

Influence of irradiation on stability and effectiveness of TiO₂/N,C photocatalysts

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The gypsum building material was enriched with photocatalytic properties for indoor air purification. The photocatalytic additive to gypsum was TiO₂ modified with carbon from various sources. The photocatalytic activity of gypsum plates was performed towards NO_x removal. Carbon doping into TiO₂ improved not only total degradation of NO_x on corresponding gypsum plates but also NO₂ selectivity was changed, limiting the production of toxic NO₂. The exhibition of photocatalysts on the visible and ultraviolet irradiation has been also carried out to examine their durability. First, the stability of modifying element – carbon in TiO₂ structure was analysed, indicating on the gradual reduction of carbon content with irradiation time, especially when the carbon source was cyclic hydrocarbon. Second, the photocatalytic activity of the gypsum plates was performed at each stage of the ageing process. Based on this insight, the correlation between carbon content in modified photocatalysts loaded to gypsum plates and photocatalytic activity of them was described in detail.

1. Introduction: The interest in photocatalysis branch grew considerably involving different areas of human life. Recently, photocatalytic building materials with the incorporation of titanium dioxide have been shown to be a promising technique to reduce the number of air contaminants such as NO_x and volatile organic compounds (VOCs) as well as their self-cleaning properties were confirmed [1, 2]. Construction materials represent the most easily available medium to distribute photoactive substances over the widest surface area possible, gaining the maximum efficiency [3]. Mainly, the cement and concrete as matrixes in photocatalytic construction materials have been studied [4]. Meanwhile, another very important material in civil engineering is gypsum, widely used in indoor applications [5].

Apart from the pure TiO₂ the modified photocatalysts with incorporated additional elements have been studied in mere applications. Non-metal doping of TiO₂ (e.g. nitrogen, carbon, fluorine and sulphur) enhance the solar efficiency of the photocatalyst and favour electron–hole separation, limiting their disadvantageous recombination [6]. Hence, the modified forms of TiO₂ in building applications seem to be more competitive and promising.

The durability in the air-purifying and self-cleaning activity is essential in photocatalytic building materials. Therefore, the ageing trials of photocatalytic building materials have been undertaken, relating to both the natural outdoor exposure and the artificially accelerated condensation cycles in a chamber. The results indicated that the durability depends greatly on the type of building material. In some cases, the photocatalytic activity was unaltered, whereas in other cases was reduced due to the removal of titanium dioxide nanoparticles from the surface. A decrease of TiO₂ content was observed, but photodegradation efficiency seemed not to be affected [7]. Other scientists assigned the decrease of photocatalytic activity of photoactive mortars in time to the soiling process [8].

However, there are still questions and doubts, on the one hand about the ‘life time’ of these photoactive building materials, on the other hand about stability of the modified forms of photocatalysts. In this Letter, both issues were concerned. The photocatalytic properties of modified gypsum building materials during their exposition to different irradiation conditions were investigated. The impact of visible as well as UV irradiation was considered. The physicochemical properties of the added modified TiO₂/N,C photocatalysts were studied at each stage of the ageing process.

2. Experimental section

2.1. Preparation of modified TiO₂/N,C photocatalysts: The commercial titanium dioxide supplied by Grupa Azoty Zakłady Chemiczne ‘Police’ S.A. (Poland) was used as a starting material for synthesis of modified photocatalysts. Before TiO₂ modification with carbon, the starting material was rinsed with ammonia water (2.5 wt%) until pH reached ca. 6.8. The obtained suspension was filtered and the remained slurry was pre-dried for 24 h at 100°C (denoted as starting TiO₂/N). Modification of the starting TiO₂/N in the carbon atmosphere was as follows: 6 g of starting TiO₂/N was placed in a central part of tubular furnace and heated (10°C/min) up to 300°C in argon flow 200 cm³/min (99.999%, Messer, Austria). After the desired temperature was reached, the inert gas was bubbled through Dreschel bottle containing 50 cm³ of carbon source (n-hexane or cyclohexane – to obtain different amount of carbon in photocatalysts structure). The final step of the preparation process was maintained for 4 h at temperature of 300°C.

The modified TiO₂/N,C photocatalysts were irradiated in different conditions in order to check their characteristic after the exposition to various kinds of environmental impact. At the beginning the modified TiO₂/N,C photocatalysts were irradiated with visible light for a period of 24 h. Then, the source of irradiation was changed to the UV light, which was applied for 15 and 30 h, successively. The starting TiO₂/N was exhibited to the same irradiation conditions for comparison.

2.2. Gypsum samples preparation: Gypsum (Dolina Nidy Sp z o.o., Poland) was used as a base material to obtain gypsum–TiO₂ composites. The mortar for plates preparation was obtained by addition of 3 wt% of photocatalyst to gypsum matrix and then the mechanical grinding for 20 min was performed. The loading of 3 wt% of TiO₂ in gypsum mass was chosen as the optimal dose on the basis of our earlier works. The homogenous powders were mixed with water (water-to-gypsum ratio w/g=0.8). The obtained pastes were poured into silicone moulds (20 × 20 × 6 mm) and set aside for solidification of the materials. Then, the gypsum plates were removed from moulds and dried in the air to dry matter. Gypsum plates with the modified TiO₂/N,C photocatalysts were prepared, which were exposed to various irradiation conditions, as was described in the previous section. Pure gypsum plates and

gypsum plates with starting TiO_2/N were applied as the reference gypsum samples.

2.3. Characterisation of modified $\text{TiO}_2/\text{N,C}$ photocatalysts: The phase composition of the samples was determined by powder X-ray diffraction (Empyrean; PANalytical). The diffractometer was equipped with a wide angle detector (PIXcel 3D; PANalytical) and a monochromator which greatly lowers the signal-to-noise ratio. The X-ray radiation source was copper ($\lambda_{\text{CuK}\alpha} = 0.154056 \text{ nm}$). Copper tube with 35 kV voltage and 35 mA current was used. The measurements were performed in the range of $10\text{--}80^\circ$ in 2θ scale with 0.05° scanning step. The mean crystallite size of photocatalysts was calculated from full-width at half maximum of the corresponding X-ray diffraction peaks by the following equation (Sherrer's formula): $D = \lambda / (\beta * \cos\theta)$, where λ is the wavelength of X-ray radiation, β is the full-width at half maximum (rad) and θ is the reflected angle.

To identify the surface functional groups of the $\text{TiO}_2/\text{N,C}$ photocatalysts, the FTIR-4200 spectrophotometer (Jasco, Japan), equipped with a diffuse reflectance accessory (Harrick, USA), was used. The Fourier-transform infrared spectroscopy (FTIR) analyses were carried out in the mid-infrared region, covered wave numbers ranging from 400 to 4000 cm^{-1} .

The determination of elemental carbon in $\text{TiO}_2/\text{N,C}$ photocatalysts at different stages of irradiation exposition was obtained using an Organic Elemental Analyser Flash 2000 (Thermo Scientific, Germany). Simultaneously, the content of nitrogen in the samples, which is derived from pre-preparation process, was determined.

The light reflectance abilities of the $\text{TiO}_2/\text{N,C}$ photocatalysts were determined by UV-visible (UV-Vis)/diffuse reflectance (DR) technique using a V-650 spectrophotometer (Jasco, Japan) equipped with an integrating sphere accessory for diffuse reflectance spectra acquisition.

2.4. Photocatalytic oxidation reactions: The photocatalytic activity of the prepared gypsum plates was determined during degradation of the NO_x gases under UV-Vis irradiation tests. NO (air liquid, $1.989 \pm 0.040 \text{ ppm}$) was used as the target pollutant which was diluted with humidified air in ratio 1:1. As the result, the inlet NO_x concentration was about 1 ppm and relative humidity was 50%. The oxygen and water were necessary for $\cdot\text{OH}$ radicals production which are clue in photocatalytic reactions. A continuous flow system was used with the total mixed flow rate of $500 \text{ cm}^3/\text{min}$. The experimental set-up was shown schematically in our previous work [9]. A cylindrical Pyrex glass vessel with the inner dimension of $\phi \times H = 9 \text{ cm} \times 32 \text{ cm}$ was used as the photoreactor. The reactor was surrounded by UV lamps $4 \times 22 \text{ W}$ (Philips) with the cumulative radiation intensity of 100 W/m^2 UV and 4 W/m^2 Vis. Temperature of the whole system during the experiments was controlled at the level of 22°C using thermostatic chamber. An on-line chemiluminescent NO_x analyser (Model T200, Teledyne Advanced Pollution Instrumentation, USA) continuously monitored NO and NO_2 concentrations for gas analysis in the outlet. The test results were integrated for every 1 min. In this work, in the typical experiments eight gypsum plates were placed in a central part of the reactor using a frame to allow all samples on direct contact with gases. After assembling the samples the reactor was tightly closed and the NO gas stream was introduced under dark condition until the concentration of the NO reached equilibrium ($\sim 35 \text{ min}$ to level of $\sim 1 \text{ ppm}$). Then the samples were exposed to irradiation for 1 h. After this time the lamps were switched off and the continuous flow of NO was maintained still for 15 min. All the experiments were conducted twice and the average values were reported in this work. The blank experiments were also performed under the similar conditions: (i) gypsum plates without photocatalysts and (ii) photolysis of NO .

3. Results and discussion: X-ray diffraction patterns measurements for starting TiO_2/N , $\text{TiO}_2/\text{N,C-n-hex}$ and $\text{TiO}_2/\text{N,C-cyclohex}$

photocatalysts were performed (Fig. 1). It was found that the starting TiO_2/N and both modified samples consist of anatase phase with a small amount of rutile. The presence of rutile in the starting photocatalyst is directly connected with the production process. Generally, no significant changes were observed in the XRD patterns of the photocatalysts. The detailed phase composition and anatase crystallite size estimated on the basis of peak intensities of anatase ($2\theta = 25.3^\circ$) and rutile ($2\theta = 27.5^\circ$) are gathered in Table 1.

In the modified samples, the slight increase of rutile phase despite of the relatively low temperature of modification (300°C) was noticed. However, in Table 1 the relative crystalline phase participation (anatase to rutile) is given. It should be mentioned that the starting TiO_2 apart from rutile seeds contained also the amorphous phase of TiO_2 . The modification process of TiO_2 might contribute to the partial transformation of the amorphous to anatase phase rather than the direct transformation of the anatase to rutile phase. The inconsiderable increase of anatase crystallite size in TiO_2/N , C-n-hex and $\text{TiO}_2/\text{N,C-cyclohex}$ photocatalysts in comparison to starting TiO_2/N was also observed. In Fig. 2, the scanning electron microscopy (SEM) images of photocatalysts modified by n-hexane and cyclo-hexane are presented; there were no significant differences possible to be observed.

FTIR/DR spectra shown in Fig. 3 were applied to compare the surface character between the studied photocatalysts. In

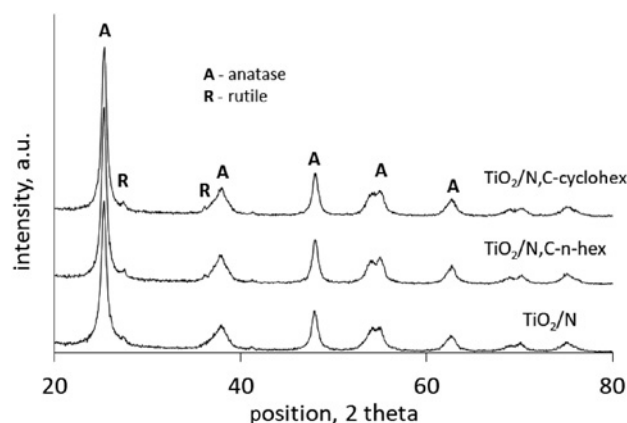


Fig. 1 XRD patterns of used photocatalysts

Table 1 Phase participation and crystallite size of the photocatalysts

Photocatalyst sample	TiO ₂ crystalline phase participation		Anatase crystallite size, nm
	Anatase, %	Rutile, %	
TiO ₂ /N	96.3	3.4	12.2
TiO ₂ /N,C-n-hex	95.8	4.2	12.8
TiO ₂ /N,C-cyclohex	95.7	4.3	12.4

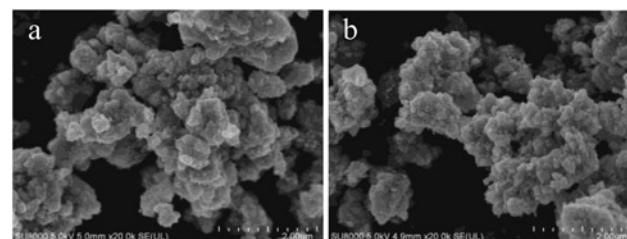


Fig. 2 SEM images of
a $\text{TiO}_2/\text{N,C-cyclohex}$
b $\text{TiO}_2/\text{n-hex}$

photocatalysts TiO_2/N , $\text{TiO}_2/\text{N,C-n-hex}$ and $\text{TiO}_2/\text{N,C-cyclohex}$, the characteristic bands appeared around 1000 cm^{-1} , which are connected with Ti–O and Ti–O–Ti bonds [10]. The next band at 1440 cm^{-1} is assigned to ammonium groups NH_4^+ [11]. Its presence is directly connected with the photocatalysts preparation step. The narrow band at about 1640 cm^{-1} is assigned to the molecular water-bending mode, while the wide bands at the range $3300\text{--}3695\text{ cm}^{-1}$ are attributed to adsorbed water and hydroxyl groups on photocatalysts surface [12].

Annealing at higher temperature (300°C) as well as the modification process caused a marked reduction in intensity of hydroxyl groups in the wavelength range of about $3800\text{--}2600\text{ cm}^{-1}$ due to the changes in content of surface –OH groups [13]. On the spectra of photocatalysts modified with carbon, new bands appeared at $1450\text{--}1470$ and $720\text{--}730\text{ cm}^{-1}$. The former one might be attributed to the $-\text{CH}_2$ bending group while the latter one could be assigned to $-\text{CH}_2$ rocking group [14]. Additionally, the $-\text{CH}_3$ group can be also present on the surface of TiO_2 modified with n-hexane, however the characteristic wavelength of the band overlaps with ammonium group [15], what prevents to identify it unequivocally. The application of UV or visible irradiation did not involve any of significant changes in FTIR spectra of modified photocatalysts. Regardless of the source of carbon, the groups $-\text{CH}_2$ were present on the photocatalysts surfaces after different type of irradiation conditions.

Table 2 includes elemental analysis of all photocatalysts towards nitrogen and carbon content. The application of carbon involved the lower nitrogen content in TiO_2 . The modified samples show the similar initial carbon content. However, a decreasing tendency in C content with increasing irradiation time was observed, especially for $\text{TiO}_2/\text{N,C-cyclohex}$. This behaviour can be explained by the structure of the carbon sources. Carbon from n-hexane can be

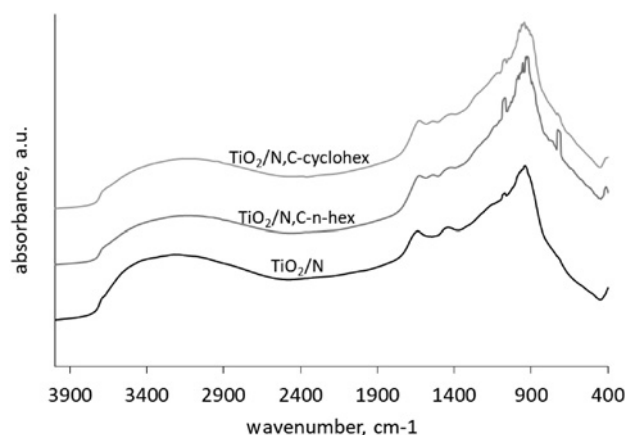


Fig. 3 FTIR spectra of starting and modified photocatalysts

Table 2 Nitrogen and carbon elemental analysis of the photocatalysts

Photocatalyst sample	Irradiation conditions	Carbon content, wt%	Nitrogen content, wt%
TiO_2/N	0 h	0.09	0.49
	24 h Vis	—	0.45
	15 h UV	—	0.41
	30 h UV	—	0.39
$\text{TiO}_2/\text{N,C-n-hex}$	0 h	0.86	0.23
	24 h Vis	0.88	0.28
	15 h UV	0.65	0.27
	30 h UV	0.62	0.27
$\text{TiO}_2/\text{N,C-cyclohex}$	0 h	0.81	0.25
	24 h Vis	0.68	0.29
	15 h UV	0.56	0.29
	30 h UV	0.47	0.29

embedded into TiO_2 in easier and stable way in comparison to the cyclic compound but the loss of C in case of $\text{TiO}_2/\text{N,C-n-hex}$ also achieved ca. 28% after 30 h of UV irradiation.

Fig. 4 shows the UV–Vis/DR spectra of starting and modified forms of TiO_2 together with the spectra obtained for the modified photocatalysts irradiated for 30 h of UV irradiation. Modification of starting TiO_2 by carbon leads to slight changes in the energy bandgap (3.32 eV for starting TiO_2/N to 3.43 and 3.41 eV for titania modified by n-hexane and cyclohexane, respectively). The redshift was insignificant and was reduced after the irradiation process (3.38 eV for both photocatalysts after the 30 h of UV irradiation). However, both modified TiO_2 powders better absorbed visible light. It was directly connected with the colour of prepared photocatalysts. After the process of modification the colour of photocatalysts was observed to change from white to dark brown. The irradiation process induced the next changes in the character of absorption spectra. As it can be seen in Fig. 4, after the same period of irradiation, the photoabsorption in the visible region was stronger for $\text{TiO}_2/\text{N,C-n-hex}$ than for $\text{TiO}_2/\text{N,C-cyclohex}$. In case of $\text{TiO}_2/\text{N,C-n-hex}$ material, colour of powder was darker during all irradiation cycles. On this basis, it was possible to believe that $\text{TiO}_2/\text{C-n-hex}$ photocatalyst contains more carbon located in a more stable way than the second one photocatalyst what was additionally confirmed by elemental analysis.

At the beginning of photocatalytic tests it was confirmed that photocatalysis on pure gypsum or photolysis of NO has not occurred. The exemplary profile of NO_x changes during photocatalytic reactions using photocatalytic gypsum plates as illustrated in Fig. 5. Generally, the photocatalytic degradation NO_x pathway

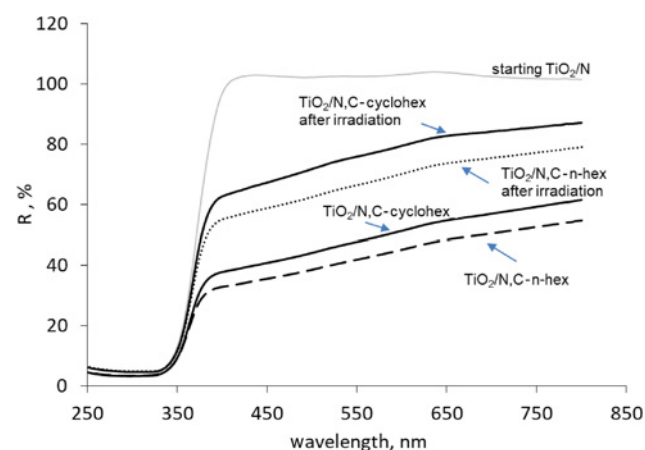


Fig. 4 UV–Vis/DR spectra of photocatalysts before and after 24 h Vis + 30 h of UV irradiation

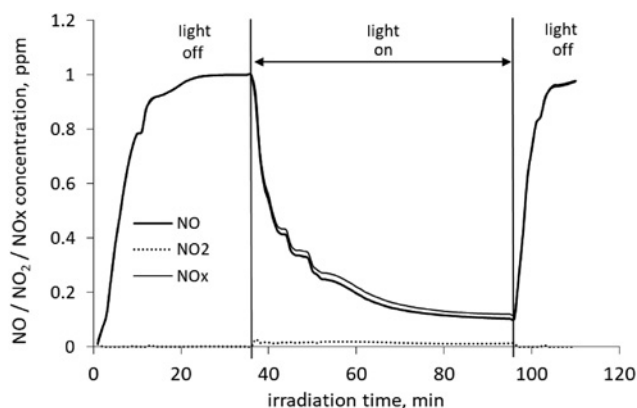


Fig. 5 Changes of NO , NO_2 and NO_x concentration versus photocatalytic process time for the exemplary gypsum sample (with $\text{TiO}_2/\text{N,C-n-hex}$)

Table 3 Photocatalytic activity of modified gypsum samples under different irradiation conditions

Gypsum sample	Irradiation conditions	NO removal, $\mu\text{g}/\text{cm}^2/\text{h}$	NO ₂ formation, $\mu\text{g}/\text{cm}^2/\text{h}$	Total loss of NO _x , $\mu\text{g}/\text{cm}^2/\text{h}$
G+TiO ₂ /N	0 h	13.4	1.5	11.9
	24 h Vis	12.9	1.1	11.8
	15 h UV	13.5	1.0	12.5
	30 h UV	13.1	1.6	11.4
G+TiO ₂ /N,C-n-hex	0 h	15.6	0.6	15.1
	24 h Vis	16.7	0.5	16.2
	15 h UV	14.4	0.7	13.7
	30 h UV	15.6	0.6	15.0
G+TiO ₂ /N,C-cyclohex	0 h	16.5	0.6	15.9
	24 h Vis	16.4	0.6	15.7
	15 h UV	13.4	0.8	12.5
	30 h UV	14.5	0.7	13.9

can be presented as follows: $\text{NO} \rightarrow \text{HNO}_2 \rightarrow \text{NO}_2 \rightarrow \text{HNO}_3$. The clue observation is that the gypsum with modified photocatalysts showed lower NO₂ selectivity than using unmodified ones (Table 3, we repeated all experiments two times and differences between the results were <5%), what is very advantageous because NO₂ is considerably more toxic than NO. The higher photocatalytic activity of gypsum with TiO₂ modified with carbon resulted from carbon presence but it should be also mentioned insignificantly bigger crystallite size and slightly higher participation of photocatalytic anatase phase in those. Despite of a gradually decrease of carbon content in TiO₂/N,C-n-hex photocatalyst, around 28% after 30 h UV, the enhanced photoactivity of corresponding gypsum plates was maintained in both NO_x removal and low conversion to NO₂.

In case of TiO₂/N,C-cyclohex, the applied irradiation considerably more reduced the modifying carbon content, what reflected in the lower photocatalytic activity of corresponding gypsum plates. However, here the carbon content after irradiation was lower about 42%, whereas the decrease of photocatalytic activity was approximately only 12% in NO removal and 13% in NO_x loss. It is highly probable that initial carbon presence in TiO₂ structure changes the electron structure of photocatalyst inducing oxygen vacancies, which presence is often responsible for the photocatalytic activity.

4. Conclusions: The gypsum building materials containing modified TiO₂ photocatalysts were successfully obtained. The main modifying element in TiO₂ structure was carbon from n-hexane or cyclohexane sources. On the basis of the conducted studies, the following conclusions were drawn:

- Modification of TiO₂ with carbon caused the enhancement of the TiO₂-loaded gypsum photocatalytic activity towards NO_x removal and decreased the production of toxic NO₂;
- The exposition of photoactive gypsum plates on the irradiation (Vis/UV) involved the slight decrease in their photocatalytic

activity in comparison to their starting properties, especially, in cases where carbon was not stable incorporated in TiO₂ structure;

- The type of carbon source influenced on the stability of TiO₂ modification indicating on the favouritism aliphatic hydrocarbons in comparison to cyclic hydrocarbons;
- Even temporary presence of modifying carbon in TiO₂ can increase their photocatalytic activity by probably creating oxygen vacancies phenomena but this issue requires further study.

5 References

- [1] Boonen E., Beeldens A., Dirckx I., *ET AL.*: 'Durability of cementitious photocatalytic building materials', *Catal. Today*, 2017, **287**, pp. 196–202
- [2] Smits M., Chan C., Tytgat T., *ET AL.*: 'Photocatalytic degradation of soot deposition: self-cleaning effect on titanium dioxide coated cementitious materials', *Chem. Eng. J.*, 2013, **222**, pp. 411–418
- [3] Diamanti M.V., Pedferri M.P.: 'Concrete, mortar and plaster using titanium dioxide nanoparticles: applications in pollution control, self-cleaning and photo sterilization'. Nanotechnology in Eco- Efficient Construction, Woodhead Publishing, Italy, 2013, pp. 299–326
- [4] Bossa N., Chaurand P., Levard C., *ET AL.*: 'Environment exposure to TiO₂ nanomaterials incorporated in building material', *Environ. Pollut.*, 2017, **220**, pp. 1160–1170
- [5] Geraldo R.H., Pinheiro S.M.M., Silva J.S., *ET AL.*: 'Gypsum plaster waste recycling: A potential environmental and industrial solution', *J. Clean. Prod.*, 2017, **164**, pp. 288–300
- [6] Pelaez M., Nolan N.T., Pillai S.C., *ET AL.*: 'A review on the visible light active titanium dioxide photocatalysts for environmental applications', *Appl. Catal. B-Environ.*, 2012, **125**, pp. 331–349
- [7] Carmona-Quiroga P.M., Martínez-Ramírez S., Viles H.A.: 'Efficiency and durability of a self-cleaning coating on concrete and stones under both natural and artificial ageing trials', *Appl. Surf. Sci.*, 2018, **433**, pp. 312–320
- [8] Diamanti M.V., Paolini R., Rossini A.B., *ET AL.*: 'Long term self-cleaning and photocatalytic performance of anatase added mortars exposed to the urban environment', *Constr. Build. Matter.*, 2015, **96**, pp. 270–278
- [9] Janus M., Zatorska J., Zajac K., *ET AL.*: 'Study of NO degradation of photoactive concrete containing N and/or C co-modified TiO₂— preliminary findings', *Micro Nano Lett.*, 2016, **11**, (5), pp. 231–235
- [10] Jagadale T.C., Takale S.P., Sonawane R.S., *ET AL.*: 'N-doped TiO₂ nanoparticles based visible light photocatalyst by modified peroxide sol-gel method', *J. Phys. Chem. C*, 2008, **112**, pp. 14595–14602
- [11] Random C., Wongnawa S., Boonsin P.: 'Bleaching of methylene blue by hydrated titanium dioxide', *ScienceAsia*, 2004, **30**, pp. 149–156
- [12] Kusiak-Nejman E., Janus M., Grzmil B., *ET AL.*: 'Methylene blue decomposition under visible light irradiation in the presence of carbon-modified TiO₂ photocatalysts', *J. Photoch. Photobio. A*, 2011, **226**, (1), pp. 68–72
- [13] Guskos N., Guskos A., Zolnierkiewicz G., *ET AL.*: 'EPR, spectroscopic and photocatalytic properties of N-modified prepared by different annealing and water-rinsing processes', *Mater. Chem. Phys.*, 2012, **136**, pp. 889–896
- [14] Murcia J.J., Hidalgo M.C., Navío J.A., *ET AL.*: 'In situ FT-IR study of the adsorption and photocatalytic oxidation of ethanol over sulfated and metallized TiO₂', *Appl. Catal. B-Environ.*, 2013, **142–143**, pp. 205–213
- [15] Janus M., Inagaki M., Tryba B., *ET AL.*: 'Carbon-modified TiO₂ photocatalyst by ethanolcarbonisation', *Appl. Catal. B-Environ.*, 2006, **63**, pp. 272–276