollutants from air and water on TiO₂ surface play an important role in the photocatalytic process and leads to an increased removal of organic contaminants both in the air and in water. The combination of TiO₂ and specific materials, such as alumino-silicates, as already reported, demonstrates that the presence of zeolite enhanced photodegradation process because of the favourable adsorption properties of the zeolite (Sarno et al., 2015).

In this work, to enhance the self-cleaning properties, TiO₂/Ag-zeolite was supported on highly porous traditional ceramic tiles and evaluated the influence on adsorption and photocatalytic properties of the anchored composite at different amounts of TiO₂/zeolite with respect to a TiO₂ coating. We mainly focus our results on the application of the composite in the discoloration of methylene blue aqueous solutions as a model fouling agent under UV light irradiation.

2. Experimental

2.1 Preparation of composite

The Ag based zeolite was prepared through ionic exchange in two steps, the first conducted at room temperature on Na, K-ferrierite with a solution of NH_4NO_3 1 M while the second ion exchange at room temperature with AgNO_3 aqueous solution for 24 h, followed by calcination at 550 °C.

Tiles, with dimensions 100 mm × 100 mm × 12 mm, were ultrasonically cleaned in surfactant and washed with water prior to the deposition process. Tiles surface functionalization was achieved with a TiO_2 sol obtained through a sol gel method (Sarno et al., 2015) mixing the reagents in the following order: titanium (IV) isopropoxide, ($\text{Ti}(\text{C}_3\text{H}_7\text{O})_4$, Sigma Aldrich), ethanol ($\text{C}_2\text{H}_5\text{OH}$, Fluka Analytical), acetyl acetone ($\text{CH}_3(\text{CO})\text{CH}_2(\text{CO})\text{CH}_3$, Sigma Aldrich), acetic acid (CH_3COOH , Aldrich Chemistry), urea (NH_2CONH_2 , Sigma Aldrich), polyethylene glycol, ($\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{H}$, MW = 5,000 – 7,000, Aldrich Chemistry) and water. In the obtained sol, Ag-zeolite and TRITON X 100, as non-ionic surfactant, were added. The functionalized ceramic tiles were finalized via steps-coating technique followed by heat-treatment in air at 550 °C. Mass ratio between zeolite and TiO_2 is equal to 0.4 g g⁻¹.

Different samples with different titanium and zeolite content were obtained increasing the number of coating steps. A functionalized tile without zeolite and Triton X 100 was also realized (tile T1).

Table 1 reports the list of the obtained samples with their titanium surface concentration and the number of coating steps realized to accomplish the achieved surface composition.

Table 1: List of samples with their titanium surface concentration.

Sample	Ti surface conc. (%)	Coating steps (n°)
Raw Tile	1.24	0
Tile T1	7.87	2
Tile R	7.96	2
Tile P	13.31	5
Tile BE	17.06	7

2.2 Characterizations of functionalized tiles

Chemical-physical characterisation of the samples was performed by different techniques.

Laser Raman spectra were obtained at room temperature with a Dispersive MicroRaman (Invia, Renishaw), equipped with 514 nm diode-laser, in the range 100 - 800 cm⁻¹ Raman shift.

X-Ray fluorescence spectroscopy (XRF) was performed using a ThermoFischer ARL QUANT'X EDXRF spectrometer equipped with a rhodium standard tube as the source of radiation and with Si-Li drifted crystal detector.

2.3 Adsorption tests

Methylene blue (MB) is used as model stain dissolved in water; since it shows good chemical stability and the concentration can be easily monitored using a UV-Vis spectrophotometer.

An aqueous solution of MB with a concentration equal to 5 ppm was prepared. Ceramic tiles were placed in a plate reactor (0.2 L in volume) realized in stainless steel (Sannino et al., 2013). The reactor was filled with the solution of methylene blue and was kept in dark. Liquid samples were monitored in continuous mode by spectrophotometric measurement. A special assembly with a flow cuvette and an external pump for the recirculation of liquid was realized, permitting to analyse continuously the change of MB concentration, measured with a Perkin Elmer UV-Vis spectrophotometer at $\lambda = 663$ nm.

2.4 Photocatalytic tests

Photocatalytic tests were performed at atmospheric pressure and ambient temperature using a steel reactor with a pyrex window of size 100 mm × 100 mm. The irradiation of photoreactor was realized by four UV lamps (nominal power 8 W each) with the main peak of emission spectrum centred at 365 nm. The photoreactor is provided of temperature controlling system, consisting of a thermal exchanger within the metal body and a cooling system.

Pre-adsorption of MB on the tiles surface was performed using an aqueous solution of MB with a concentration equal to 10 ppm. Tiles and 200 mL of the adsorption solution were placed in contact in a glass beaker and the dye was adsorbed in dark conditions for 24 h. When the remaining concentration of the dye in the solution was larger than that of the test solution, the adsorption was considered to be completed. Otherwise, the procedure was repeated for another 12 h using a fresh adsorption solution.

The initial concentration of MB for photocatalytic tests was 5 ppm. The changes of MB concentration in liquid samples were analysed in continuous way by spectrophotometric measurement at $\lambda = 663$ nm with the same device described in section 2.3.

3. Results and discussion

3.1 Samples characterization

Raman spectroscopy has been applied to evidence TiO_2 crystallographic phases since the crystal structure is an important parameter in the efficacy of the MB photo-discoloration (Vaiano et al., 2014).

Figure 1 shows the Raman spectra of the functionalized tiles in comparison with raw tile in the range 100 - 900 cm^{-1} . No bands are present for raw tile; functionalized tiles display bands at 144, 396, 514 and 637 cm^{-1} and a weak shoulder at 195 cm^{-1} , due to the Raman-active fundamental modes of titania in anatase phase (Ciambelli et al., 2008). Figure 2 reports the results of XRF analysis for raw tile in comparison with titanium functionalized tile (T1) and the tiles functionalized with the composite TiO_2/Ag -zeolite (P, R and BE samples). The surface concentration of titanium and silver in the functionalized samples reached a value of about 17 % and 0.053 % respectively for tile functionalized with the highest number of coating steps (tile BE), indicating a good performance of the deposition process under the experimental conditions employed. Moreover, as it can be seen from Figure 3 the increase of the surface concentration for these two metals is almost linear with the increase of the number of coating steps realized. These evidences clearly show that the tile surface is not completely saturated with the functionalizing composite and that the deposition method is able to induce the formation of TiO_2/Ag -zeolite layer, strongly adherent to the tile surface, in which anatase TiO_2 was present.

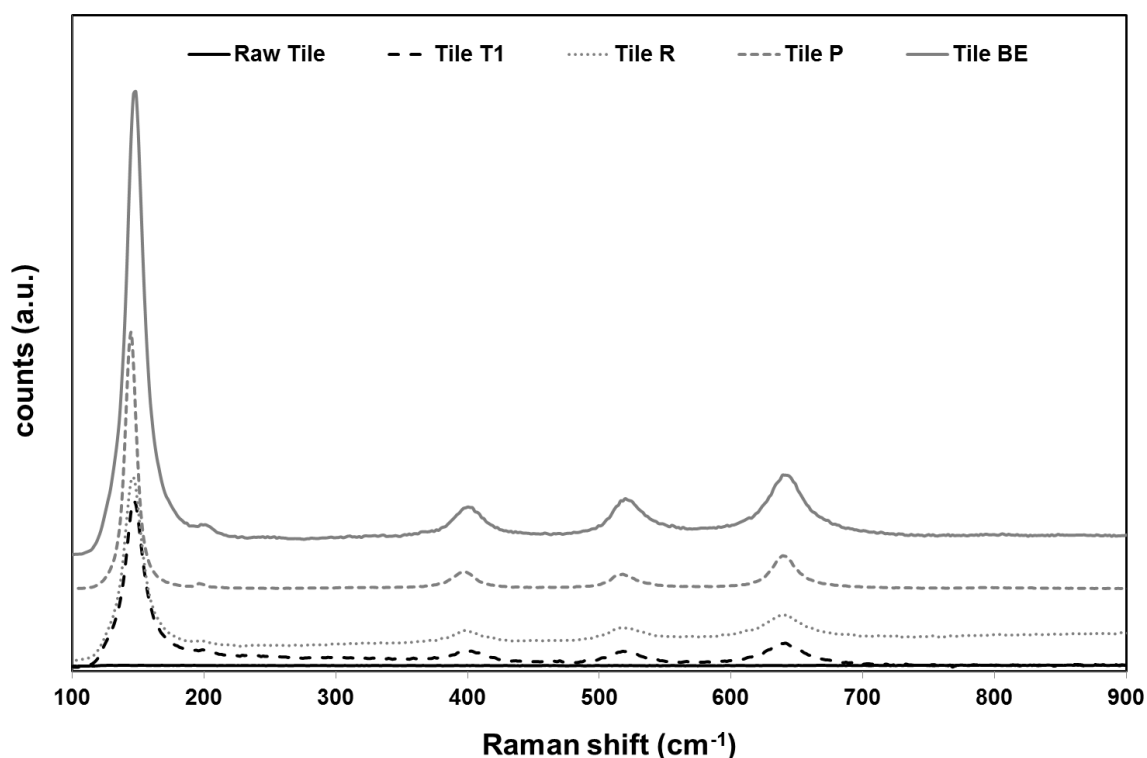


Figure 1: Raman spectra of functionalized and raw tile in the range 100 – 900 cm^{-1}

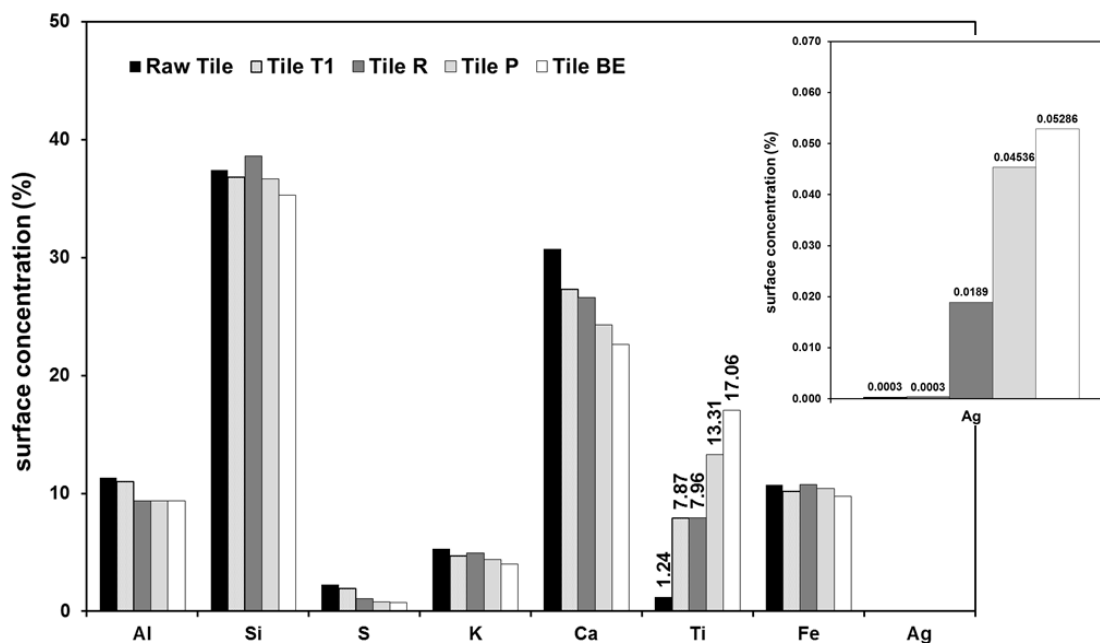


Figure 2: XRF analysis of surface for raw tile and functionalized tiles.

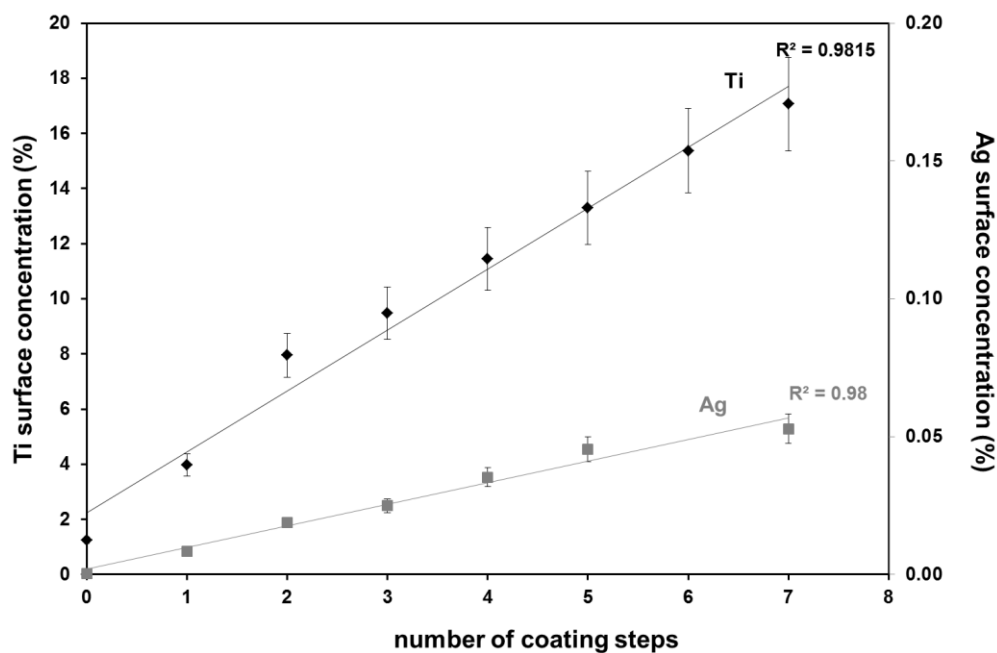


Figure 3: Behavior of the surface concentration as a function of the coating steps realized

3.2 Adsorption tests

Figure 4 shows that the relative concentration of the dye in aqueous solution decreases along the time because of the adsorption of MB on the functionalized tiles. From a certain time onwards, it reaches a constant value beyond which MB is no longer removed from the solution. For T1 sample the relative concentration of the dye decreases slower than the raw sample; this data clearly indicate that titania is able to occlude partially the porosity of the support. On the other hand the functionalization with the composite TiO_2/Ag -zeolite causes an increase of the adsorption capacity; in particular it increased of about 50 % for the sample BE with respect to the raw tile. This behaviour can be associated with an increase in the total porosity of the composite generated by the zeolite. Moreover, this capacity is directly correlated to the amount of the composite deposited on the substrate.

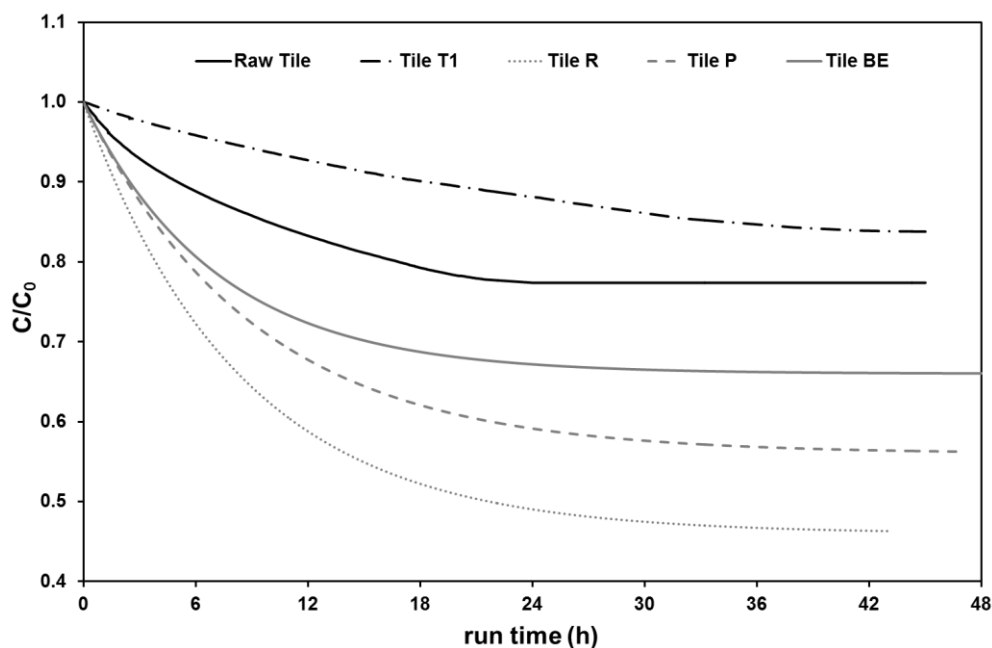


Figure 4: Behavior of MB relative concentration as a function of run time

3.3 Photocatalytic activity tests

The changes in the concentration of MB recorded in continuous mode are shown in Figure 5a. Control experiment carried out on the raw tile shows that MB relative concentration reached a maximum value and then decreased, indicating desorption phenomena of MB from the tile surface. For tile T1 the relative concentration of the dye slightly decreases reaching a discoloration of about 35 % only after 48 h of irradiation time. For the samples functionalized with the composite TiO_2/Ag -zeolite the relative concentration of MB decreases rapidly, reaching the complete discoloration in less than 42 h. At fixed irradiation time the presence of zeolite leads to higher discoloration rate (obtained following the first order kinetic with respect to the MB relative concentration). The values of kinetic constant are plotted in Figure 5b as a function of the titanium surface concentration. As it can be seen there is an optimum in the titanium surface concentration equal to 13.31 %, for which the highest value of kinetic constant is obtained. The lower photocatalytic performance at higher tile surface coverage is probably due to an aggregation of the deposited particles which shields part of the active species.

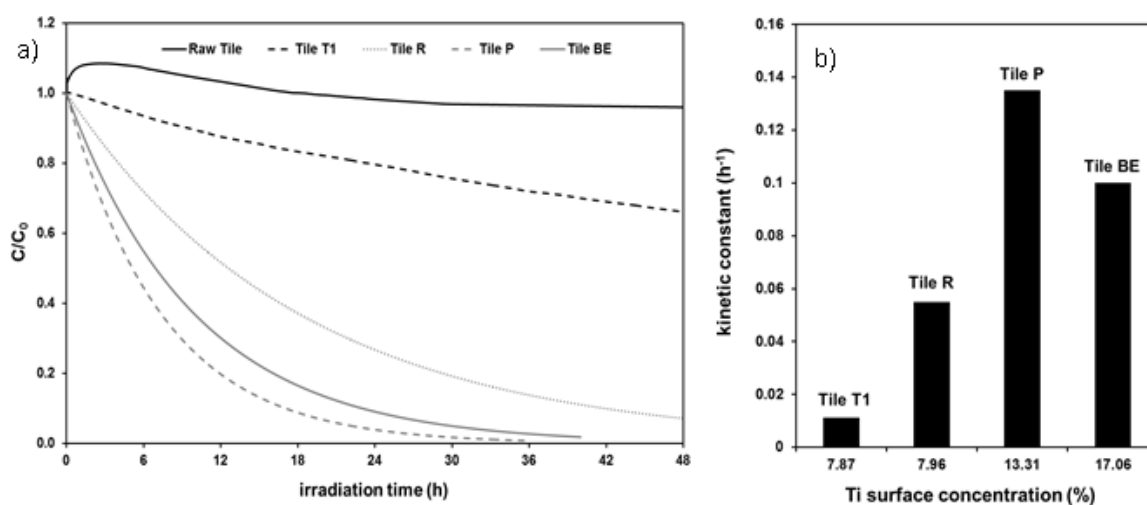


Figure 5: Behavior of MB relative concentration as a function of irradiation time (a) and kinetic constant as a function of the titanium surface concentration (b).

4. Conclusions

In this work, TiO₂-Ag-zeolite composite was supported on porous ceramic tiles to enhance the self-cleaning properties. The deposition method is able to induce the formation of a layer, strongly adherent to the tile surface, in which TiO₂ results in anatase form.

For the tile functionalized with the highest number of coating steps (tile BE) the surface concentration of titanium and silver in the functionalized samples reached a value of about 17 % and 0.053 %, respectively, indicating a good performance of the deposition process under the experimental conditions employed.

The functionalization causes an increase of the adsorption capacity; in particular MB amount adsorbed on tile surface increases of about 50 % for the sample with the highest titanium content with respect to the raw tile. On the other hand the application of the TiO₂/Ag-zeolite composite resulted in the increasing of the degradation rate of the dye with respect to the tile coated with TiO₂ alone; anyway, an optimum in the titanium surface concentration (13.31 %) for which the highest value of kinetic constant is obtained, was found. Up to this nanocomposite load, the formed coating from the adsorbent and photocatalytic particles, was completely active, being the photocatalyst well exposed to the irradiation, without self-shielding effects.

Acknowledgments

The authors wish to thanks "Ceramiche Il Pavone" for having provided the tiles used in this work.

References

- Asahi R., Morikawa T., Ohwaki T., Aoki K., Taga Y., 2001. Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science*, 293, 269-271.
- Banerjee S., Dionysiou D.D., Pillai S.C., 2015. Self-cleaning applications of TiO₂ by photo-induced hydrophilicity and photocatalysis. *Applied Catalysis B: Environmental*, 176–177, 396-428.
- Ciambelli P., Sannino D., Palma V., Vaiano V., Bickley R.I., 2008. Reaction mechanism of cyclohexane selective photo-oxidation to benzene on molybdena/titania catalysts. *Applied Catalysis A-General*, 349, 140-147.
- Durga Kumari V., Subrahmanyam M., Subba Rao K.V., Ratnamala A., Noorjahan M., Tanaka K., 2002. An easy and efficient use of TiO₂ supported HZSM-5 and TiO₂+HZSM-5 zeolite combinate in the photodegradation of aqueous phenol and p-chlorophenol. *Applied Catalysis A: General*, 234, 155-165.
- Hajaghazadeh M., Vaiano V., Sannino D., Kakooei H., Sotudeh-Gharebagh R., Ciambelli P., 2014. Heterogeneous photocatalytic oxidation of methyl ethyl ketone under UV-A light in an LED-fluidized bed reactor. *Catalysis Today*, 230, 79-84.
- Ragesh P., Anand Ganesh V., Nair S. V., Nair A., S. 2014. A review on 'self-cleaning and multifunctional materials'. *Journal of Materials Chemistry A*, 2, 14773-14797.
- Rizzo L., 2009. Inactivation and injury of total coliform bacteria after primary disinfection of drinking water by TiO₂ photocatalysis. *Journal of Hazardous Materials*, 165, 48-51.
- Sacco O., Vaiano V., Han C., Sannino D., Dionysiou D.D., 2015. Photocatalytic removal of atrazine using N-doped TiO₂ supported on phosphors. *Applied Catalysis B: Environmental*, 164, 462-474.
- Sannino D., Vaiano V., Sarno G., Ciambelli P., 2013. Smart tiles for the preservation of indoor air quality. *Chemical Engineering Transactions*, 32, 355-360.
- Sarno G., Vaiano V., Sannino D., Ciambelli P., 2015. Photocatalytic applications with TiO₂-zeolites composites anchored on ceramic tiles. *Chemical Engineering Transactions*, 43, 985-990.
- Vaiano V., Sarno G., Sannino D., Ciambelli P., 2014. Photocatalytic and Antistain properties of ceramic tiles functionalized with tungsten-doped TiO₂. *Chemical Engineering Transactions*, 39, 499-504.