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PHOTOCATALYSIS FOR URBAN DEPOLLUTION: THE CONTRIBUTION OF PLASTERS WITH TIO2 NANOPARTICLES

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Abstract

Nowadays, reducing air pollution is a critical and urgent issue. Among strategies to be pursued to improve the air quality, photocatalysis is quite interesting and viable. Titanium Dioxide TiO_2 is recognized as having an excellent manner if it is exposed to solar radiation in terms of photocatalytic behavior.

This article reports the results of a research regarding the evaluation of photocatalytic activity of degradation of organic components, activated by Titanium Dioxide (TiO_2), with the aim to assess the behavior of different dyes.

As explained in the methodology, two organic dyes contrast liquids were selected and in parallel deposited on a sample of untreated stone. The reaction and degradation speed and the organic decomposition were assessed on the basis of a direct observation and colorimetric analysis.

The results showed that the coated samples generally show faster degradation of the dye under solar irradiation compared to the uncoated one sand that a greater quantity of TiO_2 in these conditions does not lead to a significant improvement in the action enough to justify the use of a more concentrated solution.

Keywords

Photocatalytic, Titanium Dioxide (TiO_2), Easy Cleaning, Nanoparticles, Plasters.

Introduction

Air pollution is the concentration in the air of fine particulate matter, sulfur oxides, and nitrogen oxides so it represents both an environmental and human health issue with serious impacts on our lives e.g., increase in diffusion of diseases like asthma, damages on vegetation as well as on earth and water ecosystems, increase in healthcare costs, etc. In Europe, air pollution is recognized as the first cause of premature death, due to environmental factors, and Italy has recorded more than 52,000 deaths per year due to PM 2.5, equal to 1/5 of those detected in all Europe (Legambiente, 2023). According to a report of the World Health Organization (WHO) every year 7 million people die, 4.2 million of which due to outdoor pollution, 3.8 million due to household pollution (WHO, 2018). This data is relevant as people pass the 80-90% of time into buildings.

The causes of the air pollution are for a slight share natural (e.g., volcanoes activities) and mostly due to anthropic activities in all economic sectors (e.g., transportation, buildings, agriculture, fishery, industry, etc.). To reduce urban air pollution towards cleaner and safer cities, there are many solutions, such as fostering public transportation, vehicles sharing, electric vehicle charging networks, pedestrian areas, cycle paths, although they require huge investments and "courageous actions" by the Government of the Regions and Municipalities. Moreover, the recommendations of the WHO clarify that not exceeding the limit set by the new European Directive on air quality (Directorate General for Environment, 2022), which will come into force from 1 January 2030, is not sufficient to guarantee the health of citizens (Figure 1).

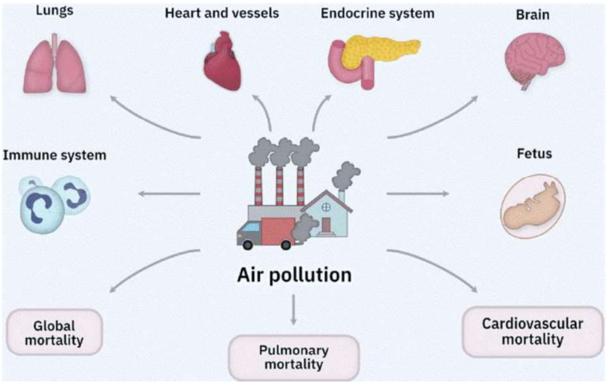

Figure 1: Effects of air pollution on human health (Source: Konduracka et Rostoff, 2022).

Air pollution exists in two phases: gas and solid. In gaseous, organic, and in-organic chemical-containments include carbon monoxide (CO), Volatile organic-compounds (VOCs), Nitrogen and Sulfur containing organic compounds (NO_x). Pathogens include bacteria, fungi, and viruses and in particles or solid phases include solid organic and inorganic pollutants (Tahir et al., 2022).

These solid and gaseous phase pollutants in air are treated by using prevention or removal approaches. At present, most common removal of air pollution techniques includes gas-adsorption filtration, ventilation, electrostatic-air purification, and air filtration (Chang et al., 2017). These physical methods have some side effects and are expensive, needing continuous replacement of materials, physical removal, and disposal. However, there are other techniques that require no physical replacement such as UV-radiation and Ozone-disinfection, but one of the major disadvantages is that they are harmful for human health (Chen et al., 2010).

Therefore, there is a serious need to use techniques for air disinfection which are environmentally friendly, inexpensive, safe, and less energy consuming, able to decompose the maximum number of air pollutants. There are several air filtration techniques, but each one has its own limitations, following explained.

Recent studies show that a concrete contribution can come from the use of materials that help sanitize polluted air, acting as photocatalysts and decomposing the organic matter that makes up the harmful VOC, transforming pollutants into harmless elements (Gowland et al., 2021; Marathe et al., 2021).

Photocatalysis (Figure 2), literally the acceleration of a chemical reaction by light, occurs when a semiconductor absorbs a quantum of electromagnetic radiation, which is a photon having energy equal or greater than to the small energy gap between the valence band completely, occupied by electrons, and the conduction band,

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initially empty (Chimmikuttanda et al., 2022).

The promotion of the electron from the valence band to the conduction one creates the chemical conditions for the coupling of redox reactions in the chain (Figure 3): in fact the electron in the conduction band can be purchased from some molecules adsorbed on the surface of the photocatalyst (in this case we talk about reduction), while the vacuum h+, which is the empty place left by the promoted electron, stimulates the transfer of an electron by adsorbed molecules (in this case it is called oxidation).

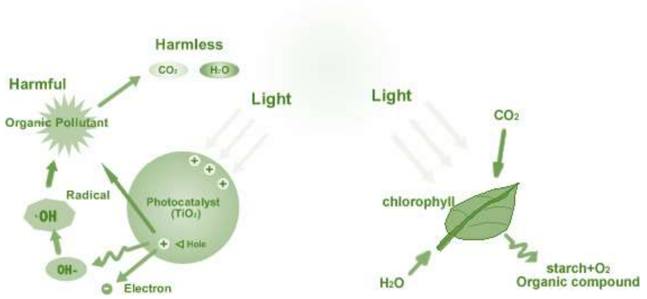

Figure 2: Scheme of photocatalysis phenomenon.

In particular, the species that is reduced is usually the Oxygen (O_2): the reduction of oxygen leads to the formation of superoxide ions; the species that is oxidized is water, generating Hydroxyl ions. The chemical species formed are highly reactive and are in turn able to decompose and transform the majority of organic and inorganic substances occurring in nature. Among all the photocatalysts in nature, one that has attracted most interest from researchers is Titanium Dioxide (TiO_2), mainly because a number of favorable properties converge on it (Armakovic et al., 2023).

Titanium Dioxide, having an energy gap that varies from 3.0 to 3.2 eV depending on the crystalline phase, which is considered, is activated by incident radiation belonging to the ultraviolet (UV) band (wavelength <400 nm) (Concordia University, 2015). It follows that the photocatalytic activity of Titanium Dioxide is dispatched in an excellent manner if it is exposed to the solar radiation, the first natural source of UV rays, or to artificial UV sources (e.g., special lamps). Moreover, studies demonstrated that the reaction rate differently depends on some key influencing factors, such as moisture, light intensity, initial contaminant concentration (Zhao et Yang, 2003).

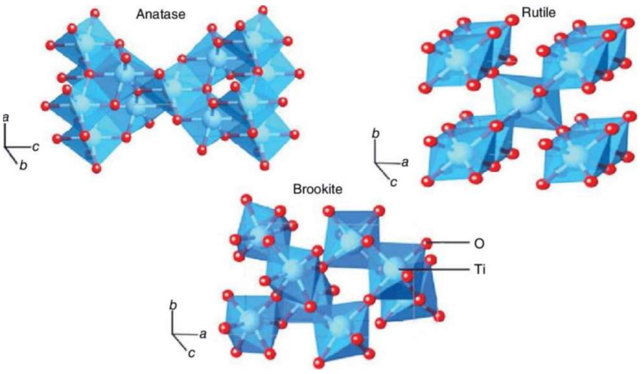

Figure 3: 3D visualization of TiO_2 crystal structures using visualization for electronic and structural analysis (Source: Karthick et al., 2019).

The air pollution is mainly caused by chlorofluorocarbons, VOC, and Nitrogen oxides, while the photocatalytic process of TiO_2 is used for purification of air as it can react with these pollutants converting them into eco-friendly substances (Dong et al., 2014; Saif et al., 2014).

Photocatalyst is used in nano form, instead of bulk form, because on the nanoscale the material has small size and higher surface area available for the reaction, increasing the reaction rate. In other words, the increase in the surface-to-volume ratio allows multiple reactants to react with the catalyst at a time e.g., Nano sized TiO_2 is more effective than bulk TiO_2.

Moreover, below 10 nm it is possible to manage some properties: by varying the size of the crystals, the redox potential of the photogenerated electron-vacuum couple is altered, with the possibility of adjustment in relation to the species to degrade (Hao et al., 2013; Magdalene et al. 2018). Furthermore, as the

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photocatalytic activity is expressed on the surface of photocatalyst, the high ratio surface-to-volume that characterizes a nanomaterial, increasing the availability of surface sites, contributes to increase the speed of the reactions of photodecomposition (Xia et al., 2008).

TiO_2 catalysts can be prepared in various nano forms, such as nanoparticle powders, nanotubes, nanorods, nanowires, and immobilized states (as thin films) (Varshney et al., 2016).

Photocatalytic treatments, in particular, show great potential against humic substances or natural organic matters. Humic substances have high molecular weight naturally occurring in yellow-brown. By using TiO_2, 80% humic acid reduction is reported (Lu et al., 2008), or 65% as reported in (Valencia et al., 2018). Also organic pollutants present in waste-water in the form of nitrates, halides, ammonia, cyanide, and thiocyanate are effectively decomposed by photocatalytic process.

TiO_2 photocatalysis shows anti-microbial effect and prevents the growth of microbes as, during the photocatalytic process, highly reactive radicals are generated that contribute to the destruction of cell-wall of bacteria causing the complete bacteria/microbes decomposition. Harmful microbes commonly present in wastewater, such as *S. mutans, S. natuss, S. cricetus, E. coli, S. cerevisisas, L. acidophilus*, etc. can be removed by heterogeneous photocatalyst (Mahmood et al., 2012). Other microbes, such as *Chlorella vulgaris*, inhibit using TiO_2 photocatalyst (Shephard et al., 2002). Similarly, photocatalyst as ZnO is used against *E. coli* and *S. aureus* (Baruah et al., 2009).

Photodegradation of some dyes was very effective in the presence of TiO_2: for example, methylene blue was photodegraded using various TiO_2 films (Matsunami et al., 2019), TiO_2 impregnated (Zuo et al., 2014), TiO_2 pretreated with varying concentrations of NaOH (Hou et al., 2018). Another dye that has attracted attention due to its frequent decomposition with TiO_2 is methyl orange. It was reported that methyl orange was photodegraded using Ag-doped TiO_2 photocatalysts (Kader et al., 2022), carbon nanotubes-TiO_2 (Wang et al., 2011), TiO_2-zeolite photocatalyst ziztyana (Aziztyana et al., 2019), etc., under visible light and UV irradiation.

In the field of building construction, after years of extensive research and continuous experiments, to date various solutions based on TiO_2 are already available on the market, such as coatings for glazed surfaces as well as photocatalytic plasters and paints for opaque surfaces, and a tendency to coat the road with photocatalytic material is also raising (Del Curto, 2014; Bazzeghini 2022; Francioso, 2017; Guerra, 2014; Garofalo, 2018; Germinario et al., 2016).

Photocatalysis process integration in building material is relevant in the debate also at normative level (OQAI, 2021; ADEME, 2013). The work that certainly can be considered as the cornerstone of the TiO_2 potentiality in architecture is the church Dives in Misericordia, built in the neighborhood of Tor Tre Teste in Rome, for the Jubilee of 2000, by the American architect Richard Meier (Figure 4).

Figure 4: Church Dives in Misericordia (Source: SacrArch).

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For Dives in Misericordia, the Italian company Italcementi, technical partner of the project, has produced a white photocatalytic cement containing nanostructured Titanium Dioxide, having the power to keep unchanged over time the beauty of surfaces due to self-cleaning properties.

Materials and Methods

Method

In this research, the photocatalytic activity of degradation of organic components, activated by TiO_2, was evaluated. For this purpose, two organic contrast liquids in aqueous solution were used; specifically: Orange G, with a concentration of 0.5 g/l, and Methylene Blue, with a concentration of 0.01 g/l. The choice to use these dyes was made to obtain readable and unmistakable results, and to be able to better follow the reaction and degradation speed, on the basis of a direct observation and colorimetric analysis aimed at identifying the change in color over time, revealing the organic decomposition. The solution used for the experimentation has a 15% concentration of TiO_2, which was diluted with distilled water in the following proportions: 1:9, 1:7, and 1:5.

Using an airbrush, a constant amount of prepared solutions was deposited onto a sample and waited for it to dry completely (3 hours).

The photocatalytic tests were carried out in several steps (Figure 5):

- Measurement of the initial color of the sample
- Application of organic dye
- Exposure of the sample to solar radiation
- Degradation monitoring.

The tests were carried out in parallel on a sample of untreated stone surface in order to evaluate the difference in action of the dye.

Application of organic dye were carried out in two steps: initially, only Methylene Blue was used as a contrast medium and by observing the behavior of the sample, with the addition of TiO_2, it was attempted to study the self-cleaning properties of the plaster mortars on which the organic compound has been deposited simulating the action of dirt on the surface.

Afterwards, the Orange G dye was also applied, to have a double basis for comparison. The application of the organic dye was carried out using a pipette, in order to deposit a precise quantity of solution on the surface of the sample and it was waited for to dry. Subsequently, the colorimetric coordinates of the original color of the sample solution were detected using a colorimeter, in order to have a term of comparison with the color detected at the end of the solar exposure time on the specimens.

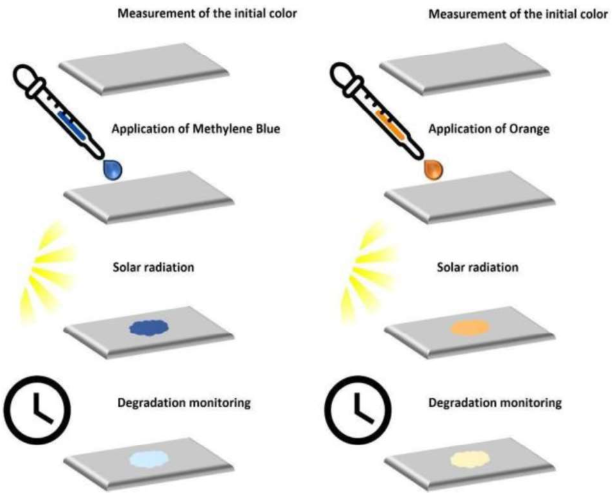

Figure 5: Steps of the photocatalytic tests.

The ZL300 colorimeter was used to measure the color difference. The CIE L*a*b* color space was used as a reference system where each color is defined by three colorimetric coordinates: L* is the coordinate of lightness; a* is the red/green coordinate and b* is the yellow/blue coordinate. For each specimen five regions, few mm^2 in size each, were examined and averaged. The total color difference, $\Delta E{*}ab$, was measured in the CIE

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L*a* b* color space and calculated using the following equation:

$$\Delta Eab = [(\Delta L) 2 + (\Delta a) 2 + (\Delta b) 2] ½$$

where ΔL is the lightness difference; Δa is the red/green difference and Δb is the yellow/blue difference.

The use of the colorimeter for the detection of the photocatalytic activity of TiO_2 has been widely used in the literature. The samples to be tested were then exposed to direct sunlight for two weeks, during which the action of the TiO_2 on the organic compound was monitored through photographic surveys.

Materials

TiO_2

Titanium Dioxide, also known as *Titania* if synthetic, is a chemical compound that occurs in the form of a colorless, whitish crystalline powder and has the chemical formula TiO_2.

TiO_2 in nature is present in five different crystalline forms: rutile, anatase, brookite, and the two very high-pressure polymorphs (due to meteorite impact) akaogiite and TiO_2II, which can be colored due to impurities present in the crystal. Rutile is the most common form: each titanium atom is surrounded octahedrally by six oxygen atoms; anatase has a tetragonal structure, more elongated than that of rutile, while brookite has an orthorhombic structure.

Due to its high refractive index, Titanium Dioxide (Figure 6) is mainly used as a white pigment in paints, plastic materials, construction cement, opacifier for colored paints (Lucas et al., 2013) and, also, to exploit solar energy to produce hydrogen from water (Chiarello et al., 2008); for this reason, it is also commonly called "titanium white". Paints made from Titanium Dioxide are excellent reflectors of infrared radiation and are therefore used extensively by astronomers.

It replaced previously used pigments, such as lead white, barium sulfate, and calcium sulfate. Compared to lead compounds it has greater covering power, is not toxic, and does not blacken if exposed to hydrogen sulfide. It is also used as a filler in plastics and rubber, as an opacifier in paper and textile fibers, and in ceramic materials to increase resistance to acids.

Titanium Dioxide is also a well-known catalyst capable of degrading numerous organic compounds by oxidation. By exploiting this property, it is possible to obtain materials which, through activation by sunlight, are capable of destroying the organic compounds deposited on them.

This property could potentially lead to the development of a new class of materials with self-cleaning and depolluting properties. In fact, when exposed to light, Titanium Dioxide molecules catalyze the oxidation of organic residues (dirt, pollution deposits, and microorganisms of various kinds) into water and carbon dioxide.

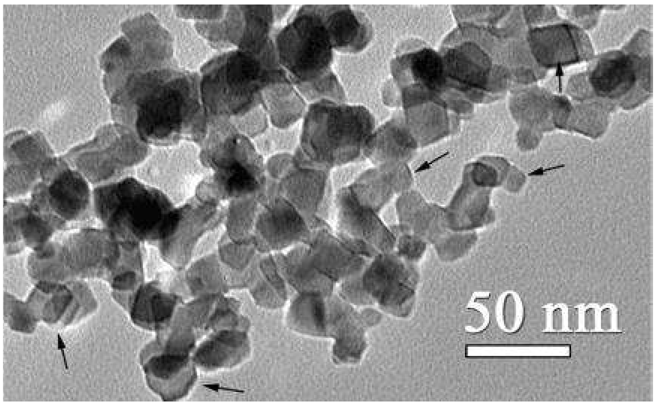

Figure 6: Transmission electron micrograph of Titanium Dioxide nanoparticles. (Source: MissioneScienza.it).

Organic dyes: Methylene blue and Orange G

Methylene Blue is an organic compound of the aromatic heterocyclic class and is used in many

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different fields. It is an almost odorless harmful compound.

At room temperature it appears as an odorless, dark green crystalline solid, stable in air and light. When methylene blue is dissolved in aqueous solution, it takes on an intense dark blue color.

Methylene blue is obtained industrially by oxidation of a mixture of dimethyl-p-phenylenediamine, sodium thiosulfate and dimethylaniline.

Orange G is a synthetic azide dye widely used in histology and laboratory practice in molecular biology. The pure compound appears in crystals or as a very minute orange-red powder; forms lumps in a humid environment. It is marketed in the form of disodium salt.

Results and Discussion

Results

It is possible to note that although organic dyes tend to decompose even on untreated surfaces, the greatest color variation was recorded i.e., a more rapid degradation of organic dye for the 1:5 ratio. This means that the use of a solution the more concentrated has greater photocatalytic activity.

However, there are not substantial differences between the 1:9 and 1:7 dilution ratios.

Figures 7 and 8 are images of the samples at different exposure time intervals and Table 1 shows the results of colorimetric analysis.

The test was therefore repeated, to further investigate the 1:9 and 1:7 ratios and compare them with the decomposition speed of the organic dye of the 1:5 diluted solution, again in relation to the untreated one. The results of the tests are reported in Table 2.

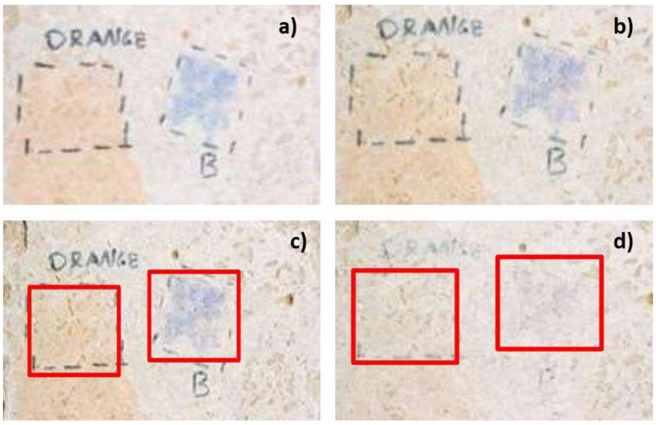

Fig. 7: White ref sample exposed to solar radiation at different time intervals: a) start of exposure; b) after 24 hours; c) after 48 hours; d) after 120 hours.

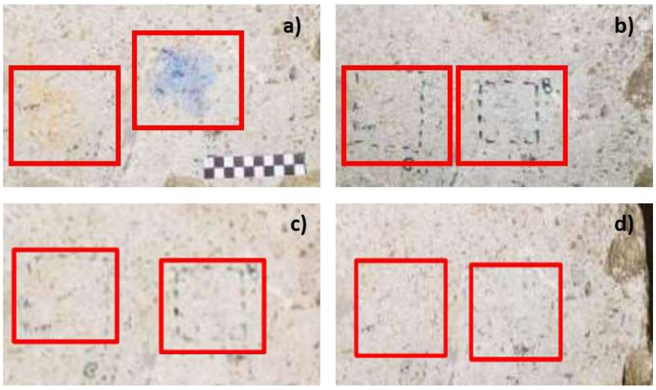

Fig. 8: Sample treated and exposed to solar radiation at different time intervals: a) start of exposure; b) after 24 hours; c) after 48 hours; d) after 120 hours.

Table 1. Colorimetric analysis results

Colorimetric data analysis		
Dilution ratio	**Methylene Blue Delta Eab**	**Orange G Delta Eab**
White Ref	10.55	5.40
1:9	17.76	3.87
1:7	16.26	5.40
1:5	23.74	5.70

Table 2. Colorimetric analysis results

Colorimetric data analysis	
Dilution ratio	**Methylene Blue Delta Eab**
White Ref	4.7
1:9	7.2
1:7	10.5
1:5	13.4

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Once again, the fastest color change was recorded compared to the untreated, for the ratio 1:5, as reported in Figures 9 and 10.

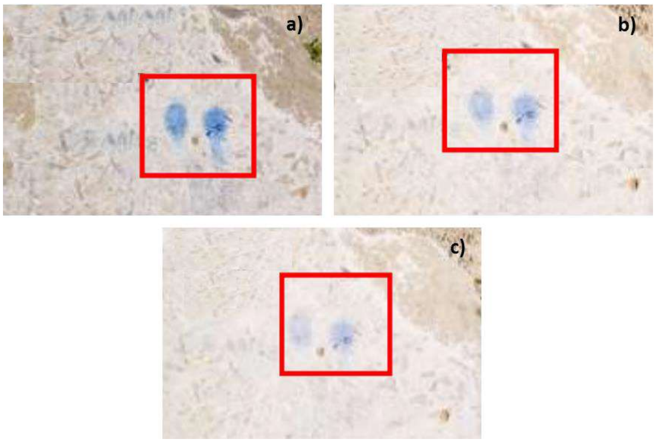

Fig. 9: White ref sample exposed to solar radiation at different time intervals: a) start of exposure; b) after 24 hours; c) after 48 hours

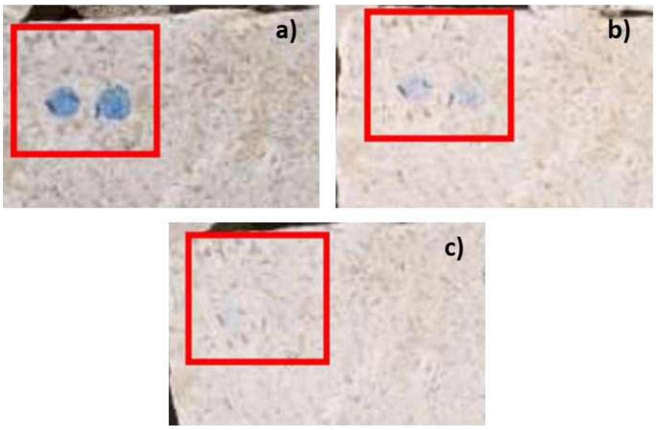

Fig. 10: Sample treated and exposed to solar radiation at different time intervals: a) start of exposure; b) after 24 hours; c) after 48 hours.

However, there is a small difference between the 1:9 and 1:7 dilution ratios, in particular for 1:7 the colour degradation was more rapid.

Further values were recorded 144 hours after the start of exposure. The results are shown in Figure 11.

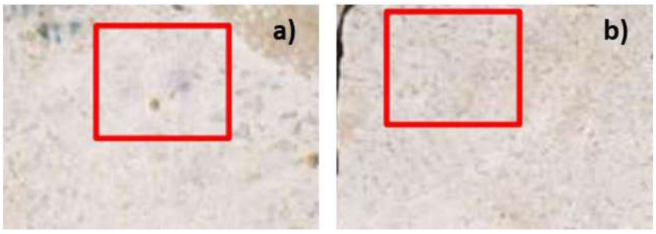

Fig.11. White ref sample (a) and treated sample (b) exposed to solar radiation after 144 hours.

Table 3 shows the results of colorimetric analysis after 144 hours. The photocatalytic activity of the Titania particles produces most of the total degradation effect on the stain in the first hours of exposure, a result also obtained from the analyzes conducted in the study by L. Bergamonti et al. (2013).

Table 3 Colorimetric analysis results after 144 h.

Colorimetric data analysis	
Dilution ratio	**Methylene Blue Delta Eab**
White Ref	16.90
1:9	14.5
1:7	16.43
1:5	21.64

Conclusions and Perspectives

Innovative nanoparticles-based photocatalyst are relevant for applications in the building sector (Vitali et al, 2016) and this article reports the results of a research regarding the evaluation of photocatalytic activity of degradation of organic components, activated by Titanium Dioxide.

The coated samples generally show faster degradation of the dye under solar irradiation compared to the uncoated ones.

From the tests conducted on the various TiO_2 solutions, it emerged that although the faster color change compared to the untreated one was recorded for the 1:5 ratio.

Moreover, after the comparative tests, there are no substantial differences between the 1:9 and 1:7 dilution ratios. Consequently, in order to reduce TiO_2 total amount, it is possible to use the TiO_2 solution in the most diluted conditions, as a greater quantity of it in these conditions does not lead to a significant improvement in the action able to justify the use of a more concentrated solution.

Author's contributions

RM: Roberta Montagno, FF: Federica Fernandez, MGI: Maria Grazia Insinga, RB: Robrta Basile, FZ: Federica Zagarella

Conceptualization: FF, RM. Data curation: RM, MGI. Formal analysis: RM, MGI, RB, FZ. Investigation: FF, MGI, RB, FZ, RM. Methodology and Supervision: FF, Validation: FF, MGI, RM.

References

1. Zhang X., Cao, S., Wu Z., Zhao S., Piao L. Enhanced photocatalytic activity towards degradation and H2 evolution over one dimensional TiO2@ MWCNTs heterojunction. Applied Surface Science. 2017, 402, 360-368 https://doi.org/10.1016/j.apsusc.2017.01.09
2. Chen F., Yan X., Mak H. K. C., Chan D. W. T. Photocatalytic oxidation for antimicrobial control in built environment: A brief literature overview. Building and Environment. 2010, 45, 8 747-1754 https://doi.org/10.1016/j.buildenv.2010.01.024
3. Gowland D., Neil C.A., Efthalia R., Photocatalytic Oxidation of Natural Organic Matter in Water. Water 2020, 13, 3,288 https://doi.org/10.3390/w13030288
4. Marathe, D.; Balbudhe, S.; Kumari, K. Persistent Organic Pollutants: A Global Issue, a Global Response. In Persistent Organic Pollutants; CRC Press: Boca Raton, FL, USA, 2021
5. Chimmikuttanda S. P., Naik A., Akple M. S. Singh R., Chapter 10 - Processing of hybrid TiO2 semiconducting materials and their environmental application, in Advanced Materials for Sustainable Environmental Remediation, Elsevier, 2022, 277-300 https://doi.org/10.1016/B978-0-323-90485-8.00011-4
6. Armaković, Sanja J., Maria M. Savanović, and Stevan Armaković. 2023. Titanium Dioxide as the Most Used Photocatalyst for Water Purification: An Overview. Catalysts 13, no. 1: 26. https://doi.org/10.3390/catal13010026
7. Zhao J., et Yang X. (2003) Photocatalytic oxidation for indoor air purification: a literature review. Building and Environment, 38(5):645-654, 2003 https://doi.org/10.1016/S0360-1323(02)00212-3
8. Dong F., Guo S., Wang H., Li X., Wu Z. Enhancement of the visible light photocatalytic activity of C-doped TiO2 nanomaterials prepared by a green synthetic approach. The Journal of Physical Chemistry C. 2011, 115 https://doi.org/10.1021/jp111916q
9. Saif M.,Aboul-Fotouh S.M.K. , El-Molla S.A., Ibrahim M.M., Ismail L.F.M. Evaluation of the photocatalytic activity of Ln3+–TiO2 nanomaterial using fluorescence technique for real wastewater treatment. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2014, 128, 153-162 https://doi.org/10.1016/j.saa.2014.02.031
10. Hao J.-Y., Wang Y., Tong X., Jin G., Guo X. SiC nanomaterials with different morphologies for photocatalytic hydrogen production under visible light irradiation. Catalysis Today. 2013, 212, 220-224 https://doi.org/10.1016/j.cattod.2012.09.023
11. Magdalane C.M., Kaviyarasu K., Arularasu M. V., Molta G. T., Isaev A. B., Al-Dhabi N. A., Arasu M. V., Jeyaraj B., Kennedy J., Maaza M. Photocatalytic decomposition effect of erbium doped cerium oxide nanostructures driven by visible light irradiation: Investigation of cytotoxicity, antibacterial growth inhibition using catalyst. Journal of Photochemistry and Photobiology B: Biology. 2018,185, 275-282 https://doi.org/10.1016/j.jphotobiol.2018.06.011

Available online at https://www.iemest.eu/life-safety-and-secrity/

12. Xia, X.H.; Liang, Y.; Wang, Z.; Fan, J.; Luo, Y.S.; Jia, Z.J. Synthesis and Photocatalytic Properties of TiO2 Nanostructures. Mater. Res. Bull. 2008, 43, 8-9, 2187-2195 https://doi.org/10.1016/j.materresbull.2007.08.026
13. Varshney, G.; Kanel, S.R.; Kempisty, D.M.; Varshney, V.; Agrawal, A.; Sahle-Demessie, E.; Varma, R.S.; Nadagouda, M.N. Nanoscale TiO2 Films and Their Application in Remediation of Organic Pollutants. Coordination Chemistry Reviews. Elsevier B.V., Amsterdam, Netherlands, 2016, 306(Part 1):43-64 http://dx.doi.org/10.1016/j.ccr.2015.06.011
14. Valencia S., Marín J., Restrepo G. Photocatalytic degradation of humic acids with Titanium Dioxide embedded into polyethylene pellets to enhance the post recovery of the catalyst. Environmental Engineering Scienc,. 2018, 35, 3 https://doi.org/10.1089/ees.2017.0091
15. Mahmood M.A., et al. Heterogeneous photocatalysis for removal of microbes from water. Environmental Chemistry Letters. 2012,10
16. Shephard G., Stockenstro M.S., De Villiers D., Engelbrecht W.J., Wessels G.F.S. Degradation of microcystin toxins in a falling film photocatalytic reactor with immobilized Titanium Dioxide catalyst. Water Research. 2002, 36, 140-146 https://doi.org/10.1016/S0043-1354(01)00213-5
17. Baruah S., SInha S. S., Ghosh B., Pal S. K. Raychaudhuri A. K. Dutta, J. Photoreactivity of ZnO nanoparticles in visible light: Effect of surface states on electron transfer reaction. Journal of Applied Physics. 2009, 105 https://doi.org/10.1063/1.3100221
18. Matsunami, D.; Yamanaka, K.; Mizoguchi, T.; Kojima, K. Comparison of Photodegradation of Methylene Blue Using Various TiO2 Films and WO3 Powders under Ultraviolet and Visible-Light Irradiation. Journal of Photochemistry and Photobiology A: Chemistry 2019, 369, 106-114 https://doi.org/10.1016/j.jphotochem.2018.10.020
19. Zuo, R.; Du, G., Zhang, W.; Liu, L.; Liu, Y.; Mei, L.; Li, Z. Photocatalytic Degradation of Methylene Blue Using TiO2 Impregnated Diatomite. Advances in Materials Science and Engineering 2014, 2014, 170148 https://doi.org/10.1155/2014/170148
20. Hou C.; Hu, B.; Zhu, J. Photocatalytic Degradation of Methylene Blue over TiO2 Pretreated with Varying Concentrations of NaOH. Catalysts 2018, 8, 575 https://doi.org/10.3390/catal8120575
21. Kader, S.; Al-Mamun, M.R.; Suhan, M.B.K.; Shuchi, S.B.; Islam, M.S. Enhanced Photodegradation of Methyl Orange Dye under UV Irradiation Using MoO3 and Ag Doped TiO2 Photocatalysts. Environ. Technol. Innov. 2022, 27, 102476 https://doi.org/10.1016/j.eti.2022.102476
22. Wang, S.; Zhou, S. Photodegradation of Methyl Orange by Photocatalyst of CNTs/P-TiO2 under UV and Visible-Light Irradiation. Journal of Hazardous Materials 2011, 185, 77-85 https://doi.org/10.1016/j.jhazmat.2010.08.125
23. Aziztyana A. P., Wardhani, S., Prananto Y. P., Purwonugroho, D., Darjito1 . Optimisation of Methyl Orange Photodegradation Using TiO2-Zeolite Photocatalyst and H2O2 in Acid Condition. In Proceedings of the IOP Conference Series: Materials Science and Engineering; IOP Publishing: Bristol, UK, 2019; Volume 546, p. 42047 https://doi.org/10.1088/1757-899X/546/4/042047
24. Pulvirenti F., Rivestimenti autopulenti nanostrutturati: sperimentazioni e applicazioni in campo civile. Tesi di laurea, Relatore prof. Del Curto, 2014, Politecnico di Milano. https://hdl.handle.net/10589/93191
25. Bazzeghini C., Fotocatalisi per la purificazione indoor dell'aria. Tesi di laurea, Relatore prof. Gasparotto, 2022, Università degli Studi di Padova.

Available online at https://www.iemest.eu/life-safety-and-secrity/

26. Francioso V. L’ossido di titanio (IV) come additivo delle malte di cemento. Tesi di laurea, Relatore prof. Fantilli, 2017, Politecnico di Torino.
27. Guerra V., Attività fotocatalitica del biossido di titanio applicato ai materiali da costruzione. Analisi delle prestazioni in funzione della tipologia di supporto e della tecnica di deposizione. Tesi di laurea, Relatore prof. Fregni, 2014, Università di Bologna.
28. Garofalo M. Abbattimento fotocatalitico di composti organici volatili. Tesi di laurea, Relatori prof. Bensaid, Piumetti, Russo, 2018, Politecnico di Torino.
29. Germinario S., Baldi G., Dami V., Cioni A., Fernandez F., Livreri P., Evaluation of nanostructured coatings for the protection of stones, International Conference YOCOCU 2016, Madrid 21-23 September 2016
30. Observatoire de la Qualité de l’Air Intérieur. (OQAI) Epuration de l’air par photocatalyse (Nº.4) 2021 https://www.oqai.fr/fr/media/brochures-et-guides/4-ateliers-bulletin-photocatalyse
31. Agence de l’Environnement et de la Maîtrise de l’Énergie (ADEME). Les fiches techniques de l’ADEME – Epuration de l’air par photocatalyse, 2013. https://www.ademe.fr
32. GianLuca Guerrini, Laurent Guillot, Realizzazioni Di Edifici Con Utilizzo Di Cementi Fotocatalitici. 16° Congresso C.T.E. - Parma, 9-11 Novembre 2006 - Volume 2 pagg. 941-950.
33. Calia A., Lettieri M., Masieri M., Pal S., Licciulli A., Arima V., Limestones coated with photocatalytic TiO2 to enhance building surface with self-cleaning and depolluting abilities - Journal of Cleaner Production Volume 165, 1 November 2017, Pages 1036-1047 https://doi.org/10.1016/j.jclepro.2017.07.193
34. Colangiuli D., Lettieri M., Masieri M., Calia A., Field study in an urban environment of simultaneous self-cleaning and hydrophobic nanosized TiO2-based coatings on stone for the protection of building surface. Science of The Total Environment - Volume 650, Part 2, 10 February 2019, Pages 2919-2930. https://doi.org/10.1016/j.scitotenv.2018.10.044
35. Graziani L., Quagliarini E., Bondioli F., D'Orazio M., Durability of self-cleaning TiO2 coatings on fired clay brick façades: Effects of UV exposure and wet & dry cycles, Building and Environment - Volume 71, January 2014, Pages 193-203. https://doi.org/10.1016/j.buildenv.2013.10.005
36. Lucas S.S., Ferreira V.M., Barroso de Aguiar J.L., Incorporation of Titanium Dioxide nanoparticles in mortars — Influence of microstructure in the hardened state properties and photocatalytic activity, Cement and Concrete Research, 43, 2013, 112-120, ISSN 0008-8846 https://doi.org/10.1016/j.cemconres.2012.09.007
37. Chiarello G. L., Selli E., Forni L. Photocatalytic Hydrogen Production over Flame Spray Pyrolysis-synthesised TiO2 and Au/TiO2. Applied Catalysis B: Environmental, 2008, 84,1–2,332-339 https://doi.org/10.1016/j.apcatb.2008.04.012
38. Bergamonti L., Alfieri I., Lorenzi A., Montenero A., Predieri G., Barone G., Mazzoleni P., Pasquale P., Lottici P. P. Nanocrystalline TiO2 by sol–gel: Characterisation and photocatalytic activity on Modica and Comiso stones Applied Surface Science- Volume 282, 1 October 2013, Pages 165-173 https://doi.org/10.1016/j.apsusc.2013.05.095
39. Vitali A., Mosquera M. J., Castro P., Piccirillo C., Pullar R.C., Fernandez F., Livreri P., Innovative hydroxyapatite nanoparticles-based photocatalyst for application on marble: evaluation of self-cleaning properties, 13th International Conference on Nanosciences & Nanotechnologies (NN16), 5-8 July 2016, Thessaloniki, Greece.

Available online at https://www.iemest.eu/life-safety-and-secrity/