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Photocatalytic Applications with TiO_2-Zeolites Composites Anchored on Ceramic Tiles

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In this work, to increase the self-cleaning properties, TiO_2/zeolite composite was supported on ceramic tiles. Functionalized tiles were prepared by a sol-gel process. Photocatalytic tests were performed at ambient temperature and atmospheric pressure using a properly designed steel reactor with a pyrex window. The irradiation of photoreactor was realized by four UV lamps. For photocatalytic activity test an aqueous solution with a 5 ppm concentration of Methylene Blue (MB) was used.
Characterization results evidenced that the deposition method is able to induce the formation of anatase TiO_2 strongly interacting with the tile surface without modifying the aesthetic properties of the ceramic tiles. The presence of zeolite increased the MB adsorption ability enhancing the photocatalytic performances.

1. Introduction

Titanium dioxide (TiO_2) is considered as one of the best semiconductor to be used as photocatalyst for pollutants degradation in liquid phase, such as methylene blue (MB) (Sannino et al., 2013a), atrazine (Sacco et al., 2015) and tannery wastewater (Vaiano et al., 2014a). In the presence of UV light irradiation redox reactions and charges separation are promoted, leading to the formation of hydroxyl radicals (•OH) and superoxide ions ($•O_2^-$) (Wu and Cheng, 2006). These species are able to induce oxidation reactions promoting the degradation of organic compounds.
To confer self-cleaning properties to ceramic tiles, TiO_2 can be fixed on their surface. Different methods have been studied to this purpose: chemical vapor deposition, sputtering, pulsed laser deposition (Yamamoto et al., 2001), hydrothermal method (Lee et al., 2002) and sol-gel deposition. Sol–gel is considered as one of the most flexible methods, because of several advantages such as low sintering temperature and good homogeneity at low cost. The deposition process is based on the hydrolysis of titanium alkoxide (Segota et al., 2011).
Some papers have demonstrated that TiO_2/zeolites composite showed an enhanced photo-degradation activity (Durga Kumari et al., 2002, Noorjahan et al., 2004), likely due to the higher adsorption properties of the zeolite and therefore facilitating the photodegradation activity of TiO_2 more effectively.
In this work, TiO_2/zeolite composite was supported on ceramic tiles to increase the self-cleaning properties.

2. Experimental

2.1 Preparation and deposition of TiO_2/zeolite composite

Silver zeolites (AgFER) were obtained through ionic exchange at room temperature of Na,K-ferrierite (Si/Al 8.4) with aqueous solution of NH_4NO_3 1 M followed by ion exchange at room temperature with $AgNO_3$ aqueous solution for 24 h and calcination at 550 °C for 2 h.
For the preparation of TiO_2 sol, the following components were used:

- Titanium (IV) isopropoxide, TTIP ($Ti(C_3H_7O)_4$, Sigma Aldrich) as titanium precursor;
- Ethanol, (C_2H_5OH, Fluka Analytical) as solvent;
- Acetic acid (CH_3COOH, Aldrich Chemistry) as catalyst;

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- Acetylacetone ($CH_3(CO)CH_2(CO)CH_3$, Sigma Aldrich) as chelating agent;
- Bidistilled water (H_2O) for gelation;
- Polyethylene glycol, PEG ($HO(C_2H_4O)_nH$, MW = 5,000–7,000, Aldrich Chemistry) as organic dispersant and binder.

Titanium isopropoxide was added to ethanol ($TTIP/C_2H_5OH$=1/40 mol mol^{-1}) and the solution was stirred continuously to mix the liquid. Then, acetylacetone (4.5 mL) and acetic acid (1.74 mL) were slowly added. The obtained solution (solution 1) was sonicated for 15 min. In a different flask, 4 g of polyethylene glycol (PEG) were added to bidistilled water under stirring and, this solution was mixed with solution 1 and stirred, obtaining a clear solution (solution 2).
Zeolite and TRITON X 100, as non-ionic surfactant, were added to the solution 2.
Functionalized ceramic tiles were obtained via impregnation technique followed by heat-treatment in air at 550 °C for 3 h. The final zeolite/TiO_2 mass ratio was equal to 0.4 g g^{-1}.

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.
The porosity, pores size, and pore size distribution of the ceramic samples were determined by a Hg intrusion porosimeter (Pascal P140-P240, ThermoElectron).

2.3 Photocatalytic tests

Photocatalytic tests were performed at ambient temperature and atmospheric pressure using a properly designed steel reactor with a pyrex window. The photoreactor is provided of temperature controlling system, consisting of a thermal exchanger within the metal body and a cooling system. The irradiation was realized by four UV lamps (nominal power 8 W) with the main peak of emission spectrum centered at 365 nm. For photocatalytic activity test an aqueous solution of Methylene Blue (MB) (concentration 5 ppm) was prepared. Then, ceramic tiles were placed in the photoreactor. The reactor was filled with methylene blue solution (100 mL), and was kept in dark condition about 24 h to achieve the equilibrium adsorption of MB on samples surface. Then, photocatalytic reaction was initiated.
Liquid samples were analysed in continuous by spectrophotometric measurement (Perkin Elmer UV-Vis spectrophotometer). In particular, an assembly with a flow cuvette and an external peristaltic pump for the recirculation of liquid allowing to measure the MB concentration at λ = 663 nm was realized.

3. Results and discussion

3.1 Samples characterization

In Figure 1 it is reported the comparison between XRF results of raw tile and functionalized samples with only TiO_2 (Tile T) and with TiO_2/zeolite composite (Tile Z). As it can be seen, the surface concentration of titanium for both functionalized samples reached a value of about 4.5 % indicating a good yield for the deposition process under the experimental conditions employed. Moreover tile Z shows a higher Ag surface concentration with respect to raw tile and tile T. This result indicates that also the zeolite was anchored on tile surface.
The Raman spectra of tile Z (Figure 2) shows only 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 (Ciambelli et al., 2008). These characteristic bands give evidence for the crystalline form of anatase for TiO_2 (Sannino et al., 2013b), as also observed on ceramic tiles functionalized with W-doped TiO_2 (Vaiano et al., 2014c) and with N-doped TiO_2 (Vaiano et al., 2014b). No bands are observed for raw tile.
Tests of Hg porosimetry performed on raw and functionalized samples are compared in Figure 3. As it can be seen, raw tile showed a total Hg intruded volume (HgIV) higher than tile T (Figure 3a). On the contrary, the addition of zeolite (tile Z) induced an increase of HgIV with respect to both raw tile and tile T. In particular, the accessible porosity was 36.0, 37.8 and 35.8 % for raw tile, tile Z and Tile T, respectively. The average pore diameter (DP) (Figure 3b) is almost similar for raw tile and tile T, while for tile Z, DP is higher than both raw tile and tile T.

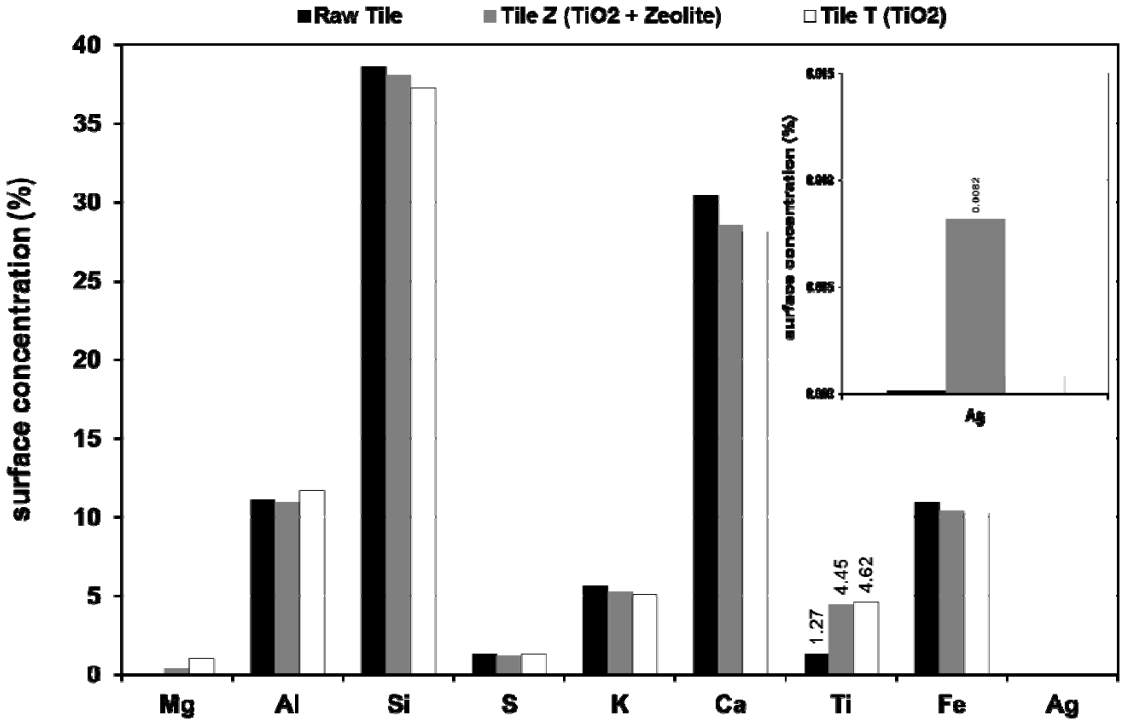

Figure 1: XRF analysis of surface for raw tile and functionalized tiles.

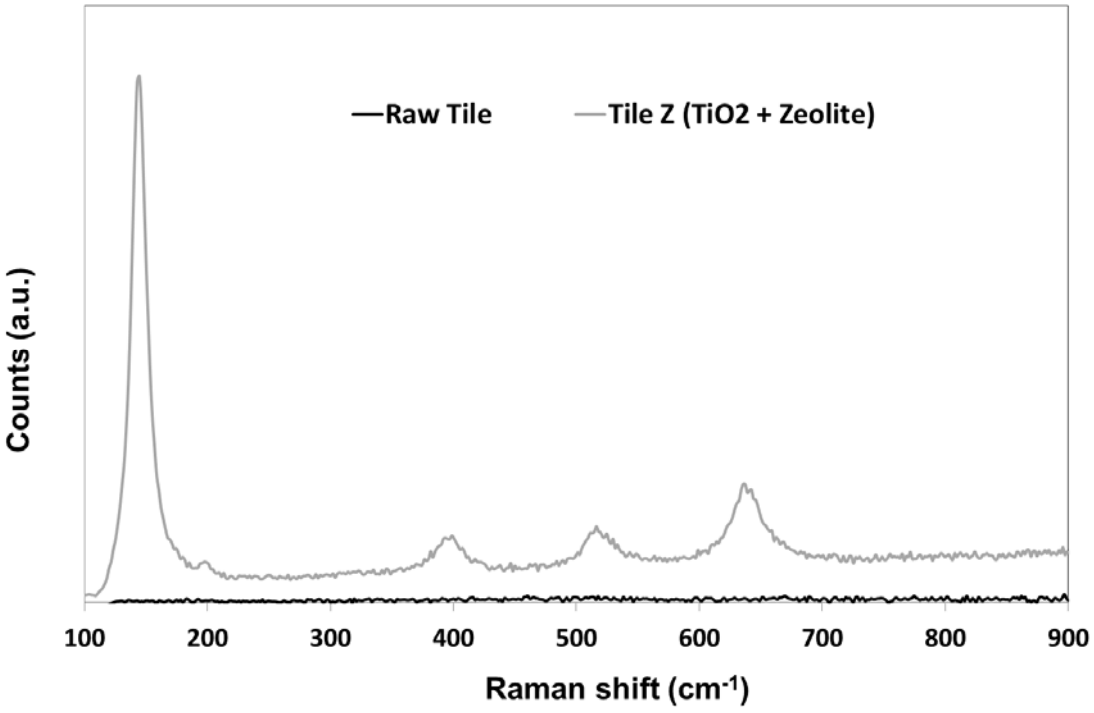

Figure 2: Raman spectra of functionalized and raw tile in the range 100 – 900 cm^{-1}.

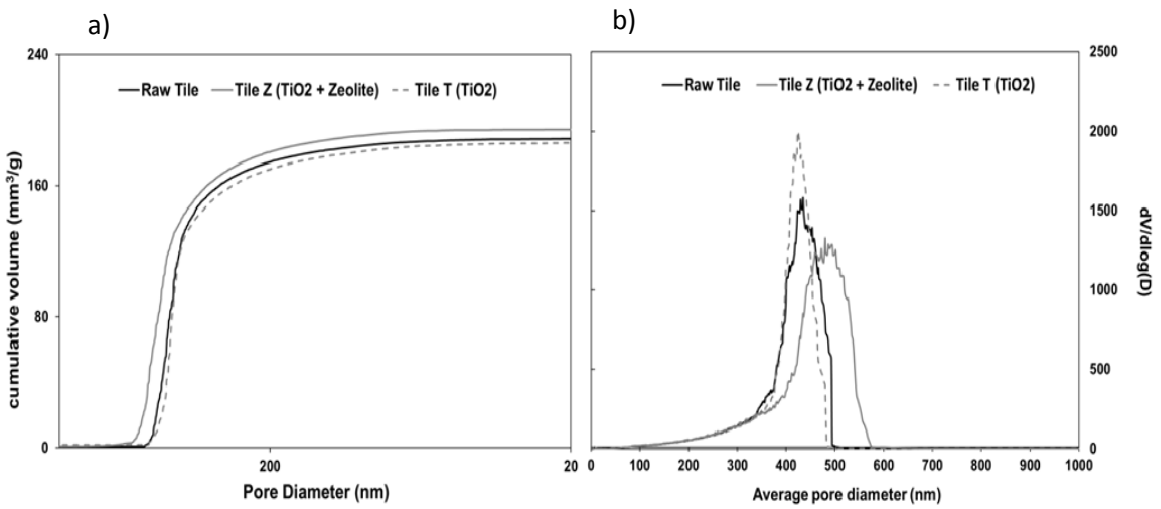

Figure 3: Cumulative volume (a) and pore size distribution (b) for Raw and functionalized tiles

3.2 Photocatalytic activity tests

The behavior of MB concentration recorded during dark adsorption and UV irradiation at specific time intervals is shown in Figure 4.

During the dark phase the amount of dye adsorbed on all the samples increases with time and, from a certain time onwards, it reaches a constant value beyond which it is no longer removed from the solution. In the case of tile T, the deposition of TiO_2 induces a decrease of the adsorption capacity with respect to raw tile, while in the presence of zeolite (tile Z) the amount of MB adsorbed is much higher than raw tile and tile T. The obtained results are in agreement with the Hg intrusion analysis (Figure 3). Moreover, this evidence is likely due to the very high specific surface area of zeolite materials (Ciambelli et al., 2002).

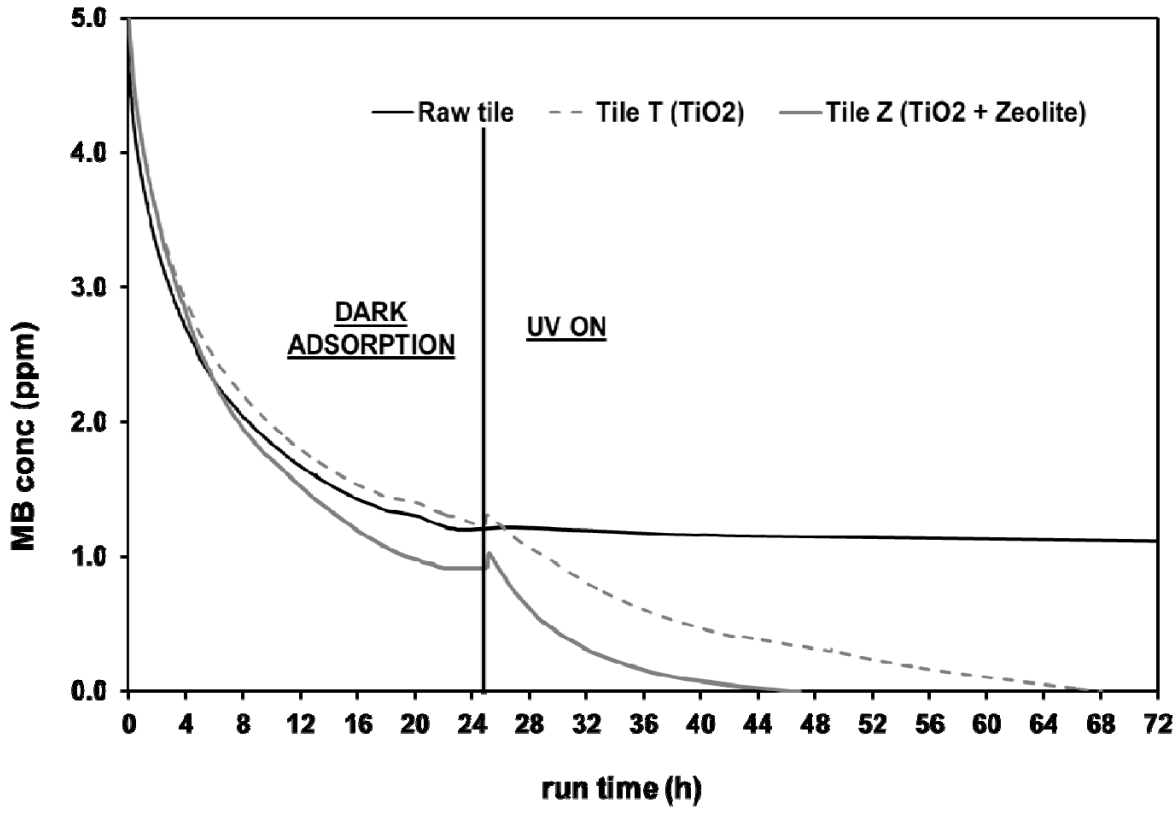

Figure 4: MB discoloration as a function of run time.

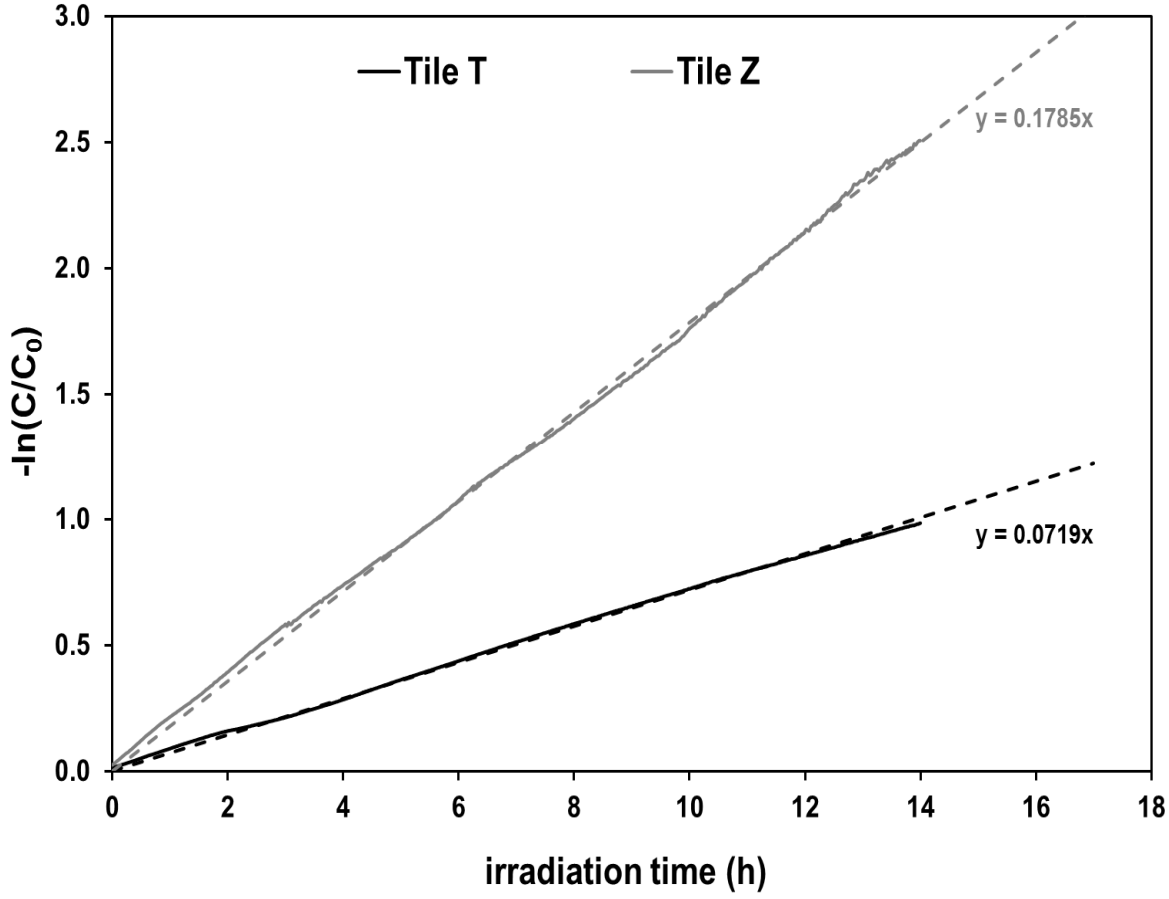

Figure 5: Evaluation of MB discoloration kinetic under UV light for Tile T and Tile Z.

Under UV irradiation, recorded in continuous mode, MB concentration on raw tile didn't change significantly. For both tile T and tile Z, MB concentration decreases progressively, reaching total discoloration. However, at fixed irradiation time, the presence of TiO_2/zeolite induces a higher discoloration rate. In particular, the total discoloration is achieved after 20 h of irradiation for tile Z, whereas for tile T the complete removal of solution colour is obtained in much longer time (44 h of irradiation). Therefore, the time required for the complete discoloration is strongly influenced by the presence of zeolite. The latter enhances the adsorption phenomena, leading to an increase of the photocatalytic reaction rate (Figure 5) and therefore to the reduction of the overall time necessary to have a complete removal of MB.

4. Conclusions

In this work, TiO_2/zeolite composite was supported on ceramic tiles to increase the self-cleaning properties.
The impregnation method is able to anchor TiO_2/zeolite inducing the formation of titania in anatase phase dispersed on the tile surface without modifying the aesthetic properties of the supports.
The addition of zeolite led to an increase of the accessible porosity, increasing it from 36 (raw tile) up to about 38 %. This increase has influenced the adsorption properties of methylene blue on ceramic support, enhancing the photocatalytic performances in terms of discoloration reaction rate. In particular, in the presence of zeolite composite, the apparent kinetic constant is almost double than that one obtained with TiO_2 alone.

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References

Ciambelli, P., Sannino, D., Gaudino, M. C. & Flytzani-Stephanopoulos, M. 2002. Ag and Co exchanged ferrierite in lean NO_x abatement with CH_4. *Studies in Surface Science and Catalysis.*

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 TiO_2 supported HZSM-5 and TiO_2+HZSM-5 zeolite combinate in the photodegradation of aqueous phenol and p-chlorophenol. *Applied Catalysis A: General,* 234**,** 155-165.

Lee, J. C., Kim, M. S. & Kim, B. W. 2002. Removal of paraquat dissolved in a photoreactor with TiO_2 immobilized on the glass-tubes of UV lamps. *Water Research,* 36**,** 1776-1782.

Noorjahan, M., Durga Kumari, V., Subrahmanyam, M. & Boule, P. 2004. A novel and efficient photocatalyst: TiO2-HZSM-5 combinate thin film. *Applied Catalysis B: Environmental,* 47**,** 209-213.

Sacco, O., Vaiano, V., Han, C., Sannino, D. & Dionysiou, D. D. 2015. Photocatalytic removal of atrazine using N-doped TiO_2 supported on phosphors. *Applied Catalysis B: Environmental,* 164**,** 462-474.

Sannino, D., Vaiano, V., Sacco, O. & Ciambelli, P. 2013a. Mathematical modelling of photocatalytic degradation of methylene blue under visible light irradiation. *Journal of Environmental Chemical Engineering,* 1**,** 56-60.

Sannino, D., Vaiano, V., Sarno, G. & Ciambelli, P. 2013b. Smart tiles for the preservation of indoor air quality. *Chemical Engineering Transactions,* 32**,** 355-360.

Segota, S., Curkovic, L., Ljubas, D., Svetlicic, V., Houra, I. F. & Tomasic, N. 2011. Synthesis, characterization and photocatalytic properties of sol-gel TiO_2 films. *Ceramics International,* 37**,** 1153-1160.

Vaiano, V., Sacco, O., Stoller, M., Chianese, A., Ciambelli, P. & Sannino, D. 2014a. Influence of the photoreactor configuration and of different light sources in the photocatalytic treatment of highly polluted wastewater. *International Journal of Chemical Reactor Engineering,* 12**,** 1-13.

Vaiano, V., Sarno, G., Ciambelli, P. & Sannino, D. 2014b. Functionalization of ceramic tiles with N-doped TiO_2 and their photocatalytic function under UV or visible light irradiation. *Journal of Advanced Oxidation Technologies,* 17**,** 193-201.

Vaiano, V., Sarno, G., Sannino, D. & Ciambelli, P. 2014c. Photocatalytic and Antistain properties of ceramic tiles functionalized with tungsten-doped TiO_2. *Chemical Engineering Transactions,* 39**,** 499-504.

Wu, J. C. S. & Cheng, Y. T. 2006. In situ FTIR study of photocatalytic NO reaction on photocatalysts under UV irradiation. *Journal of Catalysis,* 237**,** 393-404.

Yamamoto, S., Sumita, T., Sugiharuto, Miyashita, A. & Naramoto, H. 2001. Preparation of epitaxial TiO_2 films by pulsed laser deposition technique. *Thin Solid Films,* 401**,** 88-93.