Review

Challenges and Opportunities of Using Titanium Dioxide Photocatalysis on Cement-Based Materials

Angélica María Castro-Hoyos [1] , Manuel Alejandro Rojas Manzano [1] and Aníbal Maury-Ramírez [2],*

1   SIGMA Research Group, Departamento de Ingeniería Civil e Industrial, Pontificia Universidad Javeriana Cali, Santiago de Cali 760031, Colombia; angelicamariacastro@javerianacali.edu.co (A.M.C.-H.); alejandro.rojas@javerianacali.edu.co (M.A.R.M.)
2   CHOC-IZONE Research Group, Engineering Faculty, Universidad El Bosque, Bogota 111711, Colombia
*   Correspondence: amaury@unbosque.edu.co; Tel.: +57-1-6489000

Abstract: Since the early seventies with the work of Akira Fujishima on photocatalytic and superhydrophilic properties of titanium dioxide (TiO_2), also known as the Honda–Fujishima effect, photocatalysis has been investigated and progressively implemented in cement-based materials towards the development of self-cleaning, air-purifying and antiseptic materials, buildings and infrastructure. Although important achievements have been obtained at the laboratory scale, their real scale application has had some limitations mainly due to the low efficiencies obtained during adverse environmental conditions. Therefore, this article presents the challenges and opportunities of using of titanium dioxide in cement-based materials towards the development of truly efficient sustainable building materials. First, TiO_2 photocatalysis and its incorporation in cementitious materials are presented. Second, self-cleaning, air-purifying and antimicrobial properties are discussed in terms of the lab and pilot project results. Third, conclusions regarding the different multifunctional properties are given towards the real application of TiO_2 photocatalysis. Particularly, complementary technologies and strategies are presented in order to increase the above-mentioned multifunctional properties.

Keywords: TiO_2; photocatalysis; cement-based materials; air purification; self-cleaning; antimicrobial; concrete; mortar; coating

1. Introduction

Urban air pollution and global warming are one of the biggest environmental problems faced today by our planet and society. Although there are diverse pollutant sources and responsible parties, the construction industry has a great responsibility on this situation. For example, in the manufacturing phase, for every ton of produced Portland cement, approximately 700 kg of CO_2 are released to the atmosphere [1]. On the other hand, derived from other anthropogenic processes, such as transportation using vehicles with fossil fuels, volatile organic compounds (VOCs) and nitrogen oxides (NOx) are released to the atmosphere in high concentrations, which not only deteriorate air quality and increase climate change, but also cause an increased risk of acquiring respiratory diseases [2,3].

In order to mitigate air pollution, strategies such as the use of photocatalytic construction materials using nanotechnology has been considered worldwide [2]. Among the different nanomaterials, titanium dioxide (TiO_2) has been the most widely used for this purpose. When TiO_2 is incorporated into concrete or mortar it can convert dangerous pollutants into less harmful products [4]. In addition to the air purification capacity, TiO_2-loaded materials can develop self-cleaning and antimicrobial properties [5,6]. Therefore, the use of this semiconductor in building materials has not only the potential to improve air quality and mitigate global warming, but also to allow savings in maintenance (costs and operational time) by generating self-cleaning surfaces with great potential to reduce the presence of microorganisms [7–9]. As microorganisms include bacteria, viruses and fungi, recent research includes the application towards the elimination of SARS-CoV-2, which

causes COVID-19. The last one has been done by Akira Fujishima in collaboration with a Mexican research team, who studied the interface nanostructure/cell-wall microorganism to understand the annihilation mechanism [10].

As described, nanotechnology plays an important role in the field of materials' science and technology, having a great impact on building materials. This seeks not only to improve the traditional properties of cementitious materials (i.e., resistance and durability), but it also looks forward to providing building materials with new functionalities, such as self-cleaning, antimicrobial and air-purifying properties [6]. However, although intensive research has been done during almost 20 years on TiO_2 photocatalysis towards the above-mentioned properties, the current challenges in applying this light-driven technology, particularly on cementitious materials, have limited the efficient in -situ application. Therefore, this state of the art presents the TiO_2 fundamentals in relation to the main research gaps of the multifunctional properties obtained at the laboratory scale and in pilot projects. Furthermore, this article describes the effect of using TiO_2 on mechanical and durability properties of cementitious materials, which are also a point of discussion in the construction sector.

2. TiO_2 Fundamentals

Although there are several approaches and production technologies for titanium dioxide, the nanoparticles consist of thousands of atoms integrated into approx. 1–100 nm clusters. This small size translates into a high specific surface area that allows the nanomaterial to have high reactivity [1]. In principle, it was possible to obtain TiO_2 nanoparticles by simple milling of the pigmentary TiO_2 into finer particles. In spite of this, the properties of the fine powders in terms of purity, particle size distribution and particle shape were highly unsatisfactory. Therefore, several wet-chemical processes were developed during the 1980s by TiO_2 manufacturers [11].

Nanoscale titanium dioxide is a semiconductor material with photocatalytic properties, which means that when it is exposed to mainly UV-A light (315–400 nm), obtained from the sun or artificial light (lamps), it can simultaneously generate self-cleaning, air-purifying and antimicrobial properties [4,12,13].

Titanium dioxide can be found in three crystalline forms: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) (Figure 1). Among these crystalline forms, rutile is thermodynamically the most stable, while brookite and anatase transform to rutile under heating. The transformation of anatase to rutile, which is a broadly studied mechanism, occurs at temperatures between 550 and 1000 °C, while less-studied transformation of brookite to rutile has been reported between 500 and 600 °C [14,15]. The temperature of this transformation depends on impurities or dopants present in the material as well as on the morphology of the sample. Although the three varieties have been prepared synthetically using different techniques, brookite is not economically significant since there is not an abundant supply in nature; synthetically, it has been only observed as a by-product along with either anatase or rutile. Therefore, rutile and anatase have more industrial applications. Independent to the varieties, TiO_2 is the most widely used catalyst due to the stability of its chemical structure, low toxicity, biocompatibility, high reactivity, electrical, physical and optical properties, ease of synthesis and low cost [2,7,16].
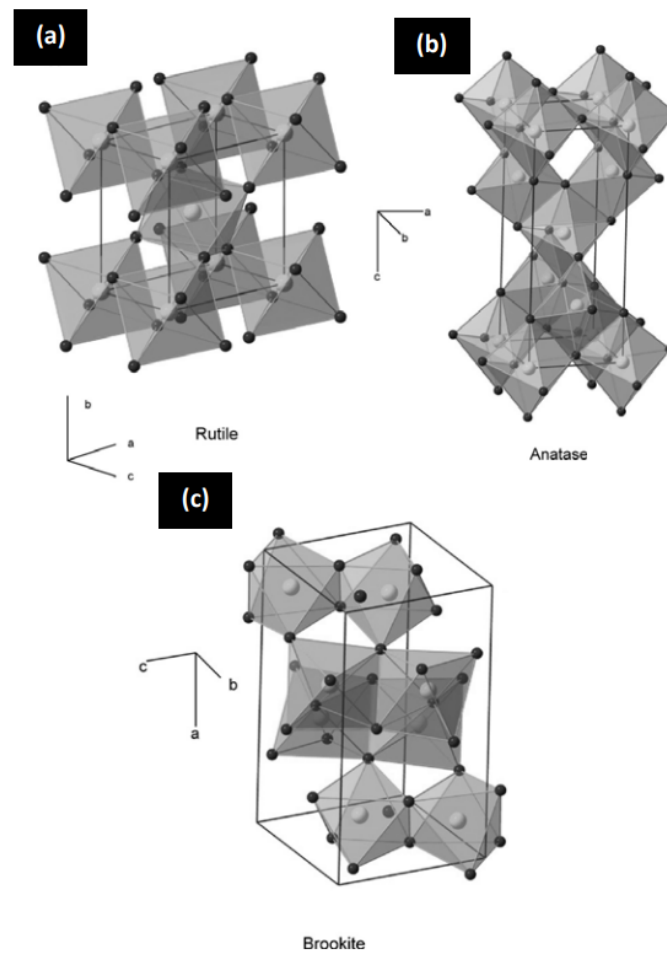
Figure 1. Crystal structure of TiO$_2$: (**a**) rutile (**b**) anatase and (**c**) brookite. Adapted with permission from Ref. [17]. Copyright 2009, Elsevier.

　　　The photocatalytic process starts with the exposure to UV-A (photons), which makes an electron (e$^-$) from the valence band move towards the conduction band, leaving a hole (h$^+$) in the valence band [7,18,19]. This is only produced if the activation light contains photons with equal or higher energy than its band gap (Eg), energy difference between the valence and conduction bands. One part of the electron-hole pair is diffused to the surface, where it is retained. Then, when oxygen (O$_2$) and water vapor (H$_2$O) present in the environment come into contact with activated titanium dioxide, reductive (O$_2^-$) and oxidative ($^-$OH) species are generated (Figure 2). Both compounds (O$_2^-$ and $^-$OH) have the ability to degrade solid and gas polluting substances [6,12]. In other words, the photocatalysis process is the acceleration of a photochemical reaction by means of a catalyst (TiO$_2$) that interacts with light with sufficient energy [20]. This reaction occurs on the surface of materials, where pollutants (organic and inorganic) are mineralized through an oxidation-reduction reaction [8]. It should be noted that TiO$_2$ is not consumed in the reaction [5].
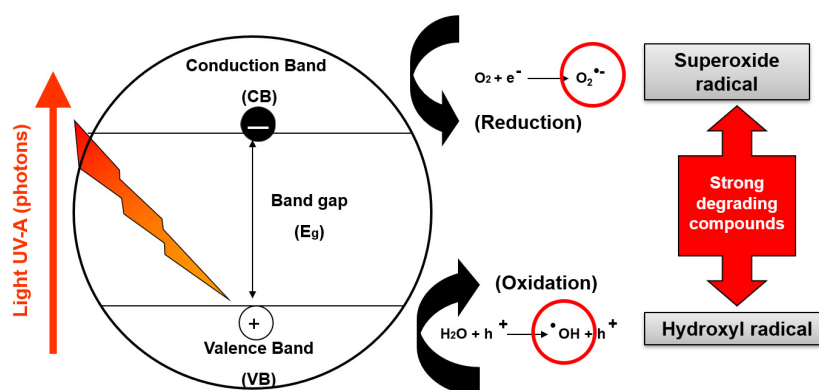
Figure 2. Illustration of the major processes occurring on a semiconductor TiO_2 particle following electronic excitation with UV-A (photons). Electron (e^-)–hole (h^+) recombination can occur at the surface or in the bulk of the semiconductor. In addition, at the surface of the TiO_2 particle, photogenerated electrons can reduce an electron acceptor A (e.g., O_2) and a photogenerated hole can oxidize an electron donor D (e.g., H_2O). Adapted with permission from Ref. [21]. Copyright 1995, American Chemical Society.

According to Pozo-Antonio et al. [20], various research projects confirm that the most remarkable photocatalytic activities are exhibited when titanium dioxide loaded materials are exposed to UV-A radiation compared with those that are exposed to visible light. Similarly, the photon efficiencies produced with artificial solar radiation are two-to-five times smaller than the efficiencies of UV-A light [20]. To ensure that the magnitude of the photocatalytic effect is retained, several strategies have been designed such as the use of metal doping (W, Fe and V) on titanium dioxide. This strategy allows increasing the sensitivity to visible light and consequently increasing the pollutant removal efficiencies, without the need to incorporate a higher concentration of nanoparticles [12,18,22]. According to Petronella et al. [23], the combination of metal nanoparticles such as Ag and Au with semiconductors such as TiO_2 allows to increase the photocatalytic efficiency due to their electrical and optical properties. However, their applications have been limited due to their chemical instability, the complex production processes and the high cost [24].

3. Cement-Based Materials Loaded with TiO_2

Cementitious materials have been loaded with TiO_2 using different coating technologies (e.g., liquid flame spraying, sol–gel, dip-coating) and mixing techniques, the latter applied during mortar and concrete mixing. Coating technologies have the advantage of using less TiO_2, having major nanoparticle exposition to light and pollutants, and they can be applied on hardened cement-based materials, i.e., that it is applicable on existing buildings and infrastructure [16,25,26]. For example, A. Maury-Ramirez et al. [27] successfully synthesized TiO_2 coatings by liquid flame spray and low temperature sol–gel technologies on autoclaved aerated concrete precast products. In the study developed by Yang et al. [25], TiO_2 nanoparticles were applied to granular quartz, and these granules were distributed on the concrete surface. The advantages of this method are that it can be implemented on a large scale and the TiO_2 remains stably bound to the surface of the substrate. Additionally, the TiO_2 mass fraction was 0.34% of the quartz mass, showing a utilization efficiency 150 times higher than in conventional photocatalytic mortars, which translates into a lower cost of implementation. In Figure 3, the aggregate with TiO_2 on the surface of a mortar is shown. On the other hand, coatings have less durability than mixing techniques, which is particularly important on pavements where concrete cracks or abrasion will expose new TiO_2 nanoparticles to pollutants and light, enhancing photocatalytic properties [2].

In the TiO_2 mixing technique, as the amount of TiO_2 nanoparticles increases the setting time of the mortar decreases [28]. This may be because the particles are so small that there is a large specific surface area available to react with water and to generate hydration products

faster and in greater quantity. Additionally, the high reactivity of TiO_2 nanoparticles allows them to act as nucleation points, promoting crystal growth during cement hydration [29].
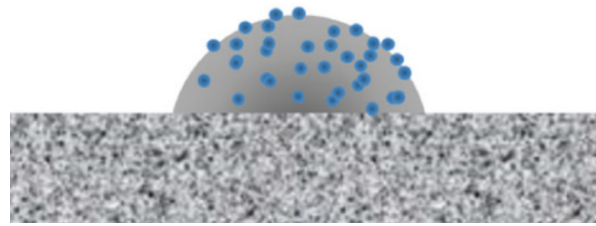

Figure 3. Aggregate with titanium dioxide on the surface of a photocatalytic mortar. Adapted with permission from Ref. [25]. Copyright 2019, Elsevier.

Using a Scanning Electron Microscope (SEM) micrograph analysis on TiO_2 added samples, the cementitious matrix evidenced a large amount of C-S-H gel and fewer pores compared with the control sample without TiO_2 [28]. Additionally, an X-ray diffraction (XRD) analysis confirmed that the addition of TiO_2 increases the amount of C-S-H gel, which has the potential to increase the microstructural properties of cementitious materials and therefore their durability. Therefore, TiO_2 not only acts as a filler by filling the voids in cementitious materials, but also accelerates the hydration process, consuming more $Ca(OH)_2$ and producing large amounts of CSH [6,13]. The last can be confirmed by Victor et al. [29], who, with calorimetry tests for concretes with the addition of 10% rutile (by weight of cement) and 10% anatase (by weight of cement), indicated greater CSH formation compared with the control sample without TiO_2. Similarly, a SEM micrograph analysis showed a better distribution and a decrease in total pore volume. All these elements show the possibility to obtain a concrete with low permeability, higher chemical and mechanical resistance and less shrinkage. The above is confirmed in the experiment developed by Daniyal et al. [28], where it was found that, when incorporating nano TiO_2 (NT) in 5% by weight of Ordinary Portland Cement (OPC) replacement to the mortar, the compressive strength after 28 days was higher than the control sample. Similarly, D. Siang Ng et al. [1] observed that when adding NT in 3 wt% of cement to the mortar it presents a compressive strength 36% higher than the control specimen. Additionally, Victor et al. [29] noticed that when incorporating anatase II and rutile I in 10% by weight to the mortar it increases the compressive strength by 17.3% and 10.5%, respectively. However, when they added the same quantity of anatase I, the compressive strength decreased by 3.7%. Moreover, Atta-ur-Rehman et al. [4] found that, when incorporating anatase to the mortar in 3 and 6% of the binder weight, the compressive strengths at 28 days were 10 and 15% higher than the control sample. Finally, Sikora et al. [13] observed that when adding 3 wt% mesoporous silica nanospheres modified with titanium dioxide ($mSiO_2/TiO_2$) to the mortar, it presented a compressive strength 15% higher than the control specimen (Table 1). Similarly, although not developed with Portland cement, the effect of the TiO_2 addition on the physicomechanical properties of a geopolymer system based on metakaolin (MK) and hydroxide and potassium silicate as activators was evaluated by L. Guzmán-Aponte et al. [30]. Three different liquid–solid systems (0.35, 0.40 and 0.45) and two titanium additions were investigated (5% and 10% of the cement content). The flowability, setting time and mechanical strength of the geopolymer mixtures and their microstructural characteristics were evaluated using techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). It was concluded that a percentage of up to 10% TiO_2 does not affect the mechanical properties of the geopolymer, although it does reduce the fluidity and setting times of the mixture.

Furthermore, D. Siang Ng et al. [1] performed flexural strength tests for mortars with NT in 3 wt% of cement. The flexural strength at 28 days was 11% higher than the control sample. Furthermore, Atta-ur-Rehman et al. [4] carried out flexural strength tests for mortar samples with anatase incorporation in 3 and 6% of the binder weight. The flexural strengths had a difference of 3.8% and −15.10% in comparison with the control specimen (Table 1).

Table 1. Mechanical and durability properties of cementitious materials with titanium dioxide.

Material	Application Process	Quantity	Geometry	Compressive Strength (28 Days)	Flexural Strength (28 Days)	Modulus of Elasticity	Durability		Observations	Reference
							Exposure Medium	Compressive Strength (360 Days)		
NT (nano TiO$_2$)	Mixing technique	5% by weight of OPC replacement	70.6 mm side.	16.21% higher than the control specimen. 26.14% higher than the control specimen. 25.80% higher than the control specimen.	- - -	- - -	Tap water. Saline water. Acidic solution.	Higher than the control specimen. Higher than the control specimen. Higher than the control specimen.	Mild steel bar of 3 mm diameter was used as embedding reinforcement.	Daniyal et al. [28]
Anatase I Anatase II Rutile	Mixing technique	10% by weight	50 mm diameter, 100 mm height.	−3.70% 17.30% 10.50%	- - -	−38.90% −26% −30.10%	- - -	- - -	- - -	Victor et al. [29]
NT (nano TiO$_2$)	Mixing technique	3 wt% of cement.	50 mm side. 40 mm side, 160 mm height.	36% higher than the control specimen. -	- 11% higher than the control specimen.	-	-	-	Fly ash was added with a dosage of 30% wt.% of cement.	Siang et al. [1]
Anatase	Mixing technique	3% of the binder weight 6% of the binder weight	25.4 mm × 25.4 mm × 279.4 mm	10% higher than the control specimen. 15% higher than the control specimen.	3.80% −15.10%	-	-	-	-	Atta-ur-Rehman et al. [4]
mSiO$_2$/TiO$_2$	Mixing technique	3 wt%	40 mm × 40 mm × 160 mm	15% higher than the control specimen.	Slightly higher than the control sample.	-	-	-	-	Sikora et al. [13]

On the other hand, according to D. Siang Ng et al. [1], small amounts of nanoparticles incorporated in the mortar decrease its porosity, causing an increase in resistance to tension and compression, compared with a conventional mortar. However, if the optimum concentration of nanoparticles is exceeded, due to its high surface energy, agglomeration can be generated, causing a reduction in the mechanical properties, as well as in the photocatalytic efficiency of the mortar [1,9]. Therefore, it is essential to find the optimal TiO_2 addition for which there is an increase in the mechanical and durability properties of the cementitious material. Normally, photocatalytic concretes and mortars have used TiO_2 contents around 5 to 10% of the cement or binder phase content by weight.

Additionally, compressive strength tests were performed at 360 days for mortars with incorporation of TiO_2 exposed to an acid solution, salt water and potable water, finding that strengths were greater than those of the control specimen and that the greater the addition of TiO_2 the greater the resistances (Table 1). This may be due to the fact that the TiO_2 nanoparticles produce a denser mortar when filling the voids, limiting the diffusion of aggressive ions in the cement matrix [28]. However, mortars with the incorporation of TiO_2 are more susceptible to attack by sulfates, which is increased if they are subjected to high temperatures. According to the study carried out by Atta-ur-Rehman et al. [4], the formation of gypsite and ettringite was evidenced in mortars with the addition of TiO_2 exposed to sulfate attack, which represents a decrease in the durability of the mortar. Therefore, it is recommended that cementitious materials with TiO_2 ought to be designed to resist attack by sulfates [4].

Similarly, the corrosion rate was evaluated in samples with the incorporation of TiO_2 and it was found that these rates are lower than those of the control mortars. For a 5% incorporation of TiO_2, the highest corrosion inhibition efficiency was observed, although for 3% incorporation considerable efficiency was also achieved [28].

According to the studies developed by Sikora et al. [13] and Victor et al. [29], the inclusion of titanium dioxide in mortars reduces water absorption, increases resistance to compression and decreases their modulus of elasticity. This can be confirmed with the tests developed by Victor et al. [29]. They added anatase I, anatase II and rutile in 10% by weight to different mortar specimens. The modulus of elasticity decreased by 38.9%, 26% and 30.1%, respectively, in comparison with the control specimen (Table 1).

As reported by Daniyal et al. [28], the resistance to bending, tension and compression in concretes with incorporation of 1% of TiO_2 increased by 25%, 67% and 18%, respectively, and the water absorption decreased by 3.68% compared with a conventional concrete. In the same way, for a concrete with the addition of 5% TiO_2 together with 25% of fly ash, the electrical resistivity increased by 257%, the permeability to chlorides decreased by 58%, the water absorption decreased by 11% and the compressive strength increased by 13%. Once again, all the aforementioned effects may be due to the increase in homogeneity, density and the improvement in the microstructure of the cementitious material when incorporating TiO_2.

However, despite the fact that the addition of TiO_2 nanoparticles increases mechanical resistance at early ages, it has a negative result in resistance at late ages [31].

It should be noted that the concretes with the addition of TiO_2 showed a superior microstructure in the transition zone, allowing a better link between the cement paste and the aggregates [31]. Additionally, the incorporation of TiO_2 in concrete decreases its fluidity [30]. Furthermore, cementitious materials are vulnerable to attack by leachate due to the dissolution of hydrated products which reduces mechanical resistance and increases porosity. However, it has been reported that the incorporation of titanium dioxide might increase the resistance of mortars to attack by leachate [8]. Similarly, concretes with the addition of TiO_2 show an increase in resistance to freezing [12].

4. Multifunctional Properties

The efficiency of the photocatalytic process on cement-based materials depends on factors such as the pollutant concentrations (incl. residence time), their nature (e.g., organic

and inorganic) and matter state (solid, liquid or gaseous). Similarly, as TiO_2 photocatalysis is a light-driven process, some environmental factors such as light intensity, relative humidity, temperature and pH play an important role [7,32,33]. Additionally, physical characteristics of materials surfaces such as porosity and roughness have been found critical towards the development of multifunctional properties such as self-cleaning and air-purification. Based on his doctoral research on cementitious materials with TiO_2, A. Maury-Ramírez states a positive effect of porosity on air purification yet a negative effect towards self-cleaning performance. Similarly, self-cleaning is negatively affected by roughness, while air-purification is not affected [34].

In terms of photocatalytic efficiency, Victor et al. [29] found that, when incorporating anatase I, anatase II and rutile in 10% by weight to the mortar, samples present NOx removal of 44.1, 11.71 and 37.24 mg $\times$ h^{-1} $\times$ m^{-2}, respectively; this for a flow rate of 1.0 L $\times$ min^{-1}, UV-A radiation of 10 ± 2 W $\times$ m^{-2}, a relative atmospheric humidity of 50 ± 5% and pollutant concentration (NOx) of 20 ppm$_v$. On the other hand, Hoda Jafari et al. [35] added Nano-TiO_2–SiO_2 to different WPC blocks by dip coating. Subsequently, they covered the mortar samples with MG, MB and MO. The decomposition of dyes was of 87%, 80% and 65%, respectively. It is important to highlight that the samples were exposed to UV irradiation and were under room temperature. Additionally, M.-Z. Guo et al. [36] incorporated P25 (composed of 75% anatase and 25% rutile) into self-compacting glass mortar (SCGM) in 2% by weight of binders (WPC and metakaolin). The samples were exposed for 24 h under UVA irradiation and presented an NOx removal rate of 28 µmol m^{-2} $\times$ h^{-1} and a NOx removal ratio of 5.8%. Similarly, A. Maury-Ramirez et al. [37] added nano TiO_2 (anatase) by dip coating and vacuum saturation methods in mortar samples. They employed a TiO_2 ethanol suspension of 0.05 g $\times$ mL^{-1} and the samples were under 24 °C and at a relative humidity of 52%. For an initial toluene concentration of 15 ppm$_v$ and a gas residence time of 3 min, they observed a toluene removal efficiency of 95 % and an elimination rate of 60–70 mg $\times$ m^{-2} $\times$ h^{-1} (Table 2).

Based on the relation of the photocatalytic efficiency with the substrate, recycled glass particles that replace fine aggregate in architectural mortars and concretes have been studied to enhance multifunctional properties. For mortars with the addition of TiO_2, the incorporation of recycled glass increases the self-cleaning capacity due to its light transmission properties. Glass allows light to enter deeper into the cementitious material, activating titanium dioxide particles that are located below the surface and have access to the pollutants, etc. It should be noted that the larger the glass particle size and the darker the glass color the lower the photocatalytic efficiency [9,38].

On a larger scale, photocatalytic paving blocks incorporating TiO_2 in the mass were placed simultaneously in a pilot sidewalk and street in Hong Kong. Results indicated that photocatalytic activity was dramatically reduced in the pavement blocks placed in the sidewalk compared with those placed in the street. This was mainly due to the accumulation of oil, dust and other substances as verified by SEM [39]. Therefore, the influence of dust and oil accumulation on the effectiveness of photocatalytic concrete surfaces was recently investigated by M. Etxeberria et al. [40]. While results showed that cleaning with water was effective in recovering the photocatalytic activity on pavement blocks exposed to dust, pavement blocks exposed to oil did not recover their photocatalytic activity with either water or detergent.

Table 2. Photocatalytic efficiency of cementitious materials with titanium dioxide incorporation.

Material	Application Process	Quantity	Efficiency	Environmental Conditions	Observations	References
Anatase I Anatase II Rutile	Mixing technique	10% by weight	$44.1 \text{ mg} \times \text{h}^{-1} \times \text{m}^{-2}$ $11.71 \text{ mg} \times \text{h}^{-1} \times \text{m}^{-2}$ $37.24 \text{ mg} \times \text{h}^{-1} \times \text{m}^{-2}$	Flow rate $1.0 \text{ L} \times \text{min}^{-1}$; UV-A radiation $10 \pm 2 \text{ W} \times \text{m}^{-2}$, relative atmospheric humidity $50 \pm 5\%$ and pollutant concentration (NOx) 20 ppm_v.	The efficiency is in terms of removal of NOx.	Victor et al. [29]
Nano-TiO$_2$–SiO$_2$	Dip coating	-	87% of MG, 80% MB and 65% MO	UV irradiation, room temperature.	The photocatalytic material was added to WPC blocks. The efficiency is in terms of percent of decomposition of dyes.	Hoda Jafari et al. [35]
P25 (75% anatase and 25%rutile)	Mixing technique	2% by weight of binders	NOx removal rate: $28 \text{ } \mu\text{mol m}^{-2} \times \text{h}^{-1}$. NOx removal ratio: 5.8%	24 h UV-A irradiation.	The TiO$_2$ was incorporated in self-compacting glass mortar (SCGM). WPC and metakaolin were used as cementitious materials.	M.-Z. Guo et al. [36]
Nano-TiO$_2$	Dip coating and vacuum saturation	TiO$_2$ ethanol suspension of $0.05 \text{ g} \times \text{mL}^{-1}$	Toluene removal efficiency: 95% elimination rate: 60–70 $\text{mg} \times \text{m}^{-2} \times \text{h}^{-1}$	24 °C, 52% relative humidity.	Initial toluene concentration: 15 ppm$_v$ gas residence time: 3 min.	A. Maury-Ramirez et al. [37]

4.1. Self-Cleaning Properties

Autonomic cleaning properties are mainly related to the level of wettability of the surfaces; high wettability promotes the definitive removal of impurities. When the photocatalysts are exposed to UV light, they increase the hydrophilicity of the surfaces, causing the water molecules to spread over the cementitious material and wash out the contaminating substances [23,41]. This phenomenon is known as photo-induced hydrophilicity [42].

When the TiO$_2$-loaded cementitious material is exposed to UV light, structural alterations are formed on the surface, which induce forces at the solid–liquid interface, decreasing the contact angle of the water. UV exposure generated O$_2$ vacancies, whereby Ti$_4^+$ ions are transformed into Ti$_3^+$ ions, increasing the affinity for water molecules. It should be noted that the greater the roughness of the nanocrystal surface the greater the self-cleaning properties at this scale [18,43]. However, this relationship does not occur at a greater scale, i.e., with the roughness of the photocatalytic surface.

On the other hand, the self-cleaning properties of a cementitious material can be measured by their ability to decompose dyes. In 1996, the first laboratory experiments about the self-cleaning activity on cementitious materials containing TiO$_2$ were reported. These tests were developed for designing the material of the church "Dives in Misericordia" (Rome, Italy). For this church a new cement type named TX Millenium was developed. To test its efficiency, white cement disks containing 5% titanium dioxide were impregnated with phenanthrenequinone (yellow dye) using an aerograph technique. A solar simulator was used to activate the TiO$_2$ photocatalyst while the reflectance (%) was used to follow the photodegradation of the dye. Results showed that in only 8 h almost a complete

color recovery was produced on the white surfaces [44]. Much more recently, in the study developed by Jafari et al. [19], the photocatalytic degradation of two colorants (methylene blue (MB) and malachite green oxalate (MG)) was evaluated in concrete blocks with Portland cement coated with SiO_2 and TiO_2 nanoparticles. More than 92% MB and 80% MG was decomposed under UV and visible light. Wang et al. [45] prepared TiO_2 with benzoic acid as a surfactant to cover some cement samples. The discoloration rates were more than 30% in 1 h and more than 80% in 15 h. It is worth highlighting that the samples were exposed to UV light (500 W). In the study carried out by Faraldos et al. [46], an aqueous suspension of nanoparticles with photocatalytic properties was applied to the surface of a cementitious material. The photocatalytic coatings degraded 90% of the NO and methylene blue to which they were exposed. It should be noted that results were independent of the method of the coating application (i.e., spraying or dip coating).

In the investigation developed by Jafari et al. [35], blocks of white Portland cement (WPC) were dip coated with a nanoparticle solution of SiO_2 and TiO_2. The photocatalytic effect of the blocks was examined according to the level of degradation of malachite green oxalate, methylene blue and methylene orange, in conjunction with oxygen demand tests. The cement blocks degraded 87 %, 80 % and 75 % of MG, MB and MO solutions, respectively. On the other hand, in the research carried out by Li et al. [47], concretes were prepared with TiO_2 and electrolytic manganese residues. The employed method was sol–gel dip coating (using different cycles) and the concretes were exposed to UV irradiation. It was found that the specimens coated using four cycles showed the highest methylene orange removal, i.e., a degradation efficiency of 94.2%.

J. Suave et al. [48] incorporated ozonated graphene (OGn) to titanium dioxide and deposited this photocatalytic material in autoclaved cellular concrete (ACC). The samples were exposed to UVC irradiation, and the photocatalytic activity was evaluated through the methylene blue degradation. It was found that, for an ACC coated with TiO_2-OGn-8%, the maximum degradation was reached after 180 min of reaction. This is due to the fact that the high specific surface area of graphene improves the photocatalytic efficiency of the degradation of organic pollutants by increasing the light absorption capacity. Similarly, it has been noted that in addition to the increase in the light absorption capacity, the nanoporous structure of TiO_2 provides more active sites for the photocatalytic reaction [49]. On the other hand, the self-cleaning properties allow to maintain a high reflectivity of the sun, contributing to reducing the phenomenon of the heat island [41]. additionally, A. Rosales et al. [50] synthesized SiO_2 together with TiO_2 to increase the durability of the photocatalytic coating without affecting its photocatalytic potential. Results indicated that using SiO_2 improved the durability of the TiO_2 coating without affecting its photocatalytic properties. Thus, a novel $SiO_2@TiO_2$ coating shows potential for developing long-lasting, self-cleaning and air-purifying construction materials.

Although several self-cleaning buildings using TiO_2 have been constructed worldwide, higher TiO_2 photocatalytic efficiencies to create real self-cleaning properties are still needed, especially when applied on white cement. As can be observed in Figure 4, a similar situation is reported in the building constructed (Residentie Commodore) on the coast of Belgium in the city of Ostend. This first Belgium self-cleaning building (includes window glasses) finished in 2007, evidenced in 2011 dirty surfaces (Figure 4a–c), different white intensities (Figure 4d,e) and even cracks (Figure 4f). Although these dirty surfaces seem to be produced by dust and not by biofouling, they also seem to be governed by the water flow patterns on the facade which are linked to the architectural design. Therefore, the architectural design seems to be another determining factor for the development of self-cleaning buildings. Therefore, more realistic laboratory studies should be conducted prior to application, because indication of the self-cleaning capability of the TiO_2-loaded cementitious materials only based on dye degradation tests does not allow to extrapolate the conditions to real life pollution cases under different weather and lighting conditions.

Figure 4. Residentie Commodore (Ostend, Belgium), the first Belgian self-cleaning building which evidenced low photocatalytic performance after 4 years of construction [34]. (**a**–**c**) facade, balconies and walls evidenced dirty surfaces (**d**,**e**) balconies and walls evidenced different white intensities, (**f**) cracked surfaces.

4.2. Air-Purifying Properties

Cement-based materials with TiO_2 have been studied to reduce air pollution in out- and indoor conditions. Therefore, intensive research for photocatalytic degradation under artificial and sun light of inorganic (e.g., nitrogen oxides) and organic pollutants (e.g., xylene, toluene and related ones) have been widely developed. Particularly for organic pollutants, preliminary evaluation using the rhodamine B degradation test has been used, because this dye is related to a polycyclic series of aromatic hydrocarbons as well as the most common pollutants in urban environments [12,51].

For example, the ability of cementitious materials with photocatalytic properties to degrade NO_x has been used to evaluate their air purification capacity. M.-Z. Guo et al., produced concrete blocks with a surface layer that incorporated TiO_2 in 2% by weight of binders. The samples were exposed to UVA irradiation and the photocatalytic removal rate for the blocks with TiO_2 was 28.0 μmol m^{-2} h^{-1}, while the removal rate for the control sample was 3.0 μmol m^{-2} h^{-1}; interesting results also were obtained about nitrite (NO_2) and nitrate (NO_3) formation during photocatalytic degradation. The accumulation of NO_2 and NO_3 on the sample surface led to a slight deactivation effect on the photocatalytic NOx removal ability of the samples, which in turn slowed down the production of NO_2 and NO_3.

Moreover, compared with NO_3, NO_2 could more easily be carried away from the sample surface by the flowing air stream [36]. In the PICADA project (Photocatalytic Innovative Coverings Application for Depollution Assessment), the photocatalytic effects of two different paints were studied. In laboratory tests, CristalACTiV[TM] P25 and PC500-added paints exhibited nitric acid conversion of 50% and 70%, respectively. Additionally, the paints showed a NO conversion of 80% and more than 95% for P25 and PC500, respectively, in outdoor conditions [23]. Similarly, in the experiment developed by M. Pérez-Nicolás et al. [18], different mortars with 2.5% TiO_2 incorporation were exposed under solar, UV and visible light; it was found that the high alumina content (HAC) and air lime mortars had the highest NOx removal ratios compared with low alumina cement (LAC) and Portland cement (PC) mortars. In the case of the specimens that were exposed to UV light, LAC (cured at 20 °C) and PC mortars had an NOx removal of 67.5% and 69.5%, respectively, while HAC (cured at 20 °C) and air lime mortars had an NOx removal of 78.7% and 80.8%, respectively. This can be attributed to the significant amounts of $CaCO_3$, which reacts with NO as a result of photo oxidation [18].

According to the experiment carried out by Zouzelka et al. [32], for an initial concentration of NO_2 and NO of 0.1 ppm_v (which corresponds to highly polluted urban air) with a relative humidity of 50% and a flow of 3000 cm^3 min^{-1}, the decrease in the NOx concentration reached was 50 and 75 mol m^{-2} h^{-1}, respectively. Additionally, TiO_2 P25 nanoparticles were altered with oleylamine, oleic acid and equimolar concentrations of both [52]. Cements with the incorporation of these particles showed NOx degradation rates two-to-five times higher compared with cements with unmodified TiO_2. For example, Figure 5 shows a scheme of the photo oxidation of NO_x by means of a cementitious material with incorporation of TiO_2 [6,18–20]. It should be noted that the degradation products after a photocatalytic reaction are O_2, H_2O, CO_2 and other inorganic molecules [5].
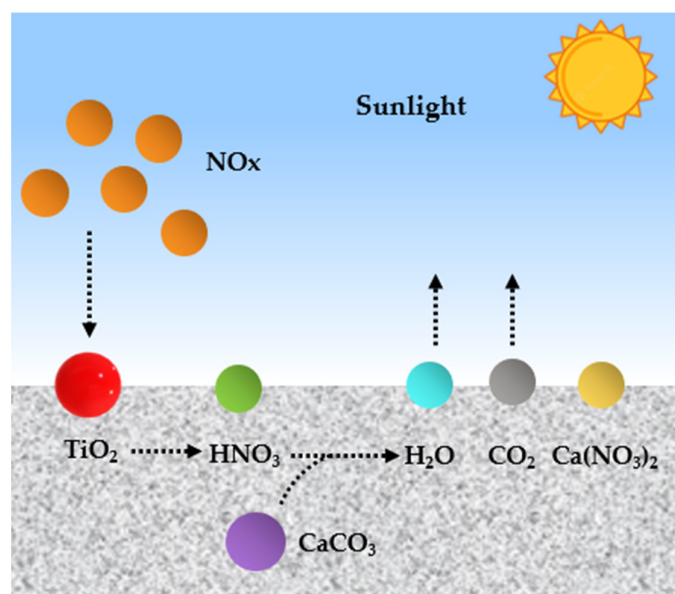

Figure 5. Oxidation of contaminants by means of cementitious materials with incorporation of TiO_2.

Additionally, in the study developed by Petronella et al. [23], the removal of ethyl-benzene, toluene, benzene and o-xylene from the air by mortars incorporating 1% TiO_2 and white Portland cement was investigated, finding removal efficiencies between 5% and 54%. However, according to Liang et al. [5], up to 78% of toluene degradation efficiency can be achieved for cementitious materials with the incorporation of titanium dioxide. Similarly, A. Maury-Ramirez et al. [37] coated autoclaved aerated concrete (AAC) with TiO_2 through vacuum saturation and dip-coating methods. The experiment was carried out in a laboratory with a photoreactor at 52% relative humidity and at 24 °C. For a gas residence time of 3 min and an initial toluene concentration of 15 ppm_v, there were removal

efficiencies of 95%. It is worth highlighting that these removal efficiencies were obtained before and after the samples were exposed to intensive weathering, which simulates a period of 25 years at central Europe weather conditions.

It should be noted that concretes with the addition of TiO_2 can also be used in pavements, which could reduce the levels of tropospheric O_3 [29]. In the investigation carried out by Wang et al. [53], a pulverized mortar with the incorporation of titanium dioxide was bonded with epoxy resin to the surface of an asphalt pavement, where an improvement in the NOx degradation efficiency was achieved.

According to the research developed by Guo et al. [36], architectural mortars with the addition of TiO_2 have a lower NOx removal capacity than pavements with the incorporation of TiO_2, since for mortars with 5% TiO_2 (by weight of binder) there was a removal efficiency of 80 μmol m^{-2} h^{-1}, while for pavement blocks with the same amount of photocatalyst there was a removal capacity of 100 μmol m^{-2} h^{-1}.

Following the promising results at the laboratory scale, pilot projects have been developed using photocatalytic building materials, particularly for application on transport infrastructure such as tunnels, highways and parking zones [54]. In the Czech Republic, a covering with the incorporation of TiO_2 was implemented in concrete walls along a frequented public road and this covering maintained its photocatalytic efficiency two years after its application [32]. Similarly, in Japan a paving stone called NOxer^{TM} was developed, which, through the photocatalytic properties of titanium dioxide, degrades part of the NOx expelled by vehicles [23]. In Bergamo, a section of street was covered by photocatalytic cobblestones and another section was used without modifications for reference. After two weeks of monitoring the NOx concentration, a 30%–40% decrease in the NOx concentration was observed in the section with TiO_2 pavers [32]. Additionally, according to the company Italcementi (which develops cements with a TiO_2 surface), if 15% of the urban surfaces of Milan were covered with concrete with TX Active$^{®}$ (one of its cements), air pollution would decrease by 50% [23].

In Colombia, the preliminary evaluation of a photocatalytic mortar (5% of the cement content) and coating (two, four and six layers) for the tunnel located at the Colombia Avenue in the city of Santiago de Cali (Figure 6a,b) was developed. The tunnel, which is located in a zone near to the city center with high traffic, is 650 m long and 14 m wide. Preliminary photocatalytic evaluation of the samples was performed at the laboratory scale, using methylene blue and rhodamine b (RhB) as dyes (Figure 6c,d) and UV-A of activation source (Figure 6e). Using the software Image J for images processing, the sample area covered with the dye was monitored before (0 h) and after the UV-A exposure (0, 4, 8 and, 24 h). Results showed that the photocatalytic coating (two layers) removed approximately 50% of the RhB compared with the 30% obtained with the photocatalytic mortar with 5% TiO_2 (Figure 6f). Additionally, it was observed that applying more coatings layers (four and six layers) did not improve the photocatalytic performance; on the contrary, the removal was reduced by up to 35% using six layers. Finally, using the street canyon model from winOSPM Software (Denmark) and the local environmental and traffic conditions, potential air pollutant removals were estimated (Figure 6g). More details can be found at Medina Medina A.F. et al. [55].
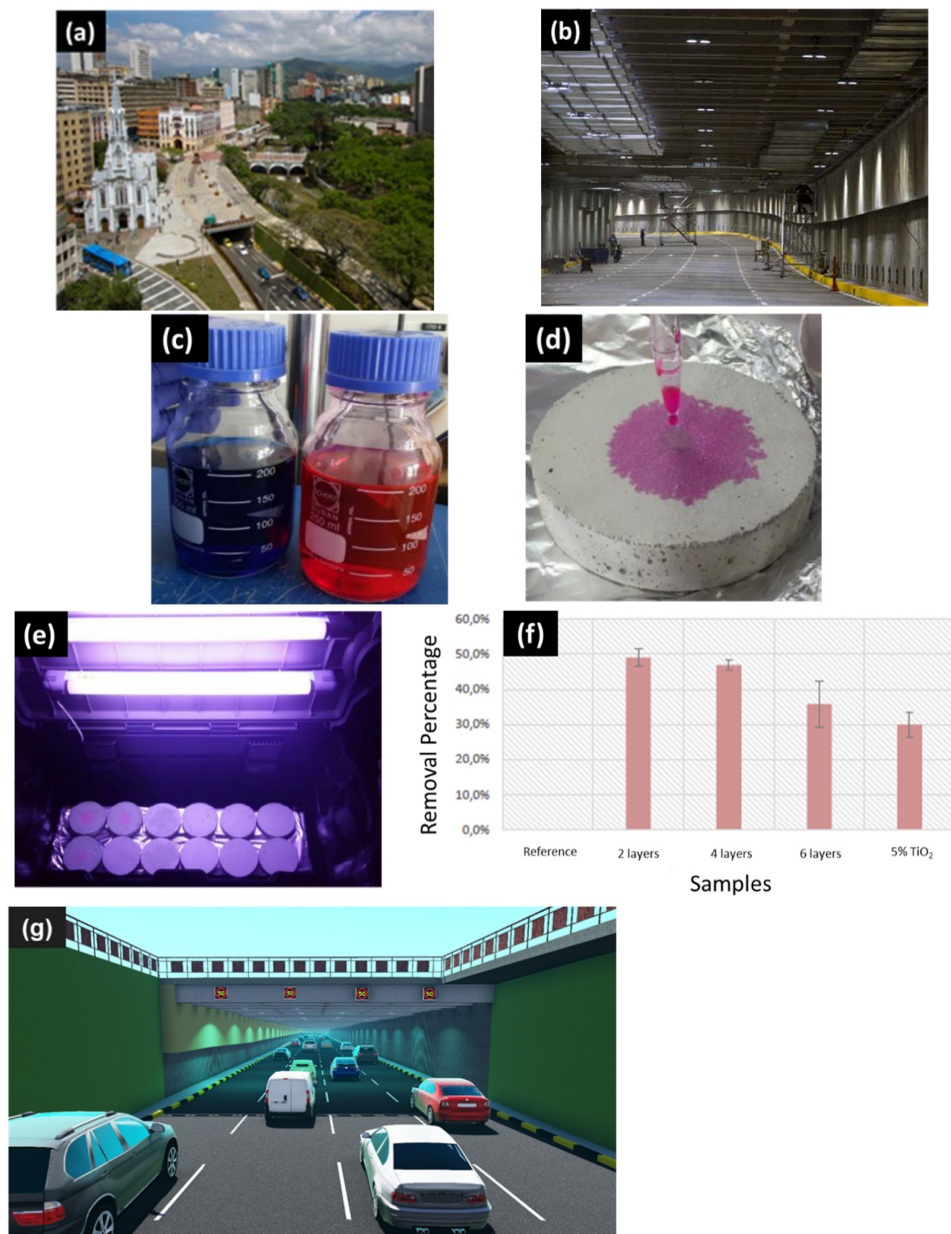
Figure 6. Preliminary evaluation of a photocatalytic coating and a mortar with 5%TiO$_2$ (related to the cement content) for application on the tunnel of the Colombia Avenue in the city of Santiago de Cali, Colombia. (**a**,**b**) Location and geometry of the Tunnel, (**c**,**d**) application of methylene blue and rhodamine B as dyes, (**e**,**f**) UV-A exposure cabinet and dye removal results, (**g**) street canyon model variables for the winOSPM Software [55].

In general, although promising results were obtained at the laboratory scale and pilot projects, complementary strategies to TiO$_2$ photocatalysis are required to make truly efficient air-purifying infrastructures. For example, current trends include the use of biological coatings such as green roofs and walls, as done by PolyU in the Green Deck Project in the Cross-Harbor Tunnel in Kowloon, Hong Kong (Figure 7) [56]. These complementary technologies not only have the potential of broadening and increasing the pollutant removal efficiency, they also have the potential of including recycled and reused materials, while improving the landscape [57,58].

Figure 7. Green Deck Project lead by the Hong Kong Polytechnique University in the Cross-Harbor Tunnel (Kowloon, Hong Kong). This project combines harmonically green roofs and walls with architectural mortar using TiO_2 and recycled glass for air-purifying purposes [56].

4.3. Antimicrobial Properties

The fixation and growth of microorganisms in cementitious materials is common due to the mineral composition, high roughness and microporosity of these materials [12]. However, by incorporating TiO_2 in concrete and mortars, antimicrobial properties are developed, that is, the development of algae, fungi and bacteria are reduced.

In the case of bacteria, TiO_2 destroys the cell wall and the cytoplasmic membrane, causing the death of the cell [7,23]. According to the study carried out by Guo et al. [51], after a mortar covered with TiO_2 was exposed to UV-A radiation for 2 h, total inactivation of *Escherichia coli* was achieved. Additionally, the antibacterial properties increase with the incorporation of metals such as Ag and Cu [12].

On the other hand, in the experiment developed by Pozo-Antonio et al. [20], there was a decrease of 20% in algae coverage on the surface for a concrete with TiO_2 coating compared with the control sample. In addition, A. Maury-Ramírez et al. [59] covered autoclaved aerated concrete with a TiO_2 coating to evaluate the algae fouling in existing structures and it was found that this coating had 20% less algae coverage in comparison with reference samples. Furthermore, they used a commercially available cement with TiO_2 incorporation to produce mortars and after 16 weeks these samples had no algal coverage. Pioneering work on doped TiO_2 developed by Linkous et al. [60] reported that a coating based on a TiO_2 dispersion (10% on a weight basis) produced a photocatalytic inhibition of around 66% of the algae growth (*Oedogonium*) when applied on a cement substrate under a combination of fluorescent and UV-A lamps, which gives in total an intensity of 12 W $\times$ m^{-2}. However, efficiencies at about 87% were found when adding 1% of noble metals such as Pt and Ir. mortars containing TiO_2 or TiO_2 doped (0.5 wt%) with Fe^{3+} (12:4:4:1; sand:lime:anatase:Portland cement on a volume basis) were tested and compared against two commercial biocides and reference samples in relation to the antimicrobial effect on a mixed culture of two green microalgae (*Stichococcus bacillaris*, *Chlorella ellipsoidea*) and one cyanobacteria (*Gleocapsa dermochroa*). Similarly, results based on averages of *chlorophyll a* fluorescence emission measurements and *chlorophyll a* contents indicated that the TiO_2 antimicrobial activity from the mortars was effective after 4 months of exposure to outdoor conditions. Algae growth ratios after the test reached 0% and 11.8% for the mortar containing TiO_2 and doped TiO_2, respectively. Application of the same photocatalyst within coatings onto two wall surfaces of the Palacio Nacional da Pena (Portugal) showed promising results concerning the degradation of lichens and other phototrophic microorganisms after two weeks of color monitoring. However, long-lasting effects of this application have still to be confirmed [61]. In a longer time frame, roofing tiles (red engobe, natural clay, black varnish) coated by a sol–gel technology were evaluated while exposed during more than 6 years to outdoor conditions in six different locations in Germany. Results based on the monitoring of the phototrophic biomass by

pulse amplitude modulation (PAM) fluorometry, image analysis and visual evaluation indicated that photocatalytic surfaces did not affect phototrophic biofilms d.

On the other hand, a TiO_2 loaded cement was tested to evaluate its fungicidal properties using a circulating flow-through chamber under artificial sunlight irradiation [62]. Fungal strains belonging to the genera *Alternaria*, *Cladosporium*, *Epicoccum Fusarium*, *Mucor*, *Penicillium*, *Pestalotiopsis* and *Trichoderma* were cultured directly from visible fouled concrete structures and later inoculated onto tiles composed of cement either containing TiO_2 or reference without TiO_2. During one week of incubation, tiles were exposed to 6 h cycles of artificial sunlight at approximately 10 W $\times$ m^{-2}, which overlapped for 3 h with sprinkler cycles of 20% potato dextrose broth (PDB), so that incubations experienced equal time under light/dark and rain/non-rain conditions. Incubations using non-photocatalytic tiles exposed to the light source exhibited a moderate amount of black, tan and red fouling (Figure 8a). However, tiles containing photocatalytic TiO_2 exhibited only a small amount of a single type of tan-colored fouling (Figure 8b,c). The reduction in biofouling observed was found to be statistically significant ($p = 0.05$). Environmental scanning electron microscope (ESEM) images revealed that hyphae-like structures were attached to the surface of the tile (Figure 8d). This tan-colored fouling was re-cultured onto solid media and identified as the *T. asperellum* isolate. However, it should be noted that the *T. asperellum* isolate was capable of surviving and being re-cultured from photocatalytic tile surfaces; this suggests that the use of TiO_2 containing cements, though effective, may not completely inhibit fungal biofouling of concrete structures.
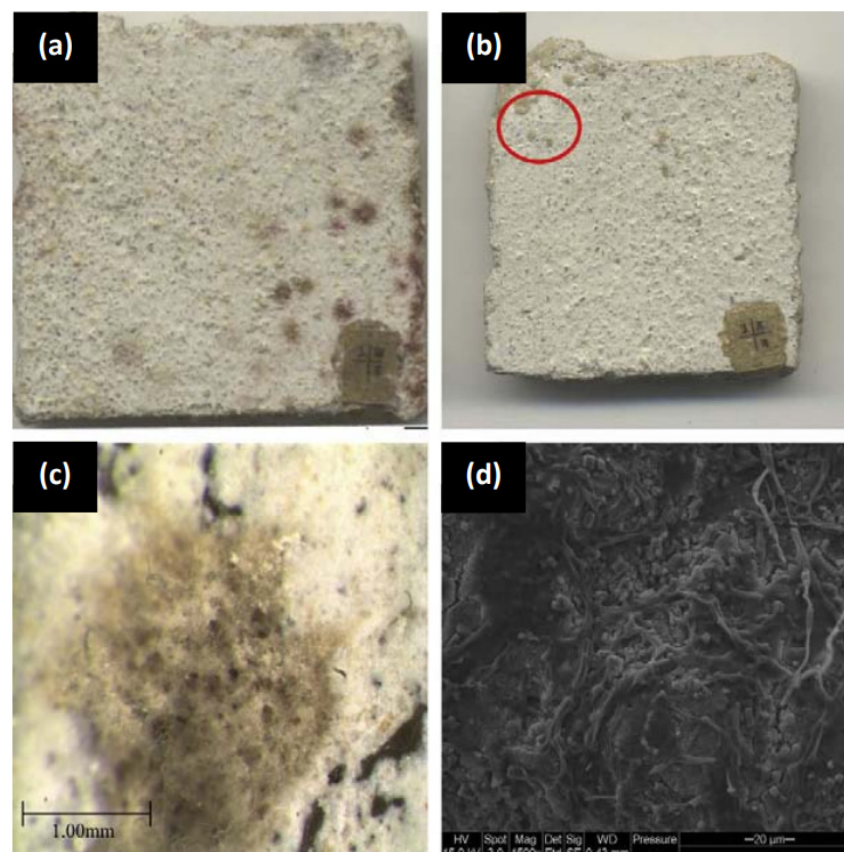

Figure 8. Fouling of tiles inoculated with eight fungal isolates incubated with 20% PDB and exposed to artificial sunlight. (**a**) Multi-colored fouling of a tile composed of non-photocatalytic cement, (**b**) fouling of a tile composed of cement containing TiO_2, red circle indicates location of growth, (**c**) stereomicroscope image of tan-colored fouling on the photocatalytic tile, (**d**) ESEM image of fouling on the photocatalytic tile. Reprinted with permission from Ref. [63]. Copyright 2009, Elsevier.

In general, although there has been inhibition of the biofouling using TiO_2-loaded cementitious materials in several tests at the laboratory scale, enhancing the TiO_2 photocatalytic activity to all fouling microorganisms and proving the long-lasting effects are still the major concerns for developing the so-called antimicrobial materials, particularly antimicrobial cement-based materials, which are of major importance as COVID-19 redefined the concept of sustainability, making crucial the inclusion of human health [64].

5. Conclusions

- First, at the laboratory scale, nano titanium dioxide (mainly anatase, rutile and its combination P25) has shown ability, under UV-A exposure, to degrade organic and inorganic substances in solid, gas and liquid phases. However, the promising efficiencies obtained at laboratory scale are not enough for in situ application in cement-based materials towards the development of air-purifying, self-cleaning and antiseptic buildings and infrastructure. This situation is mainly associated with the limited capacity of TiO_2 to be photoactivated exclusively with UV-A. Therefore, more research about doped TiO_2 and novel semiconductors should be developed to obtain higher efficiencies. Semiconductors such as ZnO, ZnS, CdS, CdSe and CdTe seem to be promising [65]. Similarly, other complementary nanotechnologies should be researched; recently promising results have been obtained with photocatalytic polyurethane coatings containing modified C_{60} fullerene additives [66] or using synthetized $SiO_2@TiO_2$ coatings [50].
- Second, although there has been wide discussion about the best method to load cement-based materials with TiO_2, it is now clear that coatings and mixing technologies have different advantages/disadvantages regarding their application. For example, coatings use less catalyst material and expose more efficiently the nanoparticles to UV-A and polluting substances. However, coatings might have durability problems when exposed to high weathering or aggressive environmental conditions. Thus, coatings result as useful for application on tunnels and buildings, while TiO_2 mixing technology is very useful for pavements and roads, where there are high weathering and aggressive environmental conditions. Loading TiO_2 during concrete or mortar mixing has been normally done in amounts around 5 to 10% of the cement or binder content (weight basis). In this addition range, generally the mechanical and durability properties have not been affected. On the contrary, most research results indicate an increase in the compressive and flexural strengths. This is mainly associated with a denser material structure, evidenced by SEM. Still, resistance to sulphate and leachate attack seem to be reduced when adding TiO_2 to cement-based materials. Therefore, it is important to adjust design methods to determine optimal TiO_2 dosage.
- Third, although countries such as Japan, China, Italy, Belgium, France, United Kingdom and the Netherlands have constructed buildings and infrastructure using TiO_2-loaded cementitious materials [67], the obtained self-cleaning, air-purifying and antimicrobial properties still need to be improved. Regarding self-cleaning buildings, particularly when using white cement and TiO_2, dirty surfaces, different white intensities and even cracks have been reported. Similarly, although high removal efficiencies towards organic and inorganic air pollutants have been reported, the environmental conditions, particularly rain and high humidity, significantly reduced TiO_2 photocatalytic efficiency. With respect to antimicrobial properties, although there has been microbial growth inhibition using TiO_2-loaded cementitious materials at laboratory scale tests, enhancing the TiO_2 photocatalytic activity to all fouling microorganisms and proving the long-lasting effect are still major concerns for developing the so-called antimicrobial cement-based materials.
- In general, although intensive research on photocatalytic cement-based materials has developed worldwide during the last 20 years, more innovative and strategic research should be done towards the massive application at real scale. Environmental and weathering conditions are demanding very efficient photocatalyst materials or even

complementary technologies, e.g., coming from the architectural design, to develop self-cleaning, air-purifying and antimicrobial properties on buildings and infrastructure. In order to achieve this goal, more realistic laboratory tests, modelling prior to real application, Life Cycle Assessments (LCA) and Social Life Cycle Assessments (S-LCA) should be performed; particularly the latter two, as self-cleaning, antimicrobial and air-purifying properties have a positive potential impact by increasing building and infrastructure durability and reducing air pollution, while nanomaterial production has a potential negative environmental impact, a life cycle thinking approach, which is about going beyond the traditional focus on production site and manufacturing processes to include environmental, social and economic impacts of a product over its entire life cycle, is required to develop truly circular economy models in the construction sector [68,69].

Abbreviations

AAC—autoclaved aerated concrete, autoclaved cellular concrete, Ag—silver, Au—gold, $Ca(OH)_2$—calcium hydroxide, $CaCO_3$—calcium carbonate, CB—conduction band, CdS—Cadmium sulfide, CdSe—Cadmium selenide, CdTe—Cadmium telluride, CO_2—carbon dioxide, CristalAC-TiVTM—titanium dioxide brand, C-S-H—calcium silicate hydrate, ESEM—Environmental scanning electron microscope, Eg—Band gap, e^-—electron, Fe—iron, Fe^{3+}—iron cation, FTIR—Fourier transform infrared spectroscopy, HAC—high alumina content, h^+—hole, LAC—low alumina cement, LCA—Life Cycle Assessment, MB—methylene blue, MG—malachite green, MK—metakaolin, MO—methyl orange, $mSiO_2/TiO_2$—mesoporous silica nanospheres modified with titanium dioxide, NHE—normal hydrogen electrode, NO_2—nitrogen dioxide, NO_3—nitrate, NO_x—nitrogen oxides, NOxerTM—paving stone with titanium dioxide, NT—nano titania, O_2—oxygen, O_3—ozone, OGn—ozonated graphene, OPC—Ordinary Portland Cement, PAM—pulse amplitude modulation, PC500—photocatalytic paint, PDB—potato dextrose broth, pH—potential of hydrogen, PICADA—Photocatalytic Innovative Coverings Application for Depollution Assessment, ppmv—parts per million by volume, RhB—rhodamine b, SCGM—self-compacting glass mortar, SEM—Scanning Electron Microscope, SiO_2—silicon dioxide, $SiO_2@TiO_2$—synthetized coating of silica and titanium dioxide, S-LCA—Social Life Cycle Assessment, Ti3+—titanium cation, Ti4+—titanium cation, TiO_2—titanium dioxide, TX Active®—cement brand with titanium dioxide, TX Millennium—cement brand with titanium dioxide, UV—ultraviolet rays, UV-A—long wavelength ultraviolet radiation, UVC—short wavelength ultraviolet radiation, V—vanadium, VB—valence band, VOCs—volatile organic compounds, W—tungsten, winOSPM—software for simulating the street canyon model, WPC—white Portland cement, XRD—X-ray diffraction, ZnO—zinc oxide, ZnS—zinc sulfide, µmol—micromol.

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