

Review

# Photocatalytic TiO<sub>2</sub>-Based Coatings for Mortars on Facades: A Review of Efficiency, Durability, and Sustainability

Jéssica D. Bersch <sup>1,\*</sup>, Inês Flores-Colen <sup>2</sup>, Angela B. Masuero <sup>1</sup> and Denise C. C. Dal Molin <sup>1</sup>

<sup>1</sup> Programa de Pós-Graduação em Engenharia Civil: Construção e Infraestrutura (PPGCI), Núcleo Orientado para a Inovação da Edificação (NORIE), Universidade Federal do Rio Grande do Sul (UFRGS), Av. Osvaldo Aranha, 99, 7th floor, Porto Alegre 90035-190, RS, Brazil

<sup>2</sup> CERIS, Departamento de Civil Engineering, Architecture and Georesources, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

\* Correspondence: jessica.beresch@ufrgs.br

**Abstract:** Due to the urgent need for a more sustainable built environment and actions against climate change, this paper presents a literature review about photocatalytic TiO<sub>2</sub>-based thin layers to be applied on mortars in facades. Photocatalysis may be a potential strategy against current environmental and climate challenges by transforming or eliminating hazardous greenhouse gases from the atmosphere. The main subjects researched were the coatings' efficiency (which encompassed their self-cleaning ability, depolluting effect, and antimicrobial properties), durability, and sustainability. The method was based on the systematic literature review approach. Self-cleaning ability was the most recurrent topic retrieved from published studies, followed by depolluting effect and durability. There are few investigations about antimicrobial properties considering TiO<sub>2</sub>-coated mortars in facades. However, sustainability studies through Life Cycle Assessment and Life Cycle Costing represented the most significant gap, even requiring broader surveys. The photocatalytic activity of the coatings is well-proven in the literature, although specific evaluations may be needed for each coating composition and testing condition to understand their performance. The type of contamination agents, TiO<sub>2</sub> dispersion and characteristics, dopants, nanocomposites, and substrate are among the principal agents influencing the results; therefore, caution must be taken when comparing research. Mainly, adhesion and photocatalytic efficiency after ageing were studied on durability. More field exposures may be recommended. Regarding the trade-offs concerning the environmental impacts of TiO<sub>2</sub>-based coatings, it is urgent to clarify whether their overall outcome is indeed advantageous and to investigate their resilience regarding climate change scenarios.

**Keywords:** TiO<sub>2</sub>-based coatings; mortar; photocatalysis; durability; sustainability



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## 1. Introduction

Some major problems that threaten the environmental balance nowadays are urban air pollution and global warming [1]. Cities are challenged due to low air quality [2], involving the emission of pollutants such as nitrogen oxides (NO<sub>x</sub>), sulphur oxides (SO<sub>x</sub>) and Volatile Organic Compounds (VOCs) [3], together with organic particulate matter, like soot [4]. Communities, human health, and the infrastructure to which they are related are affected by global warming [5]. To protect the planet and pursue more sustainable decisions, “Sustainable cities and communities” and “Climate action” are among the 17 Sustainable Development Goals adopted by the United Nations to be implemented by 2030 [6].

Regarding the sustainability of buildings, it is fundamental to adapt to the climate change scenario, even for retrofit interventions [7]. Abolhassani et al. [5], Farahani et al. [8], and Kharbouch [9], for example, studied the demands and performance involved with buildings considering future climate conditions.

In this context, photocatalysis may be assigned as a potential strategy against current environmental and climate challenges by transforming or eliminating hazardous greenhouse gases from the atmosphere; TiO<sub>2</sub> might be the most suitable alternative to convert mineral and organic compounds [10] and, thus, to assist in climate change actions.

Nano-titanium dioxide (TiO<sub>2</sub>) is recognized as a relevant alternative due to its photocatalytic behaviour and the potential to purify air and water, associated with self-cleaning performance, chemical stability [11], and antimicrobial properties [1]. Nanomaterials and their use in construction are indicated as ways to seek better environmental performance for buildings [12].

The photocatalytic process by which the TiO<sub>2</sub> operates may degrade or transform organic and inorganic substances into less harmful components, for example, degrading or mineralizing microorganisms such as viruses, bacteria, fungi, algae, and other organic compounds to CO<sub>2</sub>, H<sub>2</sub>O, and harmless inorganic anions [13]. TiO<sub>2</sub> is a semiconductor material with a bandgap energy of 3.2 eV, and thus, it absorbs energy near ultraviolet light with a wavelength of around 380 nm [14].

For the photocatalytic action of TiO<sub>2</sub>, first, irradiation incidence promotes the shift of electrons (e<sup>-</sup>) from the valence band to the semiconductor's conduction band, leaving electron holes (h<sup>+</sup>) on the valence band. Electron-hole pairs reach the surface of the TiO<sub>2</sub> particles and react with the adsorbed oxygen and water from the air [15]. Reactive oxygen species like hydroxyl (OH•), superoxide (O<sub>2</sub><sup>-</sup>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) are formed during the process, and together with oxygen (O<sub>2</sub>), they may all foster photocatalytic mechanisms, making it possible, finally, to decompose or mineralise pollutants through a reduction-oxidation process [15,16]. Hydroxyl active species can coexist with trapped holes, which are also responsible for oxidant reactions at the photocatalyst surface [17].

Regarding building facades, besides the environmental concern, aesthetic issues also integrate the objectives of applying TiO<sub>2</sub> since, when exposed to urban pollution, the coating surfaces may soil due to the deposition of atmospheric particulates [18]. Therefore, the self-cleaning property provided by TiO<sub>2</sub> can be especially beneficial. The definitive removal of impurities benefits from high levels of wettability [1]. Thus, the self-cleaning ability is favoured by the photoinduced super hydrophilicity mechanism undergone by the TiO<sub>2</sub>, which is also based on the production of excited electrons and holes through ultraviolet irradiation [19].

There are mainly two ways of using TiO<sub>2</sub> in mortars for building facades: adding it to the mixture proportion or as a surface coating [20]. The efficiency of the photocatalytic activity is affected by the way TiO<sub>2</sub> is incorporated into the substrate and by the characteristics of the substrate itself [21]. Adding the photocatalyst into the mixture provides more stability for long-term applications regarding the mortar's surface-mechanical properties [22]. According to Vulic et al. [22], the resulting photocatalytic activity of mortars with intermixed TiO<sub>2</sub> is lower than those with TiO<sub>2</sub>-based thin layers applied over their surface, although it can still be acceptable; however, it is not always satisfactory [23]. TiO<sub>2</sub> additions into mortars' mixture may not lead to the full benefit from the active material since only the nanoparticles from the outer face of the layer can be activated with UV light; on the other hand, thus, thin TiO<sub>2</sub>-based coatings might explore the photocatalyst activity more efficiently [20].

The higher photocatalytic activity of mortars coated with thin TiO<sub>2</sub>-based layers is related to the availability of more active sites on their surfaces, which can lead to greater pollutant oxidation [24]. Krishnan et al. [25] studied the performance of TiO<sub>2</sub>-based silicate coatings and TiO<sub>2</sub>-containing mortars and concluded that the coated specimens required 20 times less TiO<sub>2</sub> mass for comparable photocatalytic performance. Moreover, applying thin photocatalytic coatings or films on facades is also interesting considering that they can result in minimal changes over original aesthetic features [26] and contribute to the energy performance of the buildings [27] and the reduction of maintenance costs and efforts [28].

However, there are concerns about the durability of thin TiO<sub>2</sub>-based coatings applied on mortars since surface erosion and environmental agents can affect their stability [20].

It is a challenge to maintain a photocatalytic efficiency associated with an appropriate weathering resistance in photocatalytic building products [29]. Although self-cleaning materials in buildings are receiving increasing interest, their durability still needs to be investigated [30]. The knowledge concerning long-term performance and resilience of building materials is, however, crucial considering not only sustainability but also the expected climate changes and the initiatives for their mitigation [31].

Despite the ability of the TiO<sub>2</sub> coatings to degrade atmospheric pollutants and other components, there is also a gap concerning the knowledge of how TiO<sub>2</sub> nanoparticles affect the sustainability of cementitious materials [32]. Few studies present Life Cycle Assessments (LCAs) that are broad enough to include not only impacts such as global warming or depletion of fossil resources but also specific critical issues related to nanoparticles, such as leaching ecotoxicity [33]. In addition to investigating whether photocatalytic materials have, in fact, economic benefits, their cost-efficiency can also be determined considering Life Cycle Costing (LCC) [34], and, thus, included in the challenging context of sustainability, positioning their economic performance within the scope of durability and climate change.

The climate change scenario, the search for a more sustainable built environment, as well as the possibility of combining depolluting effects with self-cleaning properties, motivate the study of thin TiO<sub>2</sub>-based coatings to be applied on the surface of mortars in facades. Therefore, this paper aims to review some main topics regarding photocatalytic coatings with TiO<sub>2</sub>, involving their efficiency and the challenging issues related to their durability and sustainability. Well-established topics and scientific gaps are discussed, seeking consistency between the construction sector and the protection of the planet.

## 2. Methods

The search for relevant papers explicitly related to the studied subject was carried out through a systematic literature review. First, a search string was used to retrieve the literature from the Scopus database. Afterwards, a qualitative content analysis was carried out to exclude studies unrelated to the review focus [35]. The primary question [36] proposed to be answered by the selected papers was: “What are the efficiency, durability, and sustainability attributes of photocatalytic coatings with TiO<sub>2</sub> for mortars in facades?”.

The search was restricted to journals in English, and no time boundary was defined. The keyword string was set as “photocatal\* and (“titanium dioxide”) or TiO<sub>2</sub>) and coat\* and (“mortar” or “facade” or “façade”)", and the search was carried out on the title, abstract, and keywords of the papers. The studies gathered with the search criteria went through three filtering considerations: a title analysis, an abstract analysis, and, lastly, an in-depth complete document analysis [36].

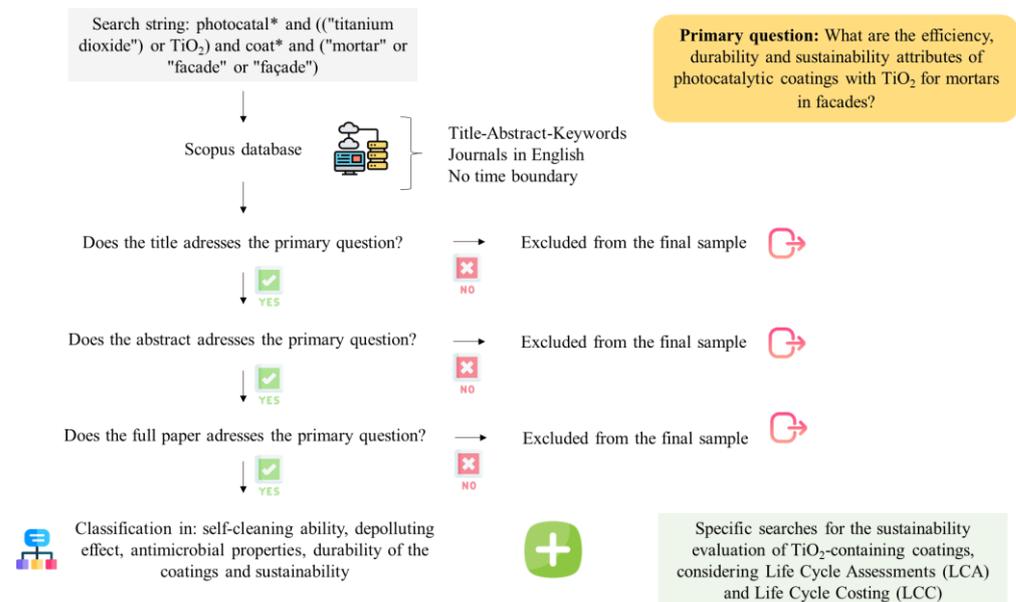
Through complete in-depth analysis, the sample of the resulting documents was further refined to consider only the TiO<sub>2</sub> form of application specified: thin TiO<sub>2</sub>-based coatings applied on mortar surfaces to be used in facades. Thus, papers addressing, for example, clay bricks [37], TiO<sub>2</sub>-soaked aggregates [38], pavements [39], application over paints [40], and TiO<sub>2</sub>-intermixed mortars [41] were left out from the selection. The remaining papers were classified according to the TiO<sub>2</sub>-related attributes they considered: self-cleaning ability, depolluting effect, antimicrobial properties, the durability of the coatings, and sustainability. Similarly, Gopalan et al. [42] also grouped the significant applications of TiO<sub>2</sub>-based building materials under environmental pollution remediation, self-cleaning, and self-disinfecting. Other properties and tests presented by the selected papers were disregarded for the classification.

In the present review, sustainability was included to examine, particularly, available LCA and LCC studies related to thin TiO<sub>2</sub>-based coatings. However, since none of the documents in the final sample used the mentioned tools, a second phase of string searches was performed in the Scopus database to provide at least an overview of the subject. Initially, two searches were conducted on the title, abstract, and keywords, the first with the string “(“titanium dioxide”) or TiO<sub>2</sub>) and coat\* and (“mortar” or “facade” or “façade”) and (“LCA” or “life cycle assess\*”),” and the second considering “(“titanium dioxide”) or

TiO<sub>2</sub>) and (coat\*) and (“LCA” or “life cycle assess\*”).” The second search string was less restrictive than the former due to the initial retrieval of only two papers [33,43]. Again, the search comprised only journals in English, and no time boundary was determined. Titles, abstracts, and full texts were subsequently analysed to filter the relevant documents related to a second proposed question: “What does the LCA indicate about the sustainability of mortars with TiO<sub>2</sub> coatings in facades?”. In this case, however, studies addressing coatings for substrates other than mortars were not directly excluded, looking for potential contributions of their LCA within the scope of the present review.

Furthermore, in the same way as for an LCA, to answer a third question, “What do LCC analyses say about the economic sustainability of mortars with TiO<sub>2</sub> coatings in facades?”, LCCs related to thin TiO<sub>2</sub>-based coatings were searched in the Scopus database. The first query string searched was “(“titanium dioxide”) or TiO<sub>2</sub>) and coat\* and (“mortar” or “facade” or “façade”) and (“LCC” or “life cycle cost\*”)”; however, it presented no results. Then, a second keyword string considering “(“titanium dioxide”) or TiO<sub>2</sub>) and (coat\*) and (“LCC” or “life cycle cost\*”)” was searched in the database.

After the final samples were filtered, classified, and organized, their methodologies and relevant findings were explored and discussed to present state-of-the-art photocatalytic efficiency, durability, and sustainability issues of TiO<sub>2</sub>-based coatings for mortars and to reveal potential research gaps. Figure 1 depicts the protocol applied to conduct this review.



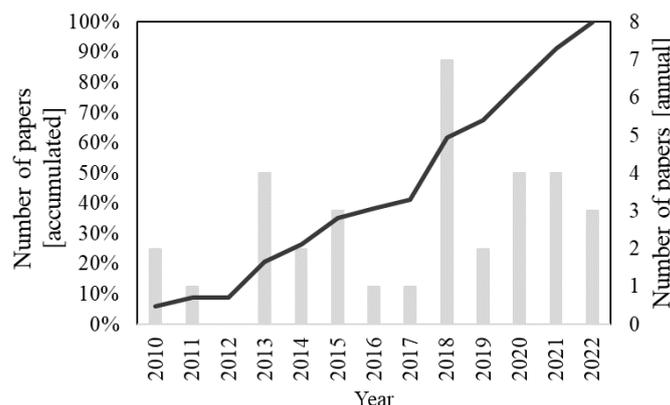
**Figure 1.** Protocol applied to conduct the literature review. This flowchart has been designed using resources from Flaticon.com (Eucalypt, Freepik, Icon mania and Vectors Market).

Due to the difficulty in comparing the results of different studies with photocatalytic materials caused by variations in reactors and parameters [44], specifically for the photocatalytic efficiency evaluation focused on the depolluting effect, discussions of the papers were further detailed based on a figure-of-merit called formal quantum efficiency (FQE), presented by Watanabe et al. [45] and Mills and Le Hunte [46]. FQE was calculated regarding Equation 1, in which the rate of reaction designates the number of molecules that are transformed or formed, while the incident light intensity applies to the incident number of photons [46].

$$\text{FQE} = \text{rate of reaction} / \text{incident light intensity} \quad (1)$$

### 3. Overview

The search of the “photocatal\* and ((“titanium dioxide”) or TiO<sub>2</sub>) and coat\* and (“mortar” or “facade” or “façade”))” string in the Scopus database retrieved 77 results. Title screening led to the exclusion of 27 documents and the abstract analysis of 14 other papers. Finally, two additional documents were removed with a full paper in-depth evaluation. The final sample, therefore, was composed of 34 articles. Figure 2 demonstrates the distribution of the selected documents over time; the final sample was entirely composed of papers published after 2010.



**Figure 2.** Distribution of the 34 papers from the final sample (after title, abstract, and full-text screening) related to the search string “photocatal\* and ((“titanium dioxide”) or TiO<sub>2</sub>) and coat\* and (“mortar” or “facade” or “façade”))” over time.

Within the final sample, five papers [1,42,47–49] were literature reviews. Among the 34 documents, 23 reported the self-cleaning performance of TiO<sub>2</sub>-based coatings for mortars to be used in facades, 18 approached their depolluting effect, three studied antimicrobial properties, and 16 presented information regarding the durability of the coatings, as indicated in Table 1. Nevertheless, none of the papers explored the sustainability of TiO<sub>2</sub> coatings or focused on the LCA or LCC tools, which are fundamental to achieving efficient and sustainable photocatalysis on building materials/systems [1].

**Table 1.** Subjects addressed by the studied papers: self-cleaning ability, depollution effect, antimicrobial effect, and durability.

Paper	Subjects Addressed			
	Self-Cleaning Ability	Depolluting Effect	Antimicrobial Effect	Durability
Khannyra et al. [50]	X	X		X
Castro-Hoyos et al. [1]	X	X	X	X
Gryparis et al. [51]	X			
Singh et al. [47]	X	X		
Pei et al. [11]	X	X		X
Zahabizadeh et al. [52]	X			
Zuena et al. [53]	X			
Gopalan et al. [42]	X	X		X
Speziale et al. [54]	X	X		X
Hot et al. [15]		X		
Rosales and Esquivel [48]	X			
Kim et al. [55]		X		X
Pondelak et al. [56]	X			X
Saeli et al. [24]		X		X
Wang et al. [57]	X			

Table 1. Cont.

Paper	Subjects Addressed			Durability
	Self-Cleaning Ability	Depolluting Effect	Antimicrobial Effect	
Krishnan et al. [58]	X			X
Rosales et al. [59]	X			X
Wu et al. [60]	X			
Pérez-Nicolás et al. [61]		X		X
Khitab et al. [49]	X	X		
Hot et al. [62]		X		
Guo et al. [29]	X			X
Mendoza et al. [63]	X	X		
Rudic et al. [64]				X
Vulic et al. [65]	X			X
Bengtsson and Castellote [66]	X	X		
Martinez et al. [67]		X		
Krishnan et al. [25]	X			X
Smits et al. [26]	X			
Guo et al. [21]		X	X	X
Vulic et al. [22]	X			
Martinez et al. [68]		X		
Fonseca et al. [69]			X	
Bengtsson and Castellote [70]		X		

Figure 3 depicts the proportion of papers that studied each one of the subjects of interest presented in Table 1 and the ones encompassing more than one research focus. In Figure 4, a bibliometric network map is shown to evaluate the co-occurrence of keywords found in the 34 papers of the final sample, aiming to understand their relevance and possible knowledge gaps. The minimum number considered for occurrences of a keyword was 5, resulting in the depiction of 20 different words. Nitrogen oxides, self-cleaning, and degradation are among the main clusters identified, following Figure 3; keywords related to the antimicrobial effect cannot be identified in Figure 4 since it was the less recurrent researched topic. Silicates are among the keywords in the cluster related to titanium dioxide, suggesting its recurrent use in the composition of TiO<sub>2</sub>-based thin films for mortars. Further details and discussions about the studies are given in Sections 4 and 5.

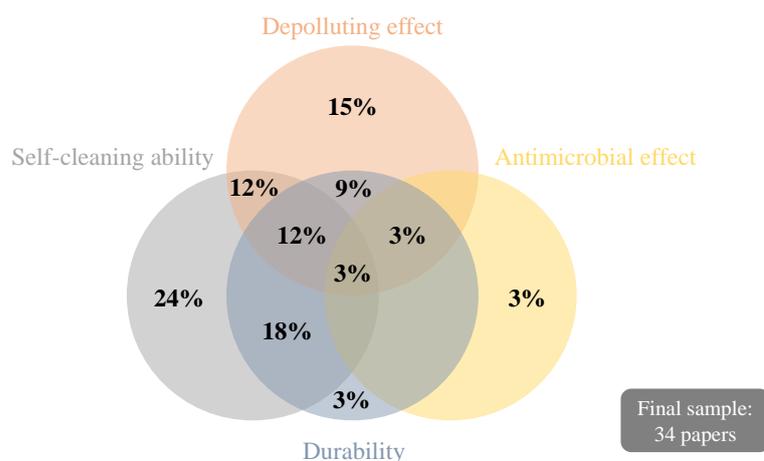
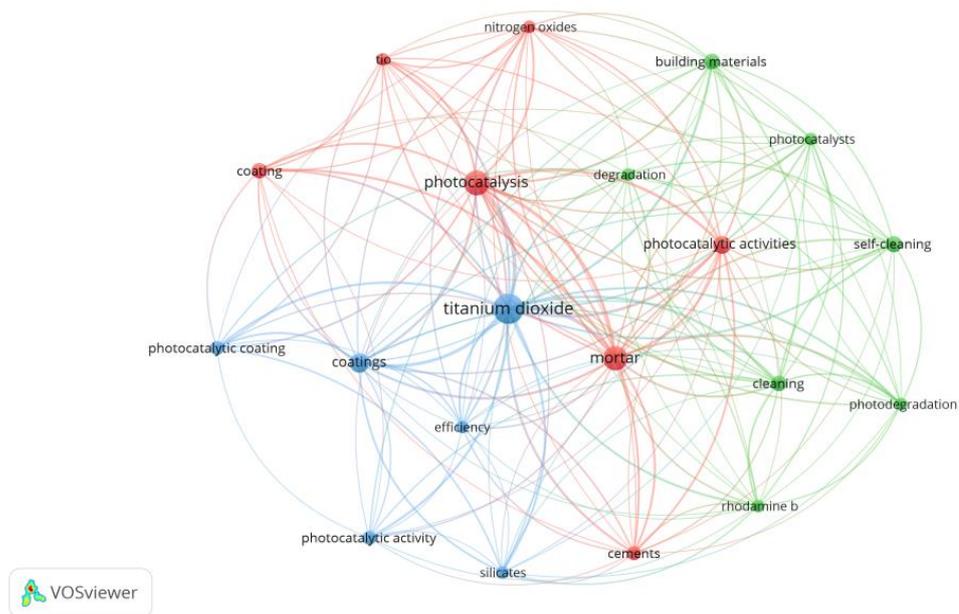


Figure 3. Proportion of papers addressing the research subjects: self-cleaning ability, depollution effect, antimicrobial effect, and durability.



**Figure 4.** Bibliometric network map referring to the co-occurrence of 20 keywords from the final sample of 34 papers related to self-cleaning ability, depollution effect, antimicrobial effect, and durability.

Table 2 compiles the core papers studied in this review relating to experimental studies on self-cleaning ability, depolluting effect, antimicrobial effect, and durability. The articles are presented chronologically, starting with the most recently published. The photocatalytic coatings are introduced considering their composition, applying method, doping substance/nanocomposite (if applicable), and evaluated substrate. Dip coating, sol-gel, covering of the surface with an n-TiO<sub>2</sub> thin layer, commercial water-based coatings, and spraying are among the principal applying methods [47].

Review articles are not presented in Table 2 since they discuss experimental results provided by several studies. Among the reviews, Castro-Hoyos et al. [1] aimed mainly to present challenges and opportunities related to using TiO<sub>2</sub> in cement-based materials, and Singh et al. [47] discussed its synthesis processes, applications, and efficiency. Gopalan et al. [42] studied the usage of modified TiO<sub>2</sub> in photocatalytic building materials, while Rosales and Esquivel [48] reviewed the synthesis and applications of SiO<sub>2</sub>-TiO<sub>2</sub> composites with modifiers or dopants. Finally, Khitab et al. [49] worked with synthesis methods, usage, and health concerns related to nano titania.

**Table 2.** Core papers presenting experimental results on self-cleaning ability, depolluting effect, antimicrobial effect, or durability. The entry “-” is for information unavailable or not applicable.

Paper	Photocatalytic Coating Composition	Applying Method	Doping Substance/Nanocomposite If Applicable	Substrate Evaluated
Khannyra et al. [50]	TiO <sub>2</sub> /SiO <sub>2</sub> and N-TiO <sub>2</sub> /SiO <sub>2</sub> synthesized via sol-gel method. TiO <sub>2</sub> proportion of 4% w/v concerning silica oligomer and concentrations of 0, 3.33, 6.66, 8 and 10 M for the nitrogen doping, regarding the synthesis of TiO <sub>2</sub> /SiO <sub>2</sub> and N-TiO <sub>2</sub> /SiO <sub>2</sub> . P25 used for comparison. (S0N0T; SN10TiO <sub>2</sub> ; SP25; SN8TiO <sub>2</sub> ; SN3.33TiO <sub>2</sub> ; STiO <sub>2</sub> ; SN6.66TiO <sub>2</sub> )	Brushed to saturation three times; sols extra removed by paper	Nitrogen	Portland cement mortar

Table 2. Cont.

Paper	Photocatalytic Coating Composition	Applying Method	Doping Substance/Nanocomposite If Applicable	Substrate Evaluated
Gryparis et al. [51]	TiO <sub>2</sub> /C-dots composites synthesized using a hydrothermal strategy. TiO <sub>2</sub> and several C-dot loadings: TC0, TC25, TC50, TC62.5 and TC75. Each catalyst was added in 4% <i>w/w</i> to a hydrophobic consolidant, synthesized using a sol-gel process. A commercial catalyst Au (1%)/TiO <sub>2</sub> (TAu) was also tested under solar conditions	Brushed three times	C-dot loading	Cement mortar
Pei et al. [11]	Graphene/TiO <sub>2</sub> nanocomposites prepared using a sol-gel assisted electrospray method. Suspensions in methanol of graphene/TiO <sub>2</sub> nanocomposites (2.5%) and commercial TiO <sub>2</sub> nanoparticles (2.5%) by weight of the cementitious materials used for the cement mortar	Sprayed	Graphene	Portland cement mortar
Zahabizadeh et al. [52]	Nano-TiO <sub>2</sub> aqueous suspension sprayed over the surface of mortar specimens after 1.5, 5, 9, 24 and 32 h and 7 days after the beginning of the hydration process	5 mg/cm <sup>2</sup> to 80 mg/cm <sup>2</sup> sprayed	-	Cement mortar
Zuena et al. [53]	Two distinct sols obtained by mixing TEOS, ethanol, TiO <sub>2</sub> nanoparticles, and loaded NC (silica nanocapsules) or MNP (silica mesoporous nanocapsules). Total nanoparticle concentration: 0.1% <i>w/w</i> . Tested coatings: Si-TiO <sub>2</sub> -NC, Si-TiO <sub>2</sub> -MNP and Si-Control	Applied using a brush until the surface remained wet for more than 1 min	Silica nanodevices loaded with a commercial biocide (2-mercaptobenzothiazole)	Lime-based mortar
Speziale et al. [54]	Two heterostructures of TiO <sub>2</sub> -ZnO (weight/weight 50/50 and 10/90). Dispersions into plain hydroalcoholic and 3D superhydrophobic medium. Further improvement by addition of superplasticizers (polycarboxylate ether (PCE), melamine sulfonate (MEL), polynaphthalene sulfonate (PNS) and polyacrylate (PA)) in a 1% <i>w/w</i> percentage concerning the weight of photocatalyst. Optimized coatings—Dispersion 1: superhydrophobic coatings (SPHB) 3 <i>w/w</i> % TiO <sub>2</sub> -ZnO 50/50 + 5% <i>w/w</i> PCE with respect to the nanoparticles. Dispersion 2: SPHB 3 <i>w/w</i> % TiO <sub>2</sub> -ZnO 10/90 + 5% <i>w/w</i> MEL with respect to the nanoparticles. Dispersion 3: SPHB 1.5 <i>w/w</i> % TiO <sub>2</sub> -ZnO 50/50 + 2.5% <i>w/w</i> PCE with respect to the nanoparticles. Dispersion 4: SPHB 1.5 <i>w/w</i> % TiO <sub>2</sub> -ZnO 10/90 + 2.5% <i>w/w</i> MEL with respect to the nanoparticles	1 mL deposited with a pipette	ZnO	Lime-based mortar
Hot et al. [15]	TiO <sub>2</sub> -based powders obtained from waste due to chemical milling baths of the aeronautical industry. 5 g of TiO <sub>2</sub> -based powder mechanically dissolved in 100 mL of distilled water solution containing 3.5 g of dispersant and 0.1 g of anti-foaming agent	Applied using a brush: 2–3 layers. 0, 1.4, 1.7, 4.4, 5.4, 5.5, 5.6, 6 g TiO <sub>2</sub> /m <sup>2</sup>	-	Cement mortar
Kim et al. [55]	Recycled TiO <sub>2</sub> nanoparticles produced from Ti-salt flocculated sludge obtained from dye wastewater. Suspension: dispersion of 20, 40, or 60 mg of TiO <sub>2</sub> powder in 5 mL of distilled water with 10 mg of mussel adhesive protein (MAP)	5 mL sprayed	-	Cement mortar

Table 2. Cont.

Paper	Photocatalytic Coating Composition	Applying Method	Doping Substance/Nanocomposite If Applicable	Substrate Evaluated
Pondelak et al. [56]	Nanocomposites based on layered double hydroxides (LDHs) associated with a photocatalytically active TiO <sub>2</sub> . Up to 10 wt.% of TiO <sub>2</sub> intercalated into the LDH. Preparation of a photocatalytic suspension	Three layers sprayed	ZnAl layered double hydroxide	Lime-based mortar
Saeli et al. [24]	Photocatalytic hydroxyapatite (TiHAp). HAp derived from Atlantic codfish bone wastes prepared with 1 wt% TiO <sub>2</sub> . Suspensions of 1 wt% and 5 wt% TiHAp in distilled water	1.5 mL deposited with a pipette	-	Natural hydraulic lime-based mortar
Wang et al. [57]	Two core-shell nanocomposites with different deposited densities of TiO <sub>2</sub> nanoparticles on each SiO <sub>2</sub> nanosphere. SiO <sub>2</sub> @TiO <sub>2</sub> photocatalysts (0.025 mg) added into water (2 mL), solution sprayed on one surface (4 cm × 4 cm) of slices. P25 used as reference	2 mL sprayed	SiO <sub>2</sub>	Cement paste and mortar
Krishnan et al. [58]	For laboratory studies: TiO <sub>2</sub> mixed in a commercial silicate coating in two contents of 1.6% or 2.5% (by volume of the liquid silicate). For field study: silicate containing 0.7% photocatalytic TiO <sub>2</sub>	Individual coatings applied in three coats	-	Cement mortar
Rosales et al. [59]	Synthesis with sonochemistry: mixing of titanium dioxide sol and silicon dioxide sol. Synthesis without sonochemistry: mixing of titanium dioxide particles and silicon dioxide sol	-	SiO <sub>2</sub>	Cement mortar
Wu et al. [60]	Photocatalytic top layer prepared by mixing a transparent silicate coating with 1.46% photocatalytic TiO <sub>2</sub> by volume. 3 layers: white silicate coating, transparent silicate coating and photocatalytic layer	Each layer applied using a brush	-	Portland cement mortar
Pérez-Nicolás et al. [61]	Dispersions with 1 wt% of the photocatalytic additive in water with superplasticizer (three polycarboxylate-based polymers and a commercial polynaphthalene sulfonate (PNS); 1 wt% in relation to the photocatalysts). Average percentage of photocatalytic additive with respect to the binder weight: 0.005%	28.5 mg sprayed	Bare TiO <sub>2</sub> , Fe-TiO <sub>2</sub> and V-TiO <sub>2</sub>	Cement and air lime mortar
Hot et al. [62]	TiO <sub>2</sub> aqueous dispersions: dilution of a commercial stable aqueous dispersion of ultrafine TiO <sub>2</sub> anatase particles. TiO <sub>2</sub> dry matter content in solution: 18 wt%, 12 wt%, 6 wt%, 5 wt%, 4 wt%, 3 wt% and 1 wt%	Applied using brush	-	Cement mortar
Guo et al. [29]	Commercially available TiO <sub>2</sub> containing paint with about 10% TiO <sub>2</sub> by weight: TiO <sub>2</sub> water suspension prepared from a 0.03 g/L P25 distilled deionized water suspension	Three layers applied using a brush	-	Self-compacting architectural mortar
Mendoza et al. [63]	Commercial TiO <sub>2</sub> suspensions and homemade titania sol (TEA)—stabilized suspension. SiO <sub>2</sub> sol applied on cement surface previously to the TiO <sub>2</sub> layer for RhB removal evaluation	SiO <sub>2</sub> and TiO <sub>2</sub> layer sprayed	-	Cement mortar
Rudic et al. [64]	Layered double hydroxides and photocatalytic active TiO <sub>2</sub> particles in suspension. 1 wt% of the synthesized nanocomposite (TiO <sub>2</sub> -LDH) in a stabilized suspension	Three layers sprayed	Zn and Al salts	Lime-based renders

Table 2. Cont.

Paper	Photocatalytic Coating Composition	Applying Method	Doping Substance/Nanocomposite If Applicable	Substrate Evaluated
Vulic et al. [65]	3 wt% TiO <sub>2</sub> suspensions introduced onto calcined ZnAl-LDH (layered double hydroxides) powder. Nanocomposite powder (1 g) suspended in 100 mL demineralized water. Nanocomposite suspension: 1 wt% of solid phase	Three layers sprayed	ZnAl-LDH	Cement and pozzolanic mortar
Bengtsson and Castellote [66]	Two commercial paints (applied directly on the surface). Six TiO <sub>2</sub> powders, applied in a solution at a concentration of 8.37 g/L, final TiO <sub>2</sub> mass load of 5 g/m <sup>2</sup> . One of the powders was a homemade S-, N-, and C-doped catalyst (S-TiO <sub>2</sub> ). Samples of the catalysts also submitted to treatments of exposure to water and calcinations (except for the paints and one powder)	300 g/m <sup>2</sup> of paint applied with metal roller. 3 mL of dispersions	S, N and C for one of the eight different catalysts tested	White cement mortar
Martinez et al. [67]	Acrylic polymer binder, water as solvent, additives (thickeners and wetting agents). Photocatalyst: particle suspension commercialized (40 wt% TiO <sub>2</sub> P25). Final photocatalytic coating with 10% (wt) of TiO <sub>2</sub>	40 g/m <sup>2</sup> (≈5 μm) applied using a brush	-	Cement mortar
Krishnan et al. [25]	Commercially available silicate coating material (containing potassium silicate, silica sol, and organic additives, solid content of 13.5%). 5%, 10%, 15%, and 20% of TiO <sub>2</sub> by mass of solid silicate mixed with the silicate coating material	Three coats	-	Portland cement mortar
Smits et al. [26]	TiO <sub>2</sub> P25, P90 and Hombikat dispersed in ethanol; E-UV commercially available in liquid form	One layer deposited with a pipette (24 ± 2 mg, 267 μg/cm <sup>2</sup> )	-	Cement mortar
Guo et al. [21]	Two coating techniques. 1: suspension of 25 g/L P25 ethanol suspension with 25 g/L glycerol; substrate materials dipped into it for 5 min. Coated mortar calcinated at 450 °C for 120 min to burn organic materials and bond the TiO <sub>2</sub> film to the substrate. 2: suspension of methanol and P25 (25g/L); mortar dipped for 5 min, and over-dried at 60 °C for 120 min	Dip-coating	-	Self-compacting glass mortars
Vulic et al. [22]	Wet impregnation of TiO <sub>2</sub> onto Zn–Al layer double hydroxides (LDHs) for the preparation of Ti–Zn–Al LDH nanocomposites. Nanocomposite suspension prepared using sol–gel method with H <sub>2</sub> O <sub>2</sub> solution	Three layers sprayed	Ti–Zn–Al LDH	Cement mortar
Martinez et al. [68]	Acrylic binder, water as solvent, additives (thickeners and wetting agents). The photocatalyst was a commercial slurry solution. Different amounts of binders (2.3%, 5.0%, 7.5%, 11.5%, 15.0%) and various concentrations of photocatalyst (0%, 5%, 10%, 15%, 20%)	40 g/m <sup>2</sup> applied using a brush	-	Mortar
Fonseca et al. [69]	Aqueous solutions of anatase photocatalyst P25 (1% (v/v) in distilled water)	Sprayed	-	Two external walls of the National Palace of Pena
Bengtsson and Castellote [70]	Colloidal suspension of TiO <sub>2</sub> in deionised water at a concentration of 8.37 g/L, final TiO <sub>2</sub> mass load of 5 g/m <sup>2</sup>	Layers of around 10 μm	-	White mortar

Some of the retrieved papers, as presented in Table 2, use TiO<sub>2</sub> with doping techniques or its combined use with other substances and nanocomposites, which may be motivated by several reasons. In general, chemical and structural modifications aim to reduce the bandgap, seeking the degradation of pollutants and contaminants with TiO<sub>2</sub> under solar or visible light irradiation [42].

Among the doping substances used in the studies, Khannyra et al. [50] applied nitrogen to understand its effect on photocatalytic activity. C-dot loading in TiO<sub>2</sub> was chosen because it might increase the photocatalytic activity, benefiting from solar light [51]; graphene/TiO<sub>2</sub> nanocomposites, likewise, might enable better exploitation of solar energy [11]. Doped structures such as Fe-TiO<sub>2</sub> and V-TiO<sub>2</sub> also aim to take advantage of visible light for photocatalytic reactions [61]. The probable more active photocatalyst behaviour under UV and visible radiation also drove the choice for heterostructures of TiO<sub>2</sub>-ZnO [54]. Layered-structured materials, like ZnAl double hydroxide, may adjust physical and chemical performance attributes during the synthesis of nano-TiO<sub>2</sub> [56], contributing, for example, to its compatibility with cement-based mortars [22]. SiO<sub>2</sub>@TiO<sub>2</sub> nanocomposites were researched mainly regarding durability issues due to the commonly weak adhesion between photocatalytic coatings and the underneath substrate; SiO<sub>2</sub> may prevent the release of TiO<sub>2</sub> nanoparticles from the surface and, thus, improve the adhesion [57].

Specifically, for the sustainability research goal, conducted as a second phase of the review, for the first string searched on an LCA, “(“titanium dioxide”) or TiO<sub>2</sub>) and coat\* and (“mortar” or “facade” or “façade”) and (“LCA” or “life cycle assess\*”)”, two papers were retrieved, and, for the second search string, “(“titanium dioxide”) or TiO<sub>2</sub>) and (coat\*) and (“LCA” or “life cycle assess\*”)”, the Scopus database identified 15 studies. The two papers found for the first string [33,43] were among the 15 identified for the second one; thus, they were considered only once.

Concerning the papers on sustainability using the LCA tool, the title and abstract screening led to the exclusion of three articles each. Full-paper reading resulted in the exclusion of two additional papers. Among the remaining seven articles, one was a literature review [71]; the other six documents from the final sample are presented in Table 3. It is essential to highlight that, as the search string was broadened to sustainability papers because specific studies related to an LCA on TiO<sub>2</sub>-based thin coatings for mortars on facades had not been retrieved from the search, some of the substrates were not mortars. Further details on the studies are given in Section 6.

**Table 3.** Papers with results assessed for sustainability and life cycle assessment (LCA). The entry “-” is for information unavailable or not applicable.

Paper	Photocatalytic Coating Composition	Deposition Method	Doping Substance/Nanocomposite If Applicable	Substrate Evaluated
Hischier et al. [33]	3 coatings: paint containing nano-TiO <sub>2</sub> together with pigment-grade TiO <sub>2</sub> ; paint containing only pigment-grade TiO <sub>2</sub> ; nano-TiO <sub>2</sub> integrated into a (protection) coating laid separately on top of a traditional paint	Painting	-	-
Pini et al. [72]	TiO <sub>2</sub> acid nanosuspension	Dip-coating	-	Softened glass
Tichá et al. [73]	TiO <sub>2</sub> photocatalytic commercial suspension	Painting	-	-
Hischier et al. [43]	Paint systems containing manufactured nanomaterials (MNM): paint containing nano-TiO <sub>2</sub> together with pigment-grade TiO <sub>2</sub> ; paint containing only pigment-grade TiO <sub>2</sub>	Painting	-	Facade
Babaizadeh and Hassan [34]	Mixture of TiO <sub>2</sub> anatase nanoparticles suspended in an aqueous liquid at 2% by volume	Sprayed	-	Residential window glass
Fufa et al. [74]	Coating with primer and stain or water-based acrylic blue tinted paint with brush. Treatments modified with TiO <sub>2</sub> and clay nanoparticles or a combination of the two	Applied with brush	-	Norway spruce wood

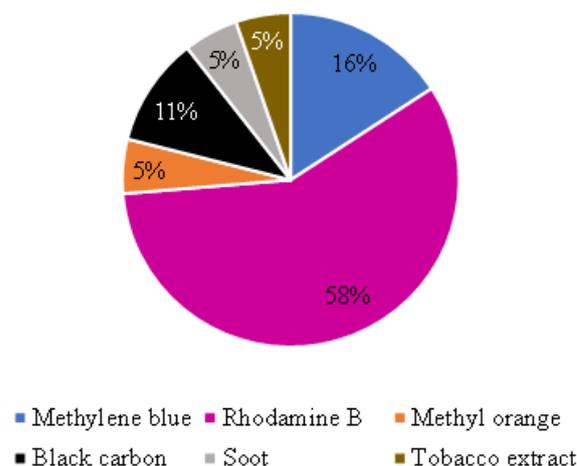
Finally, regarding sustainability and LCC, although the “(“titanium dioxide”) or TiO<sub>2</sub>) and coat\* and (“mortar” or “facade” or “façade”) and (“LCC” or “life cycle cost\*”)” query string did not match any articles, the second, “(“titanium dioxide”) or TiO<sub>2</sub>) and (coat\*) and (“LCC” or “life cycle cost\*”)” resulted in two papers published in journals [34,75]. The study of Wu et al. [75] was excluded because it did not refer to life cycle costing; the LCC abbreviation meant lightweight cement composite. Therefore, only the work of Babaizadeh and Hassan [34], already mentioned in Table 3, resulting from the advanced search on sustainability, used the LCC tool.

#### 4. Photocatalytic Efficiency

This section is divided into self-cleaning ability, depolluting, and antimicrobial effects, aiming to cover all the main topics related to the photocatalytic efficiency of thin TiO<sub>2</sub>-based coatings to be applied on mortars in facades.

##### 4.1. Self-Cleaning Ability

Among the papers retrieved by the review, the self-cleaning ability evaluation of thin TiO<sub>2</sub>-based coatings for mortars was done with methylene blue (MB) [22,50,51], rhodamine B (RhB) [11,25,29,52,54,56,57,59,63,65,66], methyl orange (MO) [53], black carbon [58,60], soot [26], or tobacco extract [66], as illustrated in Figure 5. Table 4 details the applied dye or contamination agents and the main exposure conditions for the experimental tests.



**Figure 5.** Application of different dyes or contamination agents to evaluate self-cleaning ability. Note: one of the papers [66] used tobacco extract and Rhodamine B.

**Table 4.** Details on the applied dye or contamination agents and the main exposure conditions for testing the self-cleaning ability.

Paper	Dye or Contamination Agent	Exposure Conditions
Khannyra et al. [50]	20 $\mu\text{L}/\text{cm}^2$ of 1mM MB solution dissolved in ethanol dropped over the treated and untreated samples	A 2500 W xenon arc lamp. 300 W/ $\text{m}^2$ of irradiance. 60 min of irradiation
Gryparis et al. [51]	Two drops (around 0.025 mL each) of MB applied over the coatings	UV-A light: 36 W LED curing lamp, with 33.6 mW/ $\text{cm}^2$ irradiance. Artificial solar light: two 15 W tubular fluorescent lamps, around 13.6 mW/ $\text{cm}^2$ irradiance. 48 h of irradiation
Pei et al. [11]	0.1 mL of RhB $10^{-3}$ mol/L deposited on the mortar surfaces = 5 $\text{cm}^2$ circular homogenous stained area	Three visible light lamps, resulting in 3.5 W/ $\text{m}^2$ of irradiation. 72 h of irradiation
Zahabizadeh et al. [52]	Immersion of samples in 30 mL of a 5 mg/L (5 ppm) RhB solution	Lamp with 300 W to simulate solar irradiation with 1 mW/ $\text{cm}^2$ irradiance. 8 h of irradiation

Table 4. Cont.

Paper	Dye or Contamination Agent	Exposure Conditions
Zuena et al. [53]	Covering with 750 $\mu\text{L}$ of a solution of 1 mM of methyl orange in ethanol	Laboratory test: samples in a ventilated chamber and irradiated for 72 h with 365 nm UV light. In-situ: specimens exposed to natural solar light over the month of November 2020 in Rome
Speziale et al. [54]	0.2 mL of RhB solution ( $10^{-3}$ M) poured with a micropipette on the surface of the specimens	UV-vis illumination with 300 W lamp. Loss of colour observed at different times over 48 h of irradiation
Pondelak et al. [56]	Preabsorption test (24 h) with RhB solution, after which the RhB solution was replaced	UV-A intensity: 0.8 mW/cm <sup>2</sup> . Visible light intensity: 0.3 W/m <sup>2</sup> . Irradiation for 30 min, 90 min, 150 min, 210 min and 24 h
Wang et al. [57]	2 mL of RhB solution (80 mg/L) sprayed onto the surface of treated cement pastes	UV lamp (20 W). Intensity of UV light on the surface: 0.04 mW/cm <sup>2</sup> . 9 h of irradiation
Krishnan et al. [58]	Black Carbon loadings of 8 mg/cm <sup>2</sup> and 24 mg/cm <sup>2</sup>	Three xenon lamps, 200 h of irradiation
Rosales et al. [59]	RhB solution (concentration of 50 ppm) evenly applied with a pipette to 3 standardized positions on the samples	Light with a peak wavelength of 360 nm and an intensity of 10.3 W/m <sup>2</sup> . UV-A irradiation for 26 h
Wu et al. [60]	50 mg of commercially available black carbon powder dispersed in 100 g of deionized water. 8 $\mu\text{g}/\text{cm}^2$ applied on the surface of the coated specimens	Simulated solar irradiation with wavelength from 295 to 3000 nm, intensity of 0.55 W/m <sup>2</sup> /nm at a wavelength of 340 nm. Exposure for 300 h
Guo et al. [29]	0.1 mL RhB solution (concentration of $5 \times 10^{-4}$ g/mL) applied evenly on 3 standardized positions (5 cm <sup>2</sup> e.a.)	Intensity of 3.1–3.4 W/m <sup>2</sup> and 0.5–0.6 W/m <sup>2</sup> for UV-A and visible light irradiation. Irradiation for 26 h
Mendoza et al. [63]	1.5 mL of $10^{-4}$ M RhB deposited on the surfaces in a circular homogeneous spot with $1.56 \times 10^{-4}$ moles m <sup>-2</sup> RhB	Six fluorescent lamps: 30 W/m <sup>2</sup> of irradiance. 5 days of irradiation
Vulic et al. [65]	Preabsorption with RhB solution (24 h) and then RhB solution replaced (10 ppm dm <sup>-3</sup> )	Intensity of UV-A and visible light spectra: 8 W/m <sup>2</sup> and 0.3 W/m <sup>2</sup> , respectively. Irradiation for 210 min
Bengtsson and Castellote [66]	RhB initial concentration: $1.368 \times 10^{-4}$ mol/m <sup>2</sup> ; tobacco solution initial concentration: 2.359 g/m <sup>2</sup>	UV light. Irradiance: 5 W/m <sup>2</sup> . Irradiation for 22 h
Krishnan et al. [25]	RhB dissolved in deionized water (concentration of 0.05 g/L), 5 mL applied on the specimen surface. Surface loading: 4.2 $\mu\text{g}/\text{cm}^2$	UV light: wavelength from 295 nm to 400 nm with average intensity of $\approx 0.35$ W/m <sup>2</sup> and peak intensity of 0.68 W/m <sup>2</sup> at 340 nm. Irradiation for 100 h
Smits et al. [26]	Dispersion of 0.1% carbon black in 8:2 water:isopropanol solution. Four drops applied on each sample = thickness of the soot layer around 0.12 $\mu\text{m}$ ( $\approx 22$ $\mu\text{g}/\text{cm}^2$ )	UV-A illumination: five lamps of 25 W; most intense wavelength at 368 nm; maximum incident light intensity: 340 $\mu\text{W}/\text{cm}^2$ ; luminance: 4600 lux. Artificial solar irradiation: four full spectrum daylight lamps of 14 W with reflectors; maximum incident light intensity: 70 $\mu\text{W}/\text{cm}^2$ and 31,000 lux. Irradiation for over 400 h
Vulic et al. [22]	Bottomless glass tube (inner diameter 33 mm, height 70 mm) fixed on each specimen and filled with a 10 ppm dm <sup>-3</sup> MB solution. Specimens surrounded by the same MB solution. Preabsorption test (24 h), after which the MB solution was replaced	UV irradiation with light intensity of 0.922 mW/cm <sup>2</sup> for 30, 90, 150 and 210 min

Even though, in general, the studied papers focused on the search for stable aesthetic appearance in buildings by combining photocatalytic oxidation activity with photo-induced hydrophilicity [42], comparisons between different studies must be made carefully. The thickness and structure of the thin TiO<sub>2</sub>-based coatings, applying method, nanoparticles' crystallographic parameters, and the presence of dopants affect the photocatalytic ability [47]. The efficiency of catalysts may also depend on variables such as the type of contaminant or pollutant assessed and the exposure conditions [60,66]. Pondelak et al. [56], for example, reported RhB removal of around 2% in 30 min of testing and almost 16% after

24 h of irradiation. For Vulic et al. [22], however, mortars with nanocomposite coatings enabled 28% MB removal after 3.5 h of irradiation. On the other hand, for Khannyra et al. [50], around 25% and 27% of MB degradation were verified for untreated samples and samples solely with silica (SONOT), probably due to the dye's sensitivity to UV–vis light.

The amount of exposed TiO<sub>2</sub> and, consequently, of active sites over the mortar surface is probably the main reason for using thin photocatalytic coatings instead of TiO<sub>2</sub>-intermixing techniques [22,25]. Krishnan et al. [25] observed that a silicate coating containing 15% TiO<sub>2</sub> by mass achieved a similar RhB degradation to mortars intermixed with 2% and 4% TiO<sub>2</sub> by weight of cement but required at least 20 times less TiO<sub>2</sub>. In this context, Zahabizadeh et al. [52] suggested that applying a photocatalytic coating on mortars still in a fresh state could improve the immobilization of TiO<sub>2</sub> nanoparticles on their surface.

Colour compatibility is an essential criterion to be considered when applying coatings on mortar surfaces. Aiming to preserve their original aesthetic appearance after the application of thin TiO<sub>2</sub>-based coatings, Pondelak et al. [56], for example, observed minor initial colour differences ( $\Delta E < 3$ ) and no whitening or yellowing since  $\Delta L^*$  was nearly zero, possibly indicating a high level of compatibility with the substrate. Khannyra et al. [50], on the other hand, identified significant total colour changes ( $\Delta E > 5$ ), which points out the importance of individual assessment of proposed photocatalytic coatings.

Although Pei et al. [11] and Mendoza et al. [63] worked with UV–vis diffuse reflectance spectra (DRS) to study the self-cleaning ability, most of the papers [25,29,50,51,54,57–60,66] used spectrophotometers. Then, mainly CIELab colour space enabled the assessment of colour variation ( $\Delta E$ ), calculated according to Equation 2, and the colourimetric coordinates  $L^*$ ,  $a^*$ , and  $b^*$  [57]. The coordinate  $L^*$  refers to the lightness and luminance and varies from white (100) to black (0),  $a^*$  expresses values ranging from red ( $+a^*$ ) to green ( $-a^*$ ), and, finally,  $b^*$  represents values from blue ( $-b^*$ ) to yellow ( $+b^*$ ). In Equation 2,  $L_0^*$ ,  $a_0^*$ , and  $b_0^*$  represent the initial colourimetric coordinates, and  $L_t^*$ ,  $a_t^*$ , and  $b_t^*$  are the coordinates after a particular irradiation time [57].

$$\Delta E = \sqrt{(L_t^* - L_0^*)^2 + (a_t^* - a_0^*)^2 + (b_t^* - b_0^*)^2} \quad (2)$$

Some authors [29,59] investigated RhB removal efficiencies after 4 and 26 h of UV-A or visible light irradiation, expressed as  $R_4$  and  $R_{26}$ . Equation 3 demonstrates the calculation of  $R_4$ ;  $R_{26}$  determination is the same as  $R_4$ , but the value of  $a^*$  for 4 h is changed for  $a^*$  after 26 h [29].  $R_4 > 20\%$  and  $R_{26} > 50\%$  indicate that the material can be considered photocatalytic [76,77]. In Rosales et al. [59], for example, SiO<sub>2</sub>@TiO<sub>2</sub>-containing coatings achieved UNI 11259-2016 [77] photocatalytic requirements, with  $R_4$  and  $R_{26}$  of 25% and 55%, respectively; sonochemistry further improved the efficiencies of RhB degradation to 30.4% and 70.5%, probably due to a better dispersion of TiO<sub>2</sub> on the SiO<sub>2</sub> matrix. Coatings solely TiO<sub>2</sub>-based led to even higher photocatalytic activity, reaching  $R_4$  and  $R_{26}$  of 79% and 92%, and layers with SiO<sub>2</sub> only led to a significantly lower 0.5% and 8% removal [59], as expected.

$$R_4 (\%) = [(a^*(0h) - a^*(4h))/(a^*(0h))] \times 100\% \quad (3)$$

More research is needed concerning using SiO<sub>2</sub> and TiO<sub>2</sub> as a composite, especially regarding their physical and chemical properties, synthesis methods, and applications [48]. RhB degradation provided by coatings with SiO<sub>2</sub>@TiO<sub>2</sub> nanocomposites prepared by Wang et al. [57] was higher than the efficiency promoted with TiO<sub>2</sub> P25 up to 1 h of the test, different from that observed by Rosales et al. [59]. After 9 h, however, 63.4%, 66.7%, 68.3%, and 55.1% of RhB removal was verified for coatings with the nanocomposites with higher and lower deposited density of TiO<sub>2</sub> on SiO<sub>2</sub> nanospheres, P25, and, lastly, for untreated surfaces [57].

Rosales and Esquivel [48] referenced a hydrophobic potential of SiO<sub>2</sub>-TiO<sub>2</sub> composites but indicated that TiO<sub>2</sub> decreased these properties because it led to a lower contact angle; the angle can be increased, however, with compounds like siloxanes. Speziale et al. [54] identified a synergistic effect between photocatalysts and hydrophobic components on the

coatings, which avoided bonds between the applied dye and the underneath substrate. RhB discolouration, observed through the variation on the colour coordinate  $a^*$ , was enhanced by 2–16% for lime mortars with active optimized TiO<sub>2</sub>-ZnO-containing coatings with superplasticizers [54]. In this context, for Zuena et al. [53], Si-TiO<sub>2</sub>-MNP coating with silica mesoporous nanoparticles and TiO<sub>2</sub> nanoparticles led to a worse dye discolouration performance compared to loaded silica nanocapsules due to the probable loss of contact between the dye agent, methyl orange, and the TiO<sub>2</sub>, caused by an entrapment of the photocatalytic nanoparticles within the MNP. Therefore, it is essential to understand clearly the interaction between SiO<sub>2</sub> and TiO<sub>2</sub> since the contact between them and other substances may influence the resulting performance.

Furthermore, in the study of Mendoza et al. [63], a SiO<sub>2</sub> interlayer between the mortar and the TiO<sub>2</sub>-coating led to extremely low reaction rates at the initial stages of testing when compared with specimens without the interlayer concerning RhB photodegradation. Wu et al. [60], on the other hand, after 300 h of testing, observed that a white silicate coating incorporating photocatalyst (PSWC) enabled a 99% recovery of solar reflectance and  $L^*$  values, evidencing the removal of black carbon, different from that observed for transparent silicate coating (TSC) and white silicate coating (WSC). Therefore, even with possibly corresponding components, each study can identify specific photocatalytic behaviour, which refers to the particularities of the researched layers and the applied tests.

In Gryparis et al. [51], testing with different irradiation did not significantly influence the results. Smits et al. [26], however, for daylight irradiation, observed much lower degradation rates than for UV light; more than 150 h of daylight irradiation were necessary to degrade half of the initially deposited soot. However, the soot quantity was higher than in reality, indicating that, under realistic conditions, the TiO<sub>2</sub> coating could remove the actual soot particles from the surfaces and provide self-cleaning ability [26].

Still considering different types of irradiation, in Guo et al. [29], for UV-A incidence, both the tested commercial paint containing TiO<sub>2</sub> and the water dispersion with TiO<sub>2</sub> P25 presented satisfactory photocatalytic performance, reaching, respectively,  $R_4$  of 51.4% and 57.2%;  $R_{26}$  was 63.6% for both types of coating. The resulting values were, thus, higher than the recommended targets of 20% and 50%, respectively. For visible light irradiation, similar to Smits et al. [26], the samples of Guo et al. [29] presented lower RhB removal than for UV-A:  $R_4$  was 42.0% and 43.2% for the commercial TiO<sub>2</sub>-containing paint and the aqueous dispersion, respectively, and  $R_{26}$ , 61.7% and 51.2%. The dye-sensitized photoreaction undergone using RhB probably contributed to the final high activity identified with visible irradiation [29,78].

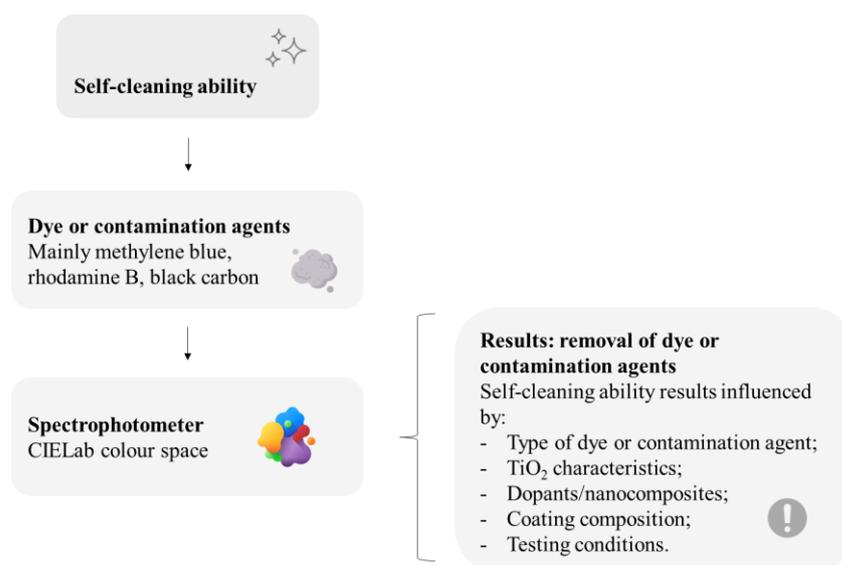
Regarding the doping of TiO<sub>2</sub> or its use as nanocomposite, Vulic et al. [65] observed similar RhB removal for TiO<sub>2</sub>/ZnAl layered double hydroxide coated cement mortars and pozzolanic mortars, which achieved 10% and 8% removal, respectively, after 3.5 h of exposure to UV light; the similar behaviour was possibly due to a comparable nature and quantity of active surface sites. For coatings containing TiO<sub>2</sub> and/or those which were N-doped, after 60 min of irradiation, Khannyra et al. [50] observed MB degradation efficiencies of 85%, 83%, 79.5%, 79%, 78%, and 72%, respectively, for SN10TiO<sub>2</sub> > SP25 > SN8TiO<sub>2</sub> > SN3.33TiO<sub>2</sub> > STiO<sub>2</sub> > SN6.66TiO<sub>2</sub>. In Pei et al. [11], cement mortar samples coated with TiO<sub>2</sub> nanoparticles and graphene/TiO<sub>2</sub> nanocomposites led to 20.25% and 69.74% of RhB degradation, respectively, while untreated mortar degraded 3.51% of RhB after 48 h of irradiation.

For Gryparis et al. [51], which studied TiO<sub>2</sub>/C-dots composites synthesized using a hydrothermal strategy, TC0 (pure TiO<sub>2</sub>) and TAU had the best performances, reaching  $\Delta E$  below five (comparing the colour difference of the surfaces after the degradation of the MB stain and before the MB application) within 48 h. A double layer composed of a consolidant layer plus a consolidant with TC25 also led to considerable self-cleaning activity, achieving  $\Delta E$  of 7.21 and 5.76 under UV-A and visible light exposure, respectively. As expected, untreated surfaces and surfaces applied only with consolidant had an insignificant colour decline [51].

Among the papers that studied the doping of TiO<sub>2</sub> or its combined use with other substances, thus, the results indicate that the efficiency of photocatalytic activity may be increased or negatively affected depending on the composition of the adjoining substance. Khannyra et al. [50], for example, verified that nitrogen doping probably extended the absorption of light that enables the photocatalytic reactions to the visible region, improving MB degradation kinetics. Additionally, Pei et al. [11] reported that the low bandgap energy presented using graphene/TiO<sub>2</sub> nanocomposites compared to solely TiO<sub>2</sub> provided the exploitation of more photons and the consequent generation of more electron-hole pairs with lower recombination rates, contributing to the photocatalytic efficiency of the studied coatings. Gryparis et al. [51], on the other hand, concluded that nanocomposites without C-dot loading into TiO<sub>2</sub> led to faster MB degradation.

Considering different TiO<sub>2</sub> proportions on coatings, all TiO<sub>2</sub>-coated and untreated surfaces of Zahabizadeh et al. [52] presented similar photocatalytic efficiency up to 4 h of irradiation. After 8 h, however, increasing coating rates resulted, in general, in higher RhB degradation; a coating rate of 80 mg/cm<sup>2</sup> led to 21% of efficiency [52]. In the study of Krishnan et al. [58], higher amounts of TiO<sub>2</sub> also led to the fastest surface recovery after testing with black carbon; less soot over the surfaces required lower TiO<sub>2</sub> content to achieve self-maintenance for a more extended period. For Smits et al. [26], all the tested coatings, with different commercially available TiO<sub>2</sub>, removed the soot deposited over the samples, although with different performances. The best behaviour, obtained with a coating containing TiO<sub>2</sub> P25, led to the complete mineralization of 60% of the soot in 24 h, resulting in its total transformation into CO<sub>2</sub> [26].

The great exposure of facades to sunlight and rainfall speeds up the implementation of self-cleaning on their surfaces [42,49]. For the spreading and consolidation of TiO<sub>2</sub> usage in buildings worldwide, however, higher photocatalytic efficiencies may still be needed, which could be enabled by large-scale or more realistic experimental studies, considering real-life pollution, weather, and lighting, further than dye degradation laboratory tests; architectural designs must also be correlated with the use of TiO<sub>2</sub> in facades since construction details might be decisive on the self-cleaning performance [1]. To summarize, Figure 6 depicts some main recurrent issues related to this review on the self-cleaning evaluation of mortar samples with thin TiO<sub>2</sub>-based coatings.



**Figure 6.** Main recurrent issues reviewed on the self-cleaning evaluation of mortar samples with thin TiO<sub>2</sub>-based coatings. This figure has been designed using resources from Flaticon.com (Creatype, Freepik, Good Ware).

#### 4.2. Depolluting Effect

Different from that verified for the self-cleaning ability, whose evaluation was done with varied dyes and contamination agents, the study of the depolluting effect on TiO<sub>2</sub>-based coatings was mainly carried out by observing the degradation of nitrogen oxides (NO<sub>x</sub>). NO<sub>x</sub> represents two different gases, nitrogen oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) [42]. Differently, Martinez et al. [67] observed the degradation of a volatile organic compound (VOC) mixture composed of benzene, toluene, ethylbenzene, and xylenes, or BTEX, to represent atmospheric pollution. VOCs are converted into CO<sub>2</sub> and H<sub>2</sub>O under UV irradiation using TiO<sub>2</sub> action [42].

Several papers [15,50,54,55,61,62,66–68,70] reference ISO 22197-1:2016 [79] or its anterior versions for the method applied (some with adaptations), or, still, UNI 11247:2010 [63,80]. ISO 22197-1:2016 [79] recommends the exposure of the tested samples in a flow-type photoreactor and their activation using UV illumination. NO is the typical air pollutant used for the experiment, during which it is partly converted to NO<sub>2</sub>. The air-purification performance is obtained through the net removal of NO<sub>x</sub>, which considers the discount of the NO<sub>2</sub> formed from the NO removed [79]. The photocatalytic degradation of NO involves two stages: first, NO is oxidized to NO<sub>2</sub> and, afterwards, NO<sub>2</sub> is further oxidated into nitrate ions NO<sub>3</sub><sup>-</sup> or nitric acid (HNO<sub>3</sub>) [42,79]; TiO<sub>2</sub> accelerates the chemical reactions without its consumption [49]. Table 5 presents information about the gas flow and exposure conditions used by the studied papers to assess the depolluting effect.

**Table 5.** Details on the gas flow and exposure conditions used for the depolluting effect assessment by the studied papers.

Paper	Gas Flow	Exposure Conditions
Khannyra et al. [50]	NO gas supply volume fraction ranging from 1136 ppb to 1188 ppb depending on the sample	UV-A light, irradiation intensity of 1 mW/cm <sup>2</sup> . Irradiation for 5 h
Pei et al. [11]	Gas mixture with a flow rate of 3 L/min and a NO concentration of 1 ppm	Two visible lamps, 420 nm, irradiation intensity of 10 W/m <sup>2</sup> . Irradiation for 12 h
Speziale et al. [54]	Initial NO concentration of 500 ppbv at a 3.0 L/min	UV-vis radiation. Illumination source: a 300 W lamp. Irradiation for 30 min
Hot et al. [15]	Initial NO concentration of 400 ppb after dilution with air	Two different UV light intensities: 20 W/m <sup>2</sup> and 5 W/m <sup>2</sup> . Irradiation for 10 min
Kim et al. [55]	1 ppm ± 0.015 ppm of NO gas at a flow rate of 3.0 L/min	UV light of 10 W/m <sup>2</sup> , 352 nm lamp. Irradiation for 5 h
Saeli et al. [24]	Inlet gas mixture prepared with synthetic air and NO <sub>x</sub> at a concentration of 0.2 ppm. Flow rate of 1 L/min	Solar lamp leading to light intensity of 3.6 W/m <sup>2</sup> in the UVA range and 25 W/m <sup>2</sup> in the visible-light range. Irradiation for 45 min
Pérez-Nicolás et al. [61]	500 ppb NO stream, 0.78 L/min flow	Two different lamps: 300 W for UV illumination, and 250 W for solar and visible irradiation, with intensities of 43.4 W/m <sup>2</sup> and 36.7 W/m <sup>2</sup> . Irradiation for 30 min
Hot et al. [62]	NO diluted to 400 ppb and flow rate constant at 1.5 L/min	Three illumination conditions: UV light at 1 W/m <sup>2</sup> , UV light at 3.3 W/m <sup>2</sup> , and visible light at 2.4 W/m <sup>2</sup> . Irradiation for 60 min
Mendoza et al. [63]	NO <sub>x</sub> concentration 0.55 ± 0.05 mg/L (0.4 mg/L NO + 0.15 mg/L NO <sub>2</sub> ) at a constant 1.5 L/min flow	300 W lamp (λ <sub>Max</sub> = 365 nm) that provides 20 W/m <sup>2</sup> of irradiance. Irradiation for 40 min
Bengtsson and Castellote [66]	Initial NO concentration: 1000 ppbv; initial NO <sub>2</sub> concentration: 50 ppbv	Irradiance 10 W/m <sup>2</sup> . Irradiation for 120 min
Martinez et al. [67]	Concentrations: 2.2 ppmV benzene, 9.5 ppmV toluene, 1.7 ppmV ethylbenzene, 1.7 ppmV o-xylene, 1.6 ppmV m-xylene, 1.6 ppmV p-xylene. Flow rate of 100 mL/min	18 W blacklight blue fluorescent tube. Light intensity of 6.0 W/m <sup>2</sup> . Conversion of VOC calculated for 24 h of UV irradiation
Guo et al. [21]	Flow of the testing gas: 1000 ppb NO. Rate of 3 L/min	UV intensity of 10 W/m <sup>2</sup> . Irradiation for 60 min
Martinez et al. [68]	Flow rate 1.5 L/min; initial NO concentrations: 400 ppb, 1000 ppb, 1500 ppb, 2000 ppb	300 W bulb with an emission spectrum close to that of daylight. Light intensity of 5.8 W/m <sup>2</sup> . Irradiation for 1 h
Bengtsson and Castellote [70]	Initial NO concentration of 1000 ppb. Flow rate of 5.2 L/min	UVA radiation at an optimum of 365 nm. Irradiation for 120 min

The characteristics of the mortar substrate may influence the depolluting of thin TiO<sub>2</sub>-based coatings. Saeli et al. [24], for example, reported that a layer with 5 wt% of TiHAp provided photocatalytic activity four times greater than with 1 wt% and even more significant than for the pure TiHAp powder (18.7% of NO<sub>x</sub> reduction after 45 min of the test), which might indicate a synergistic effect due to the high porosity of hydraulic lime mortars, enables a good spreading of the powder contained using the coating and, thus, an

increased contact area with the  $\text{NO}_x$  gas. According to Kim et al. [55], the porous surface of cementitious materials can contribute to the mass transfer of NO to the  $\text{TiO}_2$  surface, enhancing the removal rates. On the other hand, in lime mortars studied by Speziale et al. [54], coated with hydroalcoholic and superhydrophobic dispersions with 50/50 and 10/90  $\text{TiO}_2$ -ZnO nano-heterostructures, although the surface roughness should lead to increased activity, its high porosity possibly caused the absorption of active particles and, therefore, reduced the exposure of active photocatalysts to NO molecules and irradiation; optimized coatings also did not always increase the photocatalytic activity, probably due to the porosity of the substrate.

Depolluting reactions may also be influenced by the test conditions to which the samples are exposed. For Bengtsson and Castellote [70], catalyst load and light intensity were the most influential parameters on the reaction, compared with relative humidity, temperature, and contaminant concentration. Martinez et al. [68] observed that with initial NO concentrations of 400 ppb and 1000 ppb, the humidity did not significantly influence the degradation rates; however, degradation rates decreased with lower humidity values for NO concentrations of 1500 ppb and 2000 ppb. Water on the active sites at high humidity values probably did not limit the reactions; on the other hand, in low humidity conditions, a lack of oxygen-reactive species possibly affected the efficiency of NO degradation at higher pollutant concentrations [68].

Martinez et al. [67] investigated the influence of different humidity conditions on the catalytic oxidation of BTEX. Regarding an initial VOC concentration of 260 ppb, BTEX conversion reduced with increases in humidity, possibly because of competition between water vapour and pollutants at the adsorption sites of the photocatalysts. For an initial VOC concentration of 2600 ppb, the optimum humidity level was probably lower than 45%; however, oxidation rates increased with humidity below the optimum level, possibly due to the hydroxyl radical creation by dissociating the additional water under irradiation incidence [67]. Therefore, testing parameters may influence the results, and combinations among different proposed conditions, such as humidity and pollutant concentration, may also affect the observed final depolluting efficiency.

Still, regarding the NO degradation test concerning the dynamic of the experiment, Khannyra et al. [50] identified no photocatalytic activity in the absence of UV light since the photocatalytic sites were not activated. With UV-vis light irradiation, NO concentration decreased abruptly and, afterwards, remained stable through the 5 h of testing due to the complete activation of the photocatalytic sites. During this period,  $\text{NO}_2$  concentration was increased because of the reaction between NO and  $\text{O}_2$ . Even so, the total  $\text{NO}_x$  was removed stably [50]. The importance of proper definition and communication of the test conditions must be, thus, highlighted.

Concerning irradiance, Hot et al. [15], as expected, observed that NO degradation was higher under  $20 \text{ W/m}^2$  of UV lighting intensity than under  $5 \text{ W/m}^2$  due to the more extensive formation of electron-hole pairs. Considering the  $\text{TiO}_2$  obtained from waste resulting from chemical milling baths of the aeronautical industry, the maximum NO degradation was around 7%, lower than enabled using commercial products; some probable reasons are the micrometric size of the synthesized particles, resulting in fewer active sites, and the fact that more than 70% of the compounds in the powders obtained from waste were not  $\text{TiO}_2$ , but other unwanted phases [15].

Regarding the composition of the coatings, Bengtsson and Castellote [66] observed that the tested  $\text{TiO}_2$ -containing white paints and the S- $\text{TiO}_2$  solution were not photoactive. However, for the other studied catalysts, NO concentration after 120 min of irradiation was reduced from 1000 ppb to 39-175 ppb [66]. For Mendoza et al. [63], there were no significant differences in total  $\text{NO}_x$  conversion obtained with different  $\text{TiO}_2$ -based coatings applied on mortar samples; more than 53% of  $\text{NO}_x$  photodegradation was verified during the continuous flow test.

$\text{TiO}_2$  content is an important aspect influencing the results. Hot et al. [62] identified, among others, no relevant influence of  $\text{TiO}_2$  dry matter content superior to  $8 \text{ g/m}^2$  on

coatings applied on mortars, considering UV light exposure; NO degradation was considered efficient between 46% and 50%, suggesting an optimal content, above which the degradation did not improve significantly due to the absence of direct incidence of light over the photocatalyst and of contact with the pollutants. Under visible light, the same trend was observed by Hot et al. [62] but with a higher potential optimal content, 20 g/m<sup>2</sup>. For Kim et al. [55], NO removal increased with higher TiO<sub>2</sub> particle content, substantial up to a TiO<sub>2</sub>/MAP weight ratio of 4:1.

The dispersion of the photocatalyst over the mortar surfaces is fundamental to the efficiency of depolluting reactions. Agglomeration may negatively affect the TiO<sub>2</sub> photocatalytic efficiency by reducing available active sites [47]. Pérez-Nicolás et al. [61] proved the effectiveness of superplasticizers, especially polycarboxylate-based, to disperse photocatalysts and, thus, obtain high NO abatement percentages under UV light, even close to 50% (solar and visible light led to lower NO removal than UV). The polycarboxylate superplasticizers were responsible for an increase in NO abatement under UV light, on average, by 15%. Regarding solar irradiation, polycarboxylate superplasticizers led to an average of 76% higher values, especially considering air lime mortars and Fe-doped TiO<sub>2</sub>; NO removal under visible irradiation was also improved. Polynaphthalene sulfonate superplasticizer, on the other hand, caused agglomeration, leading to smaller NO<sub>x</sub> degradation values than the control coating [61]. In Speziale et al. [54], the addition of superplasticizers to the coatings also positively affected the photocatalytic activity expressed through NO<sub>x</sub> removal, in the majority of cases, except for samples with polyacrylate, which caused agglomeration; coatings with TiO<sub>2</sub>-ZnO 10/90 and superplasticizers led to the best-observed behaviour.

Doping of the TiO<sub>2</sub> may also influence depolluting efficiency. In Pérez-Nicolás et al. [61], doping enhanced the NO removal results. Under UV light, Fe-TiO<sub>2</sub> was, in general, more effective than V-TiO<sub>2</sub>; under visible light, bare TiO<sub>2</sub> still had a positive outcome because of the UV light fraction, but Fe-TiO<sub>2</sub> also led to more considerable NO degradation. In Khannyra et al. [50], the synthesized photocatalysts with nitrogen doping were less efficient than solely TiO<sub>2</sub> P25, which showed almost 39% NO conversion, compared to around 24% of SN10TiO<sub>2</sub>; up to 8 M (SN8TiO<sub>2</sub>) nitrogen doping did not cause a significant difference on the results. The lower photoactivity of the synthesized photocatalysts is possibly related to aggregation, affecting their distribution on the substrate's surface; in addition, their silica gel covering possibly prevented contact with light and the adsorption of NO on the photocatalytic surfaces [50].

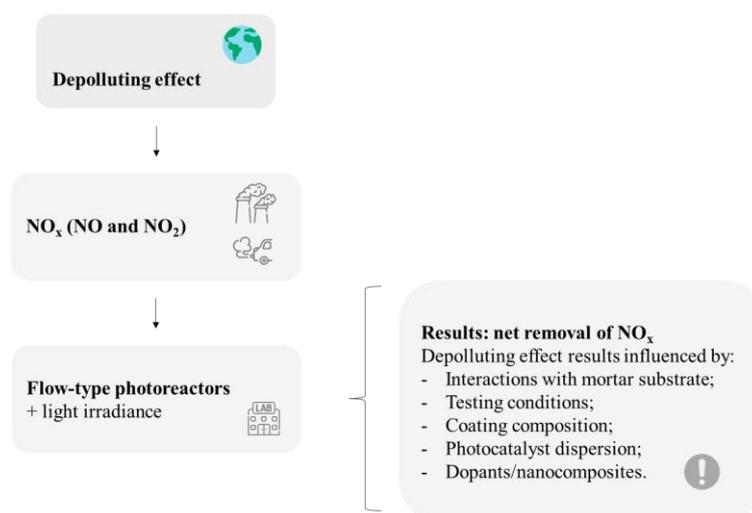
For cement mortars without coatings containing TiO<sub>2</sub> nanoparticles or graphene/TiO<sub>2</sub> nanocomposites, Pei et al. [11] verified almost no change in the total concentrations of NO and NO<sub>2</sub> throughout 12 h of visible light illumination. For 420 nm irradiation, a subtle reduction in the NO concentration and a low increase in the NO<sub>2</sub> concentration were verified for the TiO<sub>2</sub>-based coating, probably due to a portion of illumination belonging to the UV region; after almost 4 h, the NO concentration stabilized with nearly 5% of removal, being the photocatalyst deactivation probably due to the occupation of active sites with products like nitrite and nitrate. Mortars with graphene/TiO<sub>2</sub> nanocomposites coatings presented the most efficient NO removal rate, reaching 54.2%, with much later photocatalyst deactivation; thus, graphene incorporation enhanced photocatalytic activity with superior adsorption capacity [11]. Therefore, different dopant elements and synthesis parameters are decisive for depollutant reactions.

Among the studied papers, photocatalyst deactivation was observed or not in different situations. In Guo et al. [21], no catalyst deactivation was observed, different from Pei et al. [11]; TiO<sub>2</sub> dip-coated self-compacting glass mortars removed about 14 mg h<sup>-1</sup>m<sup>-2</sup> of NO and the two different dip-coating methods tested did not have a significant effect on the removal [21]. Martínez et al. [68] also did not identify photocatalyst deactivation since, although nitrate ions were formed over the mortar substrate, its large adsorption capacity limited or retarded the deactivation.

Relating to self-cleaning ability, it must be highlighted that, to preserve the desirable appearance of mortars in facades, the photocatalytic coatings must be able to remove pollu-

tants faster than their deposition rate [58]; additional strategies may be needed to obtain truly efficient air-purifying infrastructures, beyond the promising laboratory and pilot projects results [1]. Facades coated with white photocatalytic materials may, furthermore, assist in urban temperature control and even contribute to lower ozone formation during summer, considering the correlation between higher temperatures and smog [42]. Thin TiO<sub>2</sub>-based coatings for facades could act, in this context, as instruments in the pursuit of climate change control and global warming mitigation.

In general, the retrieved papers point to a coherent air-purification effect. Results on the depolluting effect provided using thin TiO<sub>2</sub>-based coatings applied on mortars depend on several features, as summarized in Figure 7. The influencing parameters are related to each particular study regarding surface characteristics, coating composition, and exposure conditions.



**Figure 7.** Main recurrent issues reviewed on the depollution effect of mortar samples with thin TiO<sub>2</sub>-based coatings. This figure has been designed using resources from Flaticon.com (Freepik, Tempo\_doloe, turkkub).

To mitigate comparison incompatibilities among the studied papers resulting from the main influencing parameters, the FQE was calculated relating to depolluting effect. Available information on the articles related to irradiation [W/m<sup>2</sup>], flow rates [L/min], NO concentration [ppm], NO removal [%], and samples' exposure area [m<sup>2</sup>] was used. The number of photons was estimated based on the wavelength of peak emission from the different lamps applied in the studies. When data were not available, assumptions were made based on the literature, namely for peak emission wavelengths [15,24,50,54,61,62,66,68], which were considered 340 nm for UV light [81], 365 nm for solar light [63], and 420 nm for visible light [11], and flow rates [15,50,66], which were assumed as 3 L/min [79,82]. Mean values were considered when the results for individual samples of the same composition were presented.

Figure 8 depicts the results obtained for the FQE. The highest photocatalytic efficiencies observed through NO degradation were obtained using commercial photocatalysts tested by Bengtsson and Castellote [66], followed by the samples studied by Martinez et al. [68], with increasing humidity contents. Samples tested by Hot et al. [62] under UV radiation with 1 W/m<sup>2</sup> also had high values among the studied papers, comparable to the majority of the samples studied by Guo et al. [21], Saeli et al. [24], and Kim et al. [55]. The lowest values were observed for the samples studied by Hot et al. [15] and Pérez-Nicolás et al. [61]. In Cortes et al. [44], FQEs for CO, CH<sub>4</sub>, and CO<sub>2</sub> are presented, calculated by dividing the moles of electrons passed to form products by the moles of photons; the results have the same order of magnitude as several obtained in the present review.



The FQE reinforces the caution that must be taken when comparing different studies with photocatalytic coatings and highlights, at the same time, the relevance of making parallels between research studies. A standard form of TiO<sub>2</sub> or a measuring parameter should be available so repeatability can be achieved [46].

#### 4.3. Antimicrobial Properties

The antimicrobial properties provided by TiO<sub>2</sub> within thin coatings applied on mortars may enable the reduction of the development of algae, fungi, and bacteria [1]. Table 6 presents the two experimental studies retrieved with the query string.

**Table 6.** Details on the microorganisms and methods used to investigate the antimicrobial properties provided by thin TiO<sub>2</sub>-based coatings in the studied papers.

Paper	Microorganism Studied	Method
Guo et al. [21]	<i>Escherichia coli</i> K12, a UV-resistant bacterium	Concentration of <i>E. coli</i> K12 of $\approx 1 \times 10^5$ colony forming units (CFU)/mL in sterilized 0.9% ( <i>w/v</i> ) sodium chloride solution. 1 mL of cell suspension applied with a pipette on mortar samples. Irradiation with UV lamps with 10 W/m <sup>2</sup> of intensity. After 20, 40, 60, 90, and 120 min of irradiation, collection of cell suspension by washing the sample with 20 mL of 0.9% sodium chloride. 100 $\mu$ L of diluted suspension spread on a nutrient agar plate and incubated. The examination of the viable count of the CFU indicated the loss of variability
Fonseca et al. [69]	Studies in situ encompassing two existing external walls already covered by organisms located in National Palace of Pena (Sintra, Portugal). One of the walls was directed to East-Northeast, did not receive direct sunlight, presented high humidity, and was widely colonized by lichenic and algal communities. The second wall faced East, received direct sunlight for most of the day and had a scattered presence of lichens	Photocatalytic coatings compared with conventional biocides (Biotin T applied using a brush at 2% ( <i>v/v</i> ), and Anios sprayed without dilution). Anatase aqueous solution applied on 50 cm <sup>2</sup> of the walls and compared with the biocides. Colour measurements and photograph records comparing the treated areas before and after two weeks of the suspension application used to evaluate the results

The results observed by Guo et al. [21] indicated that within 60 min of UV irradiation, *E. coli* was wholly inactivated on all the studied samples, regardless of the dip-coating method. At the beginning of the test, the photocatalytic inactivation rate was slower, and later, it was faster, resulting in two different stages: in the first step, a longer time was needed until the oxidative damage could destroy the cell wall and membrane, but afterwards, intracellular contents could flow out of the cells [21]. In Fonseca et al. [69], total colour variation indicated that the anatase suspension was the most efficient agent, with higher  $\Delta E^*$  than both biocides, especially Anios. The parameter L\*, regarding luminosity and shining of the surface, had the most significant increase for anatase if compared to the biocides due to the removal of dark organic matter; a\* also increased after applying anatase because of the elimination of photosynthetic microorganisms. After two weeks, almost all biological growth was removed from the walls [69]. Both studies, thus, suggest the efficiency of TiO<sub>2</sub> in suppressing microbial activity under appropriate exposure conditions.

Guo et al. [21] furthermore indicated that with the dip-coating method, photo-generated electrons and holes could react with oxygen and water and form highly reactive species much more efficiently than observed for TiO<sub>2</sub> intermixing techniques. It reinforces some advantages that may be obtained by using TiO<sub>2</sub> in thin coatings applied over the mortar surface. Additionally, the photoinduced hydrophilicity resulting from the coating possibly affects the bacteria inactivation [21].

To conclude, nanotechnology and preventive conservation potentially prevent the biodeterioration of building materials [69]. Some major topics to consolidate TiO<sub>2</sub> as an antimicrobial agent are improving action towards all fouling microorganisms and demonstrating its adequate durability [1]. Further studies are, therefore, needed to disseminate the photocatalyst use concerning its antimicrobial effect.

### 5. Durability of Thin TiO<sub>2</sub>-Based Coatings

Table 7 summarizes the properties evaluated using the experimental retrieved papers concerning durability issues for TiO<sub>2</sub>-based coatings applied on mortars, as well as an overview of the method used for ageing or assessing the results. Regarding the possible negative effects of coatings when exposed to adverse weathering conditions or aggressive environments [1], mainly adhesion and photocatalytic efficiency after ageing or deactivation were evaluated.

**Table 7.** Properties evaluated and method for ageing or assessing the results used by the papers to study durability-related issues for TiO<sub>2</sub>-based coatings.

Paper	Property	Method
Khannyra et al. [50]	Adhesion of the coating to the substrates	Peeling test by sticking a piece of adhesive tape on the surface and determining the increase of weight on the tape after its detachment
Pei et al. [11]	Photocatalyst regeneration after NO photodegradation	Deactivated graphene/TiO <sub>2</sub> nanocomposites exposed to UV irradiation in a continuous flow without NO under 50% RH for 0 h, 6 h, 12 h, 24 h, 36 h, and 48 h. NO removal rates of commercial TiO <sub>2</sub> assessed after 0 h, 6 h, and 12 h. The regeneration was evaluated using a subsequent photocatalysis experiment
Speziale et al. [54]	Photocatalytic activity (NO <sub>x</sub> abatement) and water repellence assessment (WCA) for optimized coatings	Exposure to accelerated climatic ageing. Cycles with changes in temperature, relative humidity, UV-vis irradiation, and rain periods. 25 min steps of: (1) 35 °C, UV-vis radiation, 40% RH; (2) 20 °C, 90% RH, rainwater; (3) 0 °C, 60% RH; (4) −5 °C, 50% RH. Steps continuously repeated for 3 days
Kim et al. [55]	Adhesion/bonding strength of the MAP-dispersed TiO <sub>2</sub> nanoparticle-coated film on substrates	Adhesion analyser (centrifugation technique)
Pondelak et al. [56]	Abrasion resistance and photocatalytic activity using RhB degradation	Exposure to rinsing (constant flow of tap water (250 mL/min) through a pipe system (nozzle diameter of 0.90 mm) for 30 min) and freezing–thawing cycles (50 cycles encompassing 5.5 h at 15 °C in water, followed by removal of the water and reduction of the temperature to −4 °C within 2 h; then, cooling of the substrates to −10 °C for 4 h. Lastly, the water was poured into the chamber again)
Saeli et al. [24]	Presence of the photocatalytically active layer on the surface and photocatalytic efficiency using NO <sub>x</sub> abatement	For the evaluation of the layer presence, exposure during 24 h in an ageing chamber at 35 °C, with aerosol of distilled water at 100% humidity, and test with X-ray diffraction (XRD). For NO <sub>x</sub> abatement, three repeated runs of the test, with no thermal or chemical regeneration treatment + test after two years of external exposure
Krishnan et al. [58]	Appearance changes	Field exposure for ~42 months in Singapore. Appearance changes monitored with L* and solar reflectance (SR) measurements
Rosales et al. [59]	Adhesion of the coating to the substrates	Grid of 1 mm × 1 mm with 11 cuts of 20 mm in length on the coated mortar. Scotch tape, three inches long, placed in the centre of the grid and soft pressed with an eraser. Removal of the tape from the opposite end of the application. Comparison with patterns. RhB removal assessed before and after adherence test (0 h, 4 h and 26 h)
Pérez-Nicolás et al. [61]	Photocatalytic activity using NO abatement	Accelerated climatic ageing. 7 cycles of 24 h, with varying conditions of temperature, relative humidity, rain, and UV light

Table 7. Cont.

Paper	Property	Method
Guo et al. [29]	Photocatalytic removal of RhB	Lab-simulated accelerated facade weathering, encompassing wet (1.5 L of tap water for 12 h) and dry (switching off the pumps for 12 h) conditions, and day (three UV-A and two visible lamps; UV-A intensity of $350 \pm 10 \text{ mW/cm}^2$ ) and night conditions (switching off the lamps). Weathering for one and two weeks
Rudic et al. [64]	Adhesion of the coating to the substrates	Two adhesion tests: one based on the standard tensile/pull-off method [83] and the other on modified test with semi-transparent pressure-sensitive tape [84]
Vulic et al. [65]	Photocatalytic activity, contact angle, surface roughness, and micro-hardness	Rain rinsing (constant tap water flow (250 mL/min) through a pipe system (nozzle diameter of 0.90 mm) for 30 min)
Krishnan et al. [25]	RhB degradation	5 cycles of 100 h, at the beginning of each RhB was applied. After each cycle, intermittent UV irradiation exposure (18 h UV and 6 h rest). Total duration of UV exposure of 2500 h, similar to at least 2.4 years on a tropical warm and humid condition
Guo et al. [21]	NO removal and antibacterial abilities	Three weathering conditions: normal weathering with no additional treatment; samples washed 10 times using 500 mL of deionized water to simulate rain; abrasive process with a wet cotton towel to scrape the surface with the TiO <sub>2</sub> layer (manually applied back and forth motion for 20 cycles)

Concerning adhesion properties, Khannyra et al. [50] reported that the application of surface treatments on mortars led to almost no removal of material from the substrate with a peeling test, while untreated samples lost  $6.57 \times 10^{-5} \text{ g/cm}^2$  of material, suggesting that the studied photocatalytic coatings could be durable for outdoor applications. Similarly, Rudic et al. [64] tested surface treatments which could preserve historical material's original properties since their application caused minor changes in the adhesion strength of the investigated porous render. Further than providing self-cleaning ability, depolluting, and antimicrobial effects, therefore, the usage of thin TiO<sub>2</sub>-based coatings with adequate compositions and durability might protect the underneath substrates.

Still, regarding the bonding strength, Kim et al. [55] identified  $6.7 \text{ N} \pm 2.1 \text{ N}$  for the studied coating applied over a cement-base substrate; it was lower than the adhesion for glass and stainless-steel substrates. However, no change in adhesion was identified after NO degradation tests, indicating that MAP could thus bind the TiO<sub>2</sub> to the substrate without deteriorating its photocatalytic performance. In Rosales et al. [59], 10% detachment was observed for SiO<sub>2</sub>@TiO<sub>2</sub> coated mortars; considering solely TiO<sub>2</sub>-based coatings, 40% detachment was observed, while for SiO<sub>2</sub>-containing only, the test indicated 5% detachment. In addition, after the adherence test, TiO<sub>2</sub>-based coating reduced its photocatalytic activity from 79% to 44% after 4 h of the test (R<sub>4</sub>) and from 92% to 70% after 26 h (R<sub>26</sub>). On the other hand, no difference was observed for SiO<sub>2</sub>@TiO<sub>2</sub> coatings, possibly reinforcing the SiO<sub>2</sub>@TiO<sub>2</sub> coatings' potential for air-purifying applications [59]. With the retrieved studies, it can be seen, thus, that improvements in the composition of the thin TiO<sub>2</sub>-based coatings may enhance their durability and long-term photocatalytic efficiency, indicating the importance of further studies to fill in the related knowledge gaps.

Weathering tests are essential to understanding the durability of TiO<sub>2</sub>-based coatings to be applied on mortars in facades since they will be exposed to climatic agents and, probably, to climate change. After weathering, Speziale et al. [54], for example, generally verified a significant loss of integrity in coatings applied over lime mortar, which caused a relevant decrease in the samples' hydrophobicity and affected NO<sub>x</sub> abatement results. On the other hand, also after ageing, Saeli et al. [24] verified, using XRD, that the photocatalytic active layer with 5 wt% TiHAp in water was still present on the surface of the studied specimens since the same species found before the ageing were identified; the photocatalytic coating could be, thus, resistant to washing and climatic conditions. Running three turns of the NO<sub>x</sub> abatement test over the TiHAp-coated mortars without any treatment for

regeneration, Saeli et al. [24] observed a slight decrease after the first cycle and an almost 20% reduction for the second cycle, which then stabilized. Different TiO<sub>2</sub>-based coatings, thus, can result in different durability conditions when subjected to ageing tests, possibly requiring specific studies.

In this context, in Guo et al. [29], regarding UV-A irradiation for RhB degradation, after weathering, the studied TiO<sub>2</sub>-based paint maintained a high efficiency, resulting in R<sub>4</sub> and R<sub>26</sub> of, respectively, 50.2% and 52.6%. The TiO<sub>2</sub>-P25 suspension, on the other hand, after one week of weathering, decreased from R<sub>4</sub> and R<sub>26</sub> of, respectively, 57.2% and 63.6% to 30.7% and 41.2%; after two weeks of weathering, the RhB removal capacity was further reduced to 25.5% and 41.7% because TiO<sub>2</sub> particles were removed from the coating. Considering the removal of RhB assessed through visible light exposure, TiO<sub>2</sub>-P25 did not have good photocatalytic activity, while the paint led to 40% and 51% removal after 4 and 26 h of testing [29].

Pérez-Nicolás et al. [61] observed that weathering worsened the NO degradation ability of the coated mortars due to washing with rain and UV light in a climatic chamber. However, durability was still considered good since moderate values of NO removal were obtained: 35% for cement mortars and 16% for air lime mortars. On average, cement mortars and air lime mortars without superplasticizers on the coatings had 33.8% and 35.2% of removal efficiency reduction, respectively; with superplasticizers, the decline was 35.2% and 16.4% [61]. Vulic et al. [65] also verified that rain rinsing caused some washing of the photocatalytic coatings over cement and pozzolanic mortars. However, at the beginning of UV irradiation for cement mortars, photocatalytic activity was higher than before the weathering, probably due to the presence of water; despite that, after some time, the washing-out effect became predominant and reduced the photocatalytic efficiency. The photoactivity of cement mortar was decreased by 10%, and of pozzolanic mortar, by 12.5%, which was considered a low decrease; both mortars showed an increase in the contact angle with water due to the washing out of the coating, which was coherent with the decrease in the photocatalytic activity [65]. It can be suggested, therefore, that even with some losses in photocatalytic efficiency after ageing, the coatings might still perform satisfactorily, depending on what is required for their long-term activity.

Moreover, Pondelak et al. [56], for example, did not identify reductions in photocatalytic degradation of RhB after rinsing, which suggests that the studied suspension may be suitable for application on mineral building materials. Moreover, a small and positive effect was found for the photocatalytic activity with freezing-thawing cycles, possibly related to a TiO<sub>2</sub>/LDH structure opening [56]. For Krishnan et al. [25], regarding coatings with silicate and TiO<sub>2</sub>, after three repeated RhB degradation cycles, the removal rate also increased, but, in this case, probably due to the degradation of organic additives from the silicate coating; after 2500 h of UV irradiation, the silicate coatings still had degradation of 95% at 26 h.

After the washing of the samples, Guo et al. [21] observed a reduction in the NO removal ability from 14.33 mg.h<sup>-1</sup>.m<sup>-2</sup> to 12.14 mg.h<sup>-1</sup>.m<sup>-2</sup> for dip-coated mortars with calcination and from 13.06 mg.h<sup>-1</sup>.m<sup>-2</sup> to 11.11 mg.h<sup>-1</sup>.m<sup>-2</sup> for dip-coated mortars with oven-drying; a similar effect was observed for bactericidal ability, with 90 min required to total inactivation. With abrasion, NO removal resulted in 8.75 mg.h<sup>-1</sup>.m<sup>-2</sup> for the mortar with coating calcination and 6.97 mg.h<sup>-1</sup>.m<sup>-2</sup> for the mortar with coating oven-drying, but no inactivation of *E. coli* was observed. The mortar porosity and rough texture were possibly positive to retain the TiO<sub>2</sub> coatings over the surface; however, the TiO<sub>2</sub> particles mainly responsible for bacteria inactivation were probably on the outer surface and removed during abrasion. TiO<sub>2</sub> particles in the pores of the mortars could still act as a bactericide but with lower efficiency [21]. Durability, thus, should be evaluated carefully, according to the activity expected from the coatings, since weathering could affect the depolluting effect differently from the antimicrobial performance, for example.

Concerning photocatalyst deactivation, Pei et al. [11] studied the regeneration of deactivated graphene/TiO<sub>2</sub> nanocomposites and found NO removal rates reaching 62.5%, 68.8%, 73.1%, 83.7%, 86.3%, and 89.7% of the initial rate after 6 h, 12h, 24 h, 36 h, and 48 h of UV irradiance, respectively, corresponding to 33.8%, 37.3%, 39.6%, 45.4%, 46.8%, and 48.6% of NO removal. Repeated cycles of 12-h UV treatments increased NO removal rates until three cycles, after which they became stable at around 41%. For commercial TiO<sub>2</sub>, the regeneration was less efficient than the graphene/TiO<sub>2</sub> nanocomposites, reaching 18.86%, 24.5%, and 30.2% of the initial removal rates [11]. Studies on the regeneration of photocatalyst activity may represent an opportunity for the long-term efficiency of TiO<sub>2</sub>-based coatings.

In field exposure, Krishnan et al. [58] did not observe significant appearance changes in panels without TiO<sub>2</sub>-based coatings after nine months; however, after 25 months, there was a relevant decrease in L\* from 72 to 67 and SR from 0.46 to 0.38, and after 3.5 years, 4 µg/cm<sup>2</sup> of black carbon equivalent was observed over the surfaces. A panel coated with silicate and 0.7% TiO<sub>2</sub> presented bleaching in the first month and, after 3.5 years, achieved satisfactory self-cleaning and depolluting results, removing around 16 g/m<sup>2</sup> of black carbon equivalent [58]. After two years of natural ageing, Saeli et al. [24] also observed a minor degradation of the depolluting activity of coated lime mortars, still resulting in an 18% NO<sub>x</sub> reduction. Monitoring samples exposed in the field might be considered of the utmost importance to confirm or, eventually, oppose conclusions from laboratory experiments and contribute to the extensive usage of thin TiO<sub>2</sub>-based coatings in facades to preserve their adequate performance.

Unfortunately, none of the articles retrieved for the durability of thin TiO<sub>2</sub>-based coatings for mortars on facades referred directly to the influence of climate change and global warming over their long-term performance. However, since effects on the longevity and resilience of building products are expected due to climate change [31], and weathering influences durability, studies on TiO<sub>2</sub> coatings considering prospects in the climate scenario represent an urgent gap to be fulfilled. To reinforce the consistency of this gap, an additional search was conducted in the Scopus database with the query string “photocatal\* and ((“titanium dioxide”) or TiO<sub>2</sub>) and durab\* and ((“clim\* chang\*”) or (“global warming”))”, regarding title, abstract, and keywords of journal papers in English. Only 1 document [85] was retrieved; however, it is not related to the construction sector.

Appropriate coatings should ensure stability and durability, further than protecting the underneath substrate and providing photocatalytic properties [42]. Durability investigations are fundamental, considering that, among others, to enable the large-scale application of photocatalytic technology, the deactivation of the photocatalysts [11] must be fully understood. Adherence and photocatalytic efficiency conditions may be improved through the coating composition, including doping or combined substances. Although many studies were found concerning the long-term performance of TiO<sub>2</sub>-based coatings, further research will be needed, mainly including field exposures and the climate change scenario.

## 6. Sustainability Potentials and Concerns

Since no specific results were found concerning sustainability for the primary question proposed for this review, potentials and concerns related to the life cycle of TiO<sub>2</sub>-coated products were raised in this section considering the broader search applied. In LCA studies related to sustainability for nanotechnology, there are several challenges in the obtainment of good results, including the definition of an adequate functional unit, the selection of inventory data, and the impact assessing factors, indicating that the problem may begin within the initial phases of the studies, in the goal and scope definition [33]. Among the retrieved papers, Fufa et al. [74], Babaizadeh and Hassan [34] and Hischer et al. [43] were published before the establishment of the Sustainable Development Goals by the member countries of the United Nations [6].

There needs to be more understanding of the long-term applications of nanoparticles regarding their benefits or, on the other hand, their toxic effects [71]. The availability of accurate information on nanoparticles' released amount is fundamental, as well as established rules determining how to consider this information on the inventory modelling and characterization factors for taking it into account effectively within the life cycle impact assessment, especially regarding toxicity potentials; however, the consideration of nanoparticles released through the life cycle, and their ecological relevance is often lacking in LCA studies [33]. For the experimental works assessed, Table 8 presents some main parameters regarding the LCA scopes, including impact assessment methods and the environmental impacts or damage categories considered; concerning data sources, only the databases used were referred to. Although all of the papers presented in Table 8 address at least one toxicity aspect, Tichá et al. [73] suggest a lack of internationally accepted characterization factors concerning, for example, human toxicity of nano-TiO<sub>2</sub> releases.

In Hischer et al. [33], one of the scenarios evaluated was the application of nano-TiO<sub>2</sub> in a separate coating over a traditional paint without modifications to the paint itself; after the end of the coating's life, only the outer layer should be replaced, and not the paint underneath. The functionality of the studied products must be accurately defined, indicating, for example, the amount of paint or coating saved [33]. This may be an interesting point to be considered when studying the application of TiO<sub>2</sub>-based coatings in facades.

For the self-cleaning glass studied by Pini et al. [72], a mild positive effect was observed regarding the reduction of airborne pollutants (toluene and NO<sub>x</sub>) in the use phase due to the nano-TiO<sub>2</sub> film. However, nano-TiO<sub>2</sub> adverse effects were primarily related to the release of particles, which may affect several impact categories. In the use phase, when particles are released into the air, they may affect human toxicity (cancer and non-cancer, indoor); when inhaled by humans in the end-of-life phase, they may impact carcinogens inhaled and human toxicity (cancer and non-cancer) [72]. In the work of Hischer et al. [33], most of the studied scenarios led to lower impacts for nano-paints or nano-coatings compared to traditional paints, except for those considered low lifetimes for the nanomaterial. However, among all the scenarios, ecotoxicity potential was identified as the most significant environmental impact. Human toxicity potential led to much lower variability than ecotoxicity; the release patterns of TiO<sub>2</sub> probably explain the difference since ecotoxicity potential considered emissions into water, while human toxicity regarded emissions into the air, which were from 3 to 4 times less significant [33]. The studies reinforce, thus, that toxicity aspects are critical when studying the sustainability of TiO<sub>2</sub>-based coatings.

According to Pini et al. [72], however, the positive effects of reducing emissions using the studied self-cleaning glass may offset the damages caused by nanoparticle releases if adequate eco-design choices are considered. Babaizadeh and Hassan [34] similarly investigated residential window manufacture and in-service life cycle phases when applied with a nano-TiO<sub>2</sub>-based coating. Positive effects were identified concerning the impact categories' acidification potential, eutrophication potential, air pollutants, and smog formation potential; however, the coating negatively affected global warming, fossil fuel depletion, water intake, human health, and ecological toxicity. The final result could be positive if an overall normalized performance were considered for the environment and air purification [34].

In Hischer et al. [43], nano-TiO<sub>2</sub> replaced part of pigment-grade TiO<sub>2</sub> in a paint system. The production of nano-TiO<sub>2</sub> was responsible for less than 10% of the total life cycle impacts, and the application of the paint in the facade and its end-of-life were even less significant; production of the pigment-grade TiO<sub>2</sub> and other substances were the main responsible for the total environmental impacts. Regarding ecotoxicity potential, the production of nano-TiO<sub>2</sub> or pigment-grade TiO<sub>2</sub> led to similar results. The presence of nano-TiO<sub>2</sub> in the paint allowed the repainting of the facade once less during the reference period of 80 years. There was high variability related to the knowledge of nanoparticle release during its lifetime, but this release could be even more relevant than the prolonged lifetime [43].

Tichá et al. [73] compared TiO<sub>2</sub>-based coatings with an air purifier, considering their ability to degrade microorganisms and pollutants from indoor spaces, and concluded, despite some standardization difficulties, that the photocatalytic option led to the best results. Similarly to Hischier et al. [43], Tichá et al. [73] suggested that the production method of the photocatalyst may have minimal influence when the whole life cycle of a TiO<sub>2</sub>-based coating application is considered.

From the studied papers, it can be observed, through the LCA tool, that there may be trade-offs between the positive effects of TiO<sub>2</sub>-based coatings and the environmental impacts related to the coatings materials and techniques, which can result, inclusively, in an overall negative impact due to the photocatalysts' usage. There is possibly a correspondence between nanoparticle release and longer lifetimes of TiO<sub>2</sub>-based surface coatings, which must be carefully considered to understand the offsets and final life cycle impacts. Fufa et al. [74], for example, suggested that if the main objective in using TiO<sub>2</sub>-based coatings is not the reduction of the period between maintenance interventions, nano-TiO<sub>2</sub> coatings may lead to higher final environmental impacts.

There are some differences between the conclusions among the papers, which reinforce the need for LCA studies directed specifically to TiO<sub>2</sub>-based coatings to be applied on mortars in facades. Knowledge related to the toxicity assessment of nanomaterials is still missing, suggesting the need for a database including information from toxicological tests and nanoparticle emissions [72]. Scientific gaps were pointed out concerning long-term emissions and impacts of the material when disposed of in landfills [43], research on by-products' effects, the long-term effectiveness of the technology and unknown harmful emissions during the life cycle [34]. Uncertainty considerations in LCA studies are also of fundamental importance [74]. Furthermore, although it does not refer directly to LCA, the work of Khitab et al. [49] concerns health and ecosystem problems that may arise from the usage of nano-TiO<sub>2</sub>; great care is recommended for its widespread application before the availability of reliable risk assessments.

Finally, regarding the economic performance of thin TiO<sub>2</sub>-based coatings, Babaizadeh and Hassan [34] applied the ASTM E917-05 method [86] for LCC and, for the interpretation, environmental and economic performance was grouped with Multi-Attribute Decision Analysis. For the functional unit, the prices were \$107.52 for the float glass and \$10.76 for 5.38 mL of nano-sized TiO<sub>2</sub>; a monthly average for 2011 was considered for the discount rate obtained from the U.S. Bureau of Labor Statistics [34]. Considering scenarios of different weights between environmental and economic performance, TiO<sub>2</sub>-coated glass presented a superior overall performance in most cases if compared with the standard float glass [34].

Since only one paper was found for the studied materials that included an economic performance evaluation, an evident gap can be highlighted. Further research needs to be published to enable comparisons and consolidate the knowledge on the cost-efficiency of TiO<sub>2</sub> coatings. The innovative character of building materials should be assessed, considering their life cycle costs. Moreover, as Babaizadeh and Hassan [34] suggested, with an increase in the incorporation of TiO<sub>2</sub> in construction, this photocatalyst may become more competitive in the market.

**Table 8.** Parameters regarding LCA scopes of the studied papers for sustainability evaluation.

Paper	Scenarios	Reference Study Period/ Functional Unit	LCA Software and Database	System Boundaries	Impact Assessment Method	Environmental Impact/Damage Categories Assessed
Hischier et al. [33]	180: 6 functionality options, 5 data sources for nano-TiO <sub>2</sub> production, 2 nanoparticles' release scenarios, 3 LCIA factors of the releases. Lifetime: traditional paint: 20 years; nano paint: 27 years (alternatives with 20% and 50% longer lifetime than traditional); nano coating: 15 years (alternatives with 10 and 20 years)	80 years/ 1 m <sup>2</sup> of wall, protected over a time period of 80 years	Software OpenLCA (version 1.4.2) and database Ecoinvent data v3.1, cut-off approach	Project-specific data for product stage (production of traditional paint, nano-TiO <sub>2</sub> , nano-paint, and nano-coating, where applicable), construction stage (1st and further application of paint/coating), use and end-of-life. Background system: production of further ingredients, and production and end-of-life of packaging materials	USEtox and ReCiPe	Global warming potential, fossil resource depletion potential, freshwater eutrophication potential, tropospheric acidification potential, freshwater ecotoxicity potential, human toxicity potential/ecosystem diversity, human health, resource availability
Pini et al. [72]	Uncoated flat glass (conventional material), nanoTiO <sub>2</sub> coated float glass (10 years or 30 years, obtained with two refunctionalization processes)	30 years/ 1 m <sup>2</sup> of nanoTiO <sub>2</sub> self-cleaning coated float glass	Software SimaPro 8 and databases included in the software (like Ecoinvent v2)	Supply of raw materials, packing, installation, and end-of-life; production, maintenance, and disposal of facilities; environmental burdens related to the production of chemicals, packaging, and auxiliary materials; emissions into air and water, solid waste; transportation of solid waste to a treatment facility	Modified IMPACT 2002+ v2.10 and USEtox method v1.03	Carcinogens, non-carcinogens, respiratory inorganics, ionizing radiation, ozone layer depletion, respiratory organics, aquatic ecotoxicity, terrestrial ecotoxicity, terrestrial acidification/nutritification, land occupation, aquatic acidification, aquatic eutrophication, global warming, non-renewable energy, mineral extraction, radioactive waste, carcinogens inhaled, human toxicity—cancer, human toxicity—non-cancer, ecotoxicity, human toxicity—cancer—indoor, human toxicity—non-cancer—indoor/human health, ecosystem quality, climate change, resources, radioactive waste, carcinogens inhaled

Table 8. Cont.

Paper	Scenarios	Reference Study Period/ Functional Unit	LCA Software and Database	System Boundaries	Impact Assessment Method	Environmental Impact/Damage Categories Assessed
Tichá et al. [73]	Application of photocatalytic coating to the ceiling (100 m <sup>2</sup> )—for the mechanical air purifier, a maximum input power of 110 W was chosen. 3 scenarios for lighting and power regime/period of operation	1 year/ Purification of 100 cubic meters of air in an enclosed space over a period of one year	Software SimaPro 8.0.4 and database Ecoinvent 3	Cradle-to-grave: from raw material acquisition through production, use, end-of-life treatment, recycling, and final disposal	CML-IA baseline V3.01/EU25	Abiotic depletion, abiotic depletion (fossil fuels), global warming (GWP100a), ozone layer depletion, human toxicity, freshwater aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, photochemical oxidation, acidification, eutrophication
Hischier et al. [43]	Substitution of nano-TiO <sub>2</sub> for parts of another active ingredient in the paint (pigment-grade TiO <sub>2</sub> )	80 years/ Protection of one square meter of (indoor or outdoor) wall during a period of 80 years	Software OpenLCA and database Ecoinvent v2.2	Foreground system: production of MNM and paint, 1st and further application of paint, use phase, end-of-life treatment (paint). Background: extraction resources, production of further ingredients, copolymer, filler materials, energy supply, production, and end-of-life packaging materials	ReCiPe method and USEtox model	Global warming potential, freshwater eutrophication potential, fossil fuel depletion potential, terrestrial acidification potential/ecotoxicity, human toxicity, ecosystem diversity, human health, resource availability
Babaizadeh and Hassan [34]	Comparison of titanium dioxide-coated glass with uncoated glass (float glass) with the same specifications	40 years/ One square meter of titanium dioxide-coated glass	-	Extracting and processing the raw data, manufacturing, use phase, and end-of-life for coated and uncoated windows	BEES 4.0 model	Global warming, acidification potential, eutrophication potential, fossil fuel depletion, indoor air quality, water intake, criteria air pollutants, human health, smog formation potential, ozone depletion potential, ecological toxicity
Fufa et al. [74]	Spruce coated with unmodified water-based paint and modified with 1 wt% nano-TiO <sub>2</sub>	50 years/ 0.01 m <sup>2</sup> coated exterior wooden cladding	-	Production, construction, use and maintenance, and demolition	ReCiPe	Global warming, human toxicity, photochemical oxidation formation, acidification, and eutrophication

## 7. Conclusions

This paper presents a literature review about thin TiO<sub>2</sub>-based coatings to be applied on mortars in facades concerning their photocatalytic efficiency, represented by the self-cleaning ability, depolluting effect, and antimicrobial properties, their durability, and an overview of life cycle sustainability. Even with no time boundary imposed for the search, all the studied papers were published after 2010.

Although the efficiency of photocatalytic TiO<sub>2</sub>-based coatings is generally reinforced, especially if compared to intermixing techniques, the studied papers suggest that an individual analysis is essential for each formulated composition. The investigation must also be particular to the specific properties of interest since the response of the same coating composition may differ under various contaminant, pollutant or microbial agents or even different exposure conditions. Doping agents, substrate properties, TiO<sub>2</sub> characteristics, and their dispersion in the coating also influence the results. Therefore, measuring parameters that allow comparison between different research on the same calculation basis may be essential. The discussion about NO degradation, based on the figure-of-merit formal quantum efficiency (FQE), might contribute to this purpose.

Among the research scopes, within the 34 papers answering the primary question proposed, “What are the efficiency, durability, and sustainability attributes of photocatalytic coatings with TiO<sub>2</sub> for mortars in facades?” self-cleaning performance was the most investigated topic in the literature, followed by depolluting effect and durability. The thin TiO<sub>2</sub>-based coatings were mainly applied by brushing, spraying, with a pipette, or by dip-coating.

Different dyes and contamination agents were used to study the self-cleaning behaviour of coated mortars, mainly methylene blue, rhodamine B, and black carbon; the results were usually assessed with CIELab colour space. The depollution effect was mainly investigated through NO<sub>x</sub> degradation in flow-type photoreactors with light irradiance; however, different exposure conditions were observed among the studied papers. Antimicrobial properties were the least characteristic tested on experimental works concerning coatings applied on mortars in facades; even so, TiO<sub>2</sub> was considered adequate for degrading bacterium and other organisms. For durability, the conclusions should be further compared and analysed and focus primarily on the resilience of TiO<sub>2</sub>-based coatings against climate changes and extreme events. Adhesion and photocatalytic efficiency after ageing or deactivation were the main focus of research related to long-term performance.

Regarding sustainability, since no results using Life Cycle Assessment (LCA) and Life Cycle Costing (LCC) tools were found for the first query string from this review, additional broad searches were required to identify coherent papers; however, the results were not necessarily related to facade mortars. For LCC, only one paper was retrieved. Different parameters were adopted within the scope of the LCA studies discussed; however, all the papers generally addressed at least one toxicity environmental impact. A clear gap was identified in this subject, which is reinforced considering the trade-offs between the advantages and disadvantages of TiO<sub>2</sub>-based coatings when environmental impacts are considered, pointing out the need for additional work in order to validate the innovative character of TiO<sub>2</sub> to be incorporated into building materials.

Further research is also especially needed to fully understand the performance over time of thin TiO<sub>2</sub>-based coatings for facade mortars and to increase its widespread application by the construction sector with more resilience under a changing climate. The potential of photocatalytic coatings is well documented, but realistic field studies and implementations would contribute to its maturity in the market; especially antimicrobial properties should be more thoroughly investigated. Regarding the current challenges related to climate change, human health, and environmental requirements, durability and sustainability studies are urgent to determine the photocatalytic activity's long-term performance and its impacts on the coatings' life cycle. Nanoparticle releases and emissions, toxicological effects, and end-of-life concerns should be addressed, aiming to obtain coatings with positive final impacts, and mitigate the drawbacks of these innovative solutions.

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