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Review

Selected Aspects Regarding the Restoration/Conservation of Traditional Wood and Masonry Building Materials: A Short Overview of the Last Decade Findings

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Abstract: Vernacular buildings are usually constructed using materials at hand, including wood, natural stone and bricks (either clay or mud bricks). All those materials are exposed to a series of environmental factors, affecting their structure and integrity. The literature review was conducted using different databases (Scopus, Web of Science, ScienceDirect, SpringerLink) using as keywords the historical material, "heritage" and the terms regarding the desired effect, within the envisaged time period (2010–2019). The assessment of the results was performed by manual inspection (reading the entire article) and the selection of the works to be inserted in the current review was made by evaluating the contribution to the field. This review summarizes different aspects related to the restoration and conservation of wooden and masonry elements of traditional buildings, including materials used for biocidal interventions, protection against abiotic factors, cleaning and consolidation agents. Finally, a critical discussion regarding the current limitations and future perspectives concludes the review work, envisaging the role of researchers specialized in materials science in the context of cultural heritage conservation.

Keywords: vernacular constructions; wood; stone; restoration; conservation

1. Introduction

Traditional buildings represent an important heritage of each civilization. These constructions are specific to each nation and region, considering a multitude of factors, including climate and availability of materials [1], without any one of them being decisive. Traditional buildings were usually constructed using the materials at hand, including wood, natural stone and bricks (either clay or mud bricks) [2,3]. All those materials are exposed to a series of environmental factors, affecting their structure and integrity. A good example of different construction materials can be observed in the Romanian traditional buildings (Figure 1) which are usually consisting of a mixture of wood and masonry (either mud or clay bricks and stones). As the traditional buildings are considered to be a proof of continuity of a civilization [4], great attention must be given to the development of appropriate materials for their restoration and conservation.

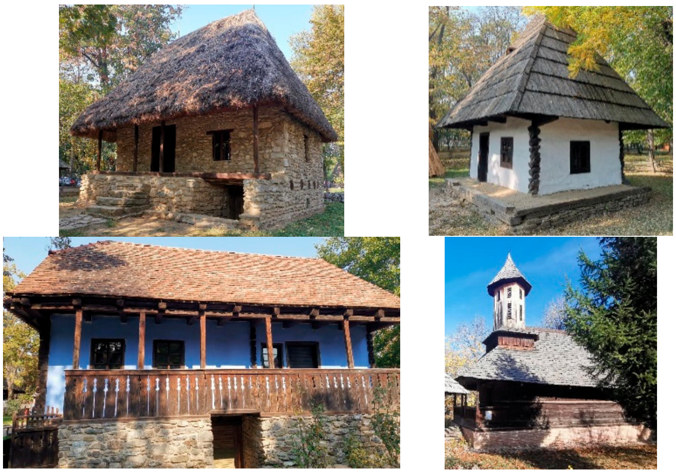

Figure 1. Examples of Romanian traditional buildings incorporating different construction materials (stone, bricks and wood)—pictures belonging to the authors' private collection.

Cultural heritage of a nation is formed not only of well-known monuments. Traditional houses and their construction methods represents an important legacy, which is transmitted from one generation to another, which was adapted to the times and needs, but permanently reflecting the environmental, cultural, technological, economic and historical conditions of the local context.

The present review focuses on the recent developments regarding the materials used for the restoration and conservation of traditional buildings (masonry, stone and wood) and represents a critical discussion of aspects related to their utilization; very useful in the transdisciplinary studies related to further development of new materials or for the use of the current ones.

The literature review was conducted using different databases (Scopus, Web of Science, ScienceDirect, SpringerLink) using as keywords the historical material ("wood", "masonry", "brick", "stone" "building", "mortar"), "heritage" and the terms regarding the desired effect ("restoration", "conservation", "biocid*" or "consolidation") within the envisaged time period (2010–2019). The assessment of the results was performed by manual inspection (reading the entire article) and the selection of the works to be inserted in the current review was made by evaluating the contribution to the field (the entire process is described in Figure 2).

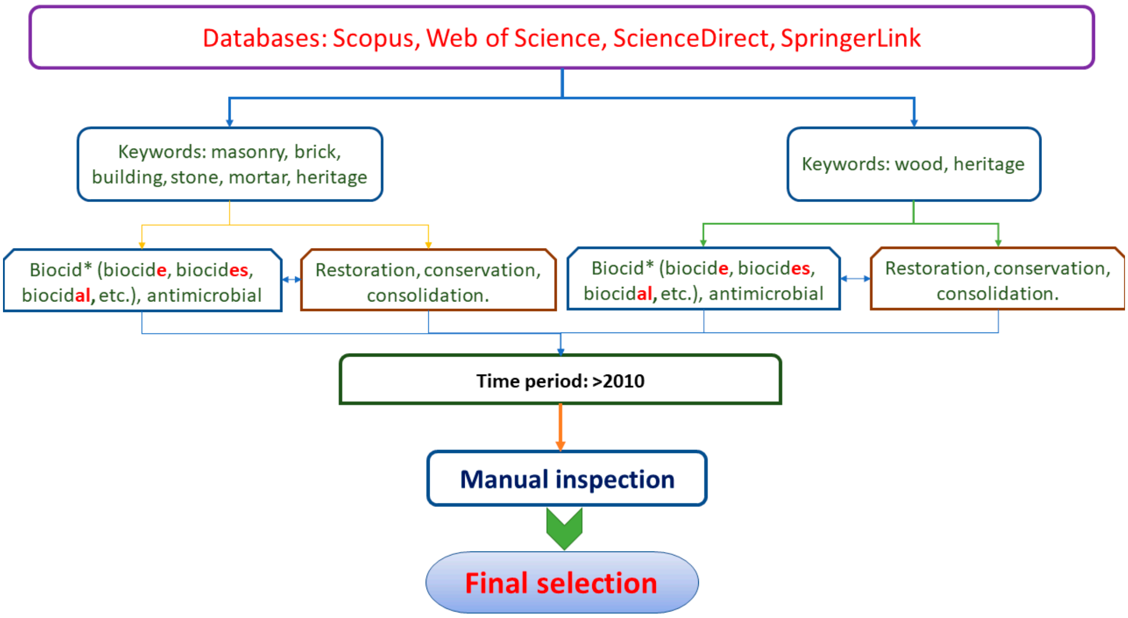

Figure 2. General procedure followed for the selection of articles to be included in the present review.

2. Materials Used for Restoration and Conservation of Wooden Elements

2.1. Biocidal Materials Used for Wooden Elements

Wood is considered to be one of the most common construction materials, with traditional buildings made of wood being encountered all over the world [5]. Due to its biodegradable nature, wood is exposed to a wide variety of biotic and abiotic agents, including fungi, insects, termites, moisture fluctuation or weathering [6]. Thus, the approach for restoration or conservation of the wood artifacts should comprise two aspects: the biocidal treatment and a chemical consolidation approach (Figure 3).

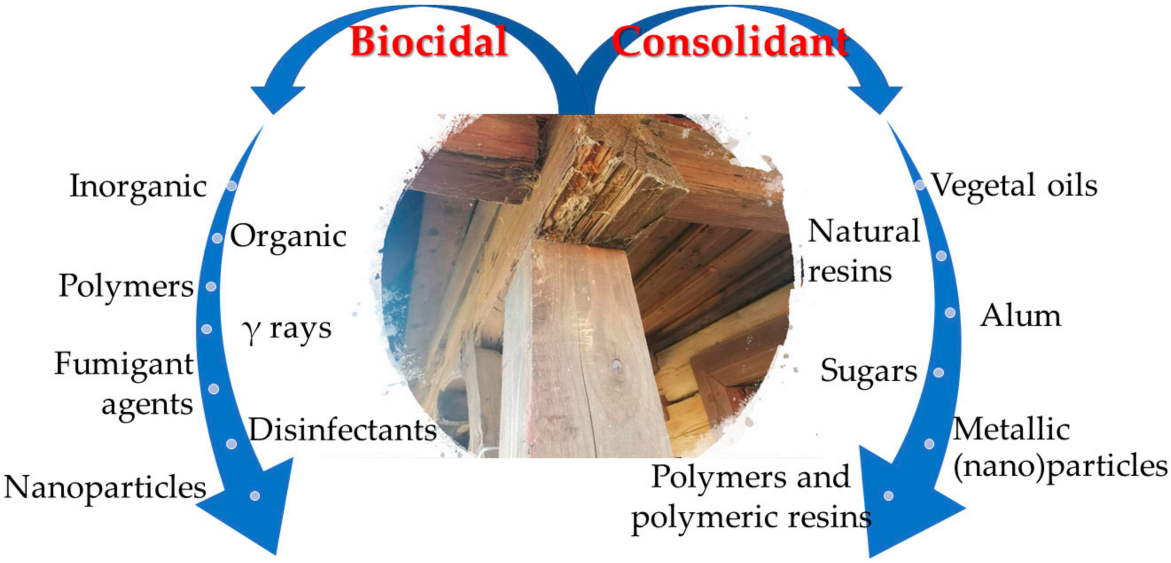

Figure 3. Aspects covered by the present review regarding the conservation and restoration of wooden building materials.

Another important biotic factor affecting all the objects belonging to the cultural heritage is represented by the human interventions. If we speak, either about interventions with negative effects (through the use of inappropriate materials or techniques), vandalism or about the lack of any intervention, these can be avoided only by increasing the awareness level, both at the level of the general population, as well as decision makers [7,8].

Wood itself can be categorized using different physical or chemical characteristics, one of the most important being the nature of the wood—softwood (gymnosperm trees—conifers, cycads, Ginkgo and gnetophytes) or hardwood (angiosperm trees) [9,10] and the conservation/restoration strategy should be adapted to its nature [11].

One of the most encountered problems in the preservation of wood artifacts is represented by its biodegradation. Unger [12] reviewed in 2012 the problems related to the historical use of inorganic (fluorides, fluorosilicates, metallic sulfates and chlorides, alkali arsenates or boron compounds) and organic biocides (chlorinated hydrocarbons, cyclodiene compounds, phenol derivatives, organometallic compounds or organophosphates), both on the artifacts themselves and to human health. The European standard EN 15003 [13] proposes the hot air methodology to eliminate fungal and insect attacks. However, the method cannot be always applied (considering the state of degradation and the characteristics of the materials). With the understanding of those negative effects, the search of new biocides represented an important research area in the last decades. In 2011, Clausi et al. [14] evaluated the antifungal effect (against white and brown rot fungi) of two widely used polymeric consolidants (Paraloid B72 and Regalrez 1126) applied on White poplar (*Populus alba*) and Norway spruce (*Picea abies* (L.) H. Karst). The authors observed that the application of individual consolidants led to different inhibition of the fungi (10% Paraloid being effective against white-rot fungus, while 5% Regalrez was effective against brown-rot fungus; the consolidant mixture inhibited both types of fungi). The results suggested that the combined application of the consolidants could slow the fungal growth in treated samples (behavior depended on wood species and treatment type); on the long-term, no treatment was proven to be effective in completely inhibiting fungal growth. Stejskal et al. [15] proposed the use of the fumigating agent hydrogen cyanide that proved to be effective against pinewood nematodes, Asian long-horned beetles and house longhorned beetles, important pests of the construction wood and historical buildings. The authors recorded a 100% mortality against the cerambycids (after 1-h exposure) and nematodes (after 18-h exposure), at a 20 g/m^3 concentration of fumigant agent. Although effective, the chemical compound was prohibited for use due to its high toxicity (together with another effective pesticide, methyl bromide) [16]. This led to the search of alternative chemical and non-chemical pesticidal agents.

Kozirόg et al. [17] evaluated several active ingredients against a series of bacteria and molds isolated from the historical wooden surfaces at the former Auschwitz II-Birkenau concentration and extermination camp. The authors noticed that the most promising active ingredients were didecyldimethylammonium chloride and *N*-(3-aminopropyl)-*N*-dodecylpropane-1,3-diamine. As a next step of the study, the effect of commercially available biocides based on those active ingredients, applied by spraying or fogging, were evaluated in terms of bacterial and fungal inhibition, the best results being obtained for Boramon and Rocima 101 (12 months effectiveness, respectively 3 months).

Goffredo et al. [18] evaluated the potential of inorganic nanoparticles (consisting of 1% TiO_2 nanoparticles solutions, supplemented with silver or copper nanoparticles, at concentrations of 0.60% and 3.15%) as antifungal agents against *Aspergillus niger*, applied on pine (*Pinus sylvestris* L.—softwood) and beech (*Fagus sylvatica* L.—hardwood). The best results were obtained for the solutions containing 3.15% metallic nanoparticles, without any significant visual alteration of the visual aspect of wooden surfaces.

Recent advances in the conservation of wood artifacts were recently reviewed by Walsh-Korb and Averous [19]. Thus, the current review will only aim to briefly present the common conservation approaches (Table 1), and to complete the cited work with the most recent developments.

2.2. Consolidants Used for Wooden Elements

Historically speaking, one of the first used consolidants were the vegetal oils (such as linseed or Tung oil) and natural resins (such as colophony) [19]. Having advantages such as being easy to obtain and apply, the main disadvantages (such as the aesthetic changes induced by the colophony, extensive drying periods of the linseed oil leading to wood structure softening or inhomogeneous film structure obtained using Tung oil) led to the search for alternative treatments [20–22]. A similar approach, is represented by the use of sugars or sugar alcohols, which, through controlled drying, give rise to crystals consolidating the material. However, development of large crystals could damage the wood materials; in the same time, sugars can be a very good source of nutrients for the development of microbial growth [23,24]. One of the first inorganic treatments of the historical wooden elements is represented by the use of potassium aluminum sulfate dodecahydrate, developed in the middle of the XIXth century. However, its major drawbacks (among which the acid degradation of cellulose is one of the most important) led to abandoning the treatment, but not the general use of inorganic consolidants [25]. More recently, several types of inorganic materials (including nanoparticles) were applied for the consolidation of wood materials. As some such types of particles also possesses antimicrobial properties, their application can also cover the biocidal need in restoration procedures [19,26–28].

With the development of polymer science, several polymeric materials or polymeric resins were successfully tested for the conservation of wood materials. Among those, several types of commercially available materials are currently applied in our days [29–34]. Finally, in recent years, the use of biobased materials (such as keratin, cellulose or chitosan) was supported by several literature studies [35–37].

Besides the materials previously presented, Cataldi et al. [38] proposed the addition of microcrystalline cellulose (5%–20%) into a UV-light curable methacrylic-siloxane resin formulation, with potential application as historical wood coating. The addition led to the increase of the dynamic moduli, flexure stiffness, and hydrophobicity, accompanied by a decrease of the thermal expansion coefficient, which suggest that the photo-curable micro-composites could be used to recover the mechanical and physical properties of damaged wood, being a good alternative to the traditional resins currently used.

Another interesting approach was presented by Moise et al. [39]. Using polyester acrylate styrene free resin and gamma curing, the authors observed the increase of thermal, chemical and photochemical stability. In the same time, the gamma curing offers the advantage of disinfection of the material. However, great attention must be payed upon gamma treatment, as the ionizing radiation can damage the cellulose structure [40]. Additionally, considering the radioprotection issues, the method cannot be usually applied for in situ interventions [19].

In our opinion, the previously described materials present advantages such as slowing the fungal growth in treated samples, in situ application (for most of the proposed solutions), recovery of damaged properties of wooden materials, etc. The main disadvantage of the current approaches is represented by the lack of long-term protection (the need for repeating the treatment). Additionally, the future research should be focused on the development of multi-phase treatments, which could adapt to environmental changes in real-time, besides offering a protection for multiple degradation causes [19].

Table 1. Classic and modern conservation agents for wood artifacts (references presented in chronological order).

Procedure	Agent	Characteristics	Application Method	Ref.
Inhibition of fungal growth	Paraloid B72 and Regalrez 1126	Slowing of fungal growth in treated samples; short-term effect	Surface application	[14]
Consolidant	Vegetable oil (linseed, Tung), natural resins (colophony)	Water repellent, crack-filling, non-toxic, easy to obtain and apply	Surface application	[20–22]
Consolidant	Polymers and polymeric resins (melamine- or urea-formaldehyde, Paraloid B72, Regalrez 1162, Poly(ethylene glycol), Acrylic resins, Silanes, Epoxy resins)	Wide-spread treatments, easy to apply, good stability; last generation treatments (acrylic or epoxy resins) although have better properties, require vacuum application	Surface application, immersion	[29–34]
Consolidant	Sugars and sugar alcohols (sucrose, lactilol, trehalose)	Reversible, non-toxic, increase stability upon crystallization of sugars	Immersion of the wood artifacts	[23,24]
Consolidant	Inorganic particles (calcium hydroxide, magnesium hydroxide, titanium dioxide, alkaline carbonate)	Ability to neutralize acids within the wood (in some cases even continuous deacidification), reduce cellulose hydrolysis; some have biocidal action	Spraying, surface applications	[26–28]
Consolidant	Biobased solutions (keratin, cellulose, chitosan)	Natural resource, easy to apply, good compatibility; can undergo the same degradation issues as the wood	Immersion	[35–37]
Biocidal	didecyldimethylammonium chloride, *N*-(3-aminopropyl)-*N*-dodecylpropane-1,3-diamine, hydrogen peroxide, glutaraldehyde, sodium hypochlorite, boric acid, lactic acid	Sprayable 30% Boramon and 8% Rocima 101 effectively protected the wood against bacterial growth for 12 months; and molds for 3 months	Spraying, fogging	[17]
Consolidant	Methacrylic-siloxane resin and microcrystalline cellulose	Increase of the dynamic moduli, systematic decrease of the thermal expansion coefficient, increase of the flexure stiffness, increase hydrophobicity	Surface application (coating)	[38]
Consolidant	Alum	Naturally occurring, can cause acidic depolymerization of cellulose	Immersion	[25]
Antifungal	Inorganic nanoparticles (TiO_2 suspension, containing silver or copper nanoparticles)	The highest antifungal efficiency was observed for suspensions containing highest level of metallic nanoparticles	Brushing	[18]
Disinfection, consolidant	Polyester acrylate and polyester resin dissolved in styrene, by gamma curing	Changes in thermal, chemical and photochemical stability	Immersion, gamma curing	[39]

3. Materials Used for Restoration and Conservation of Masonry Elements

3.1. General Considerations

Alongside wood, masonry materials (such as natural stones, fired or unfired bricks) represent the basis of traditional constructions. The use of natural stones involves the application of several types of rocks, such as the intrusive, volcanic, sedimentary or metamorphic rocks. A classification of the natural rocks used in traditional constructions is presented in Table 2, together with their compositional characteristics.

Man-made materials can be divided into cob (subsoil, water, straws and lime), adobe (mud and organic materials), mud-bricks (sun-dried materials, composing of loam, mud, sand, water and straws), fired bricks (sometimes called "artificial stones") and mortars (different composition workable paste binding the construction materials). In the following paragraphs, the materials used for restoration and conservation of masonry elements are presented, classified into biocidal materials, cleaning agents, consolidants and protective coatings. (Figure 4).

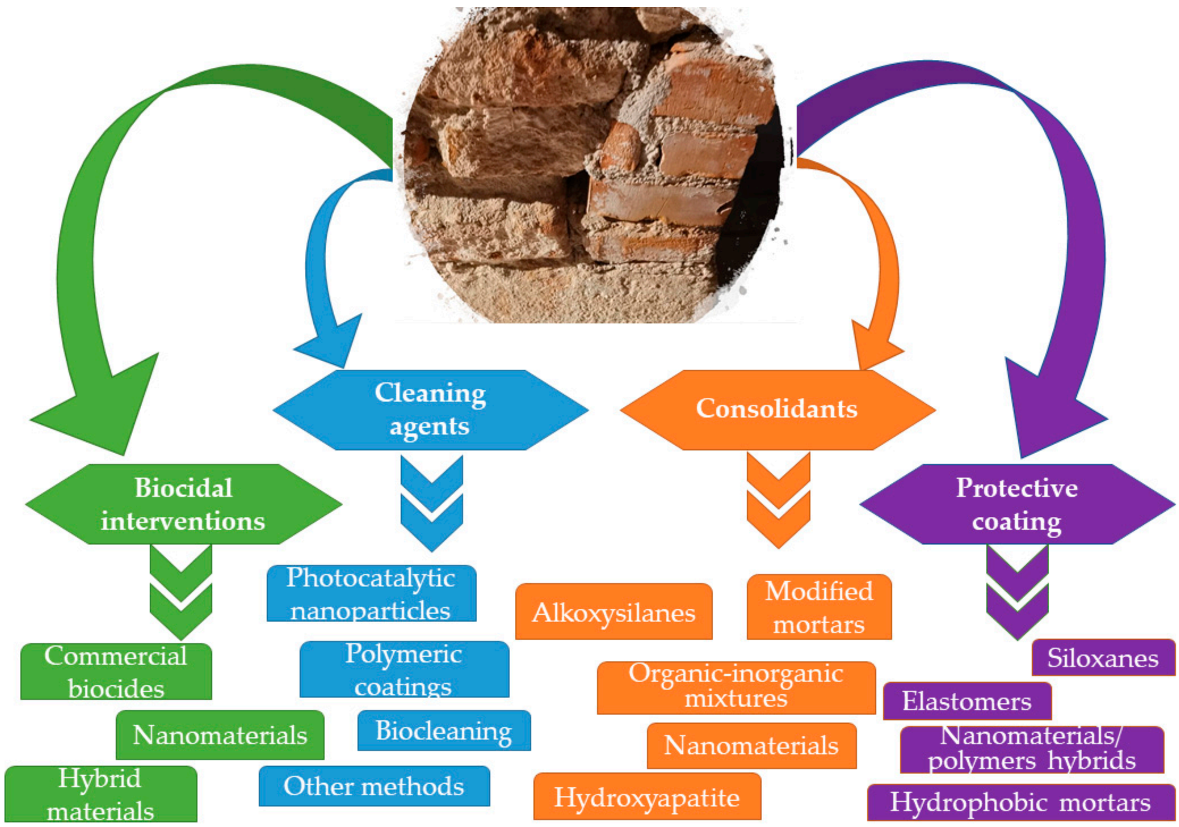

Figure 4. Aspects covered by the present review regarding the conservation and restoration of stone building materials.

Table 2. Characteristics of natural rocks used in vernacular constructions.

Class	Type	Examples	Composition	Characteristics and Uses	Ref.
Intrusive rocks	Felsic	Granite	Quartz (20%–60%), felspars, mica; ratio Plagioclase/(Plagioclase + Alkali feldspar) = 10–65	Granular, phaneritic, massive, hard and tough. Average density 2.65 and 2.75 g/cm^3, compressive strength >200 MPa; used for the construction of pyramids, lumns, door lintels, sills, wall coverings; mostly used as size stone	[41]
	Intermediate	Diorite	Plagioclase feldspar, biotite, hornblende, pyroxene	Phaneritic, occasionally porphyritic, extremely hard, usually used for sculptures, roads, drainage or inscriptions	[42]
	Mafic	Gabbro	Plagioclase and clinopyroxene	Used as ornamental facing or paving stones	[43]
	Ultramafic	Peridotite	Olivine and pyroxene	Coarse-grained, dense, uncommon at the surface, unstable, rarely used	[44]
Extrusive rocks	Felsic	Rhyolite	Quartz (>20%), alkali feldspar (>35%)	Very viscous; used as building, facing or paving stone.	[44]
	Intermediate	Andesite	Plagioclase, pyroxene, hornblende	Porphyritic structure, density 2.11–2.36 g/cm^3, used as filling material, for sculptures or monuments	[45]
	Mafic	Basalt	Pyroxene (augite), plagioclase, olivine	Aphanitic, the most encountered volcanic rock, used as building blocks, cobblestones, for statues	[46]
	Ultramafic	Komatiite	Olivine, pyroxene, anorthite, chromite	Spinifex texture, rare, not usually used for traditional construction	[47]
Sedimentary rocks	Clastic	Sandstone	Quartz or feldspar	Grain size, 0.06–2 mm, variable hardness and color; versatile uses (dependent on the composition)—construction, decoration	[48, 49]
	Biochemical	Limestone	Calcite and aragonite	Variable grain size and texture, hard; used for buildings, decorations or mortars	[50]
	Chemical	Gypsum	Calcium sulfate dihydrate	Variable color and luster, Mohs hardness 2, specific gravity 2.31–2.33; used for plasters, decorations	[51]
Metamorphic rocks		Marble	Calcite or dolomite	Usually white, medium grained, hard, relatively abundant; used for buildings, decorations, sculptures or flooring	[52]

3.2. Biocidal Interventions

3.2.1. Classical Approaches

The biodeterioration of masonry materials can be divided into three main categories, considering the microorganisms involved: deterioration caused by bacteria, by fungi or by lichen [53]. Table 3 presents some examples of biodeterioration induced by different organisms in masonry materials.

Table 3. Biodeterioration of masonry materials (selected examples).

Support Material	Site	Biodeteriogens	Effect	Ref.
Adobe	Capayán ruins (Argentina)	*Centris muralis* Burmeister bee	Massive erosion, high density of cavities	[54]
Limestone and lime stucco	Maya constructions (Mexico)	Fungi, cyanobacteria	Dissolution and recrystallization of calcite, physical breakdown	[55]
Limestone and lime mortar	San Roque church, (Mexico)	Cyanobacteria and Bryophyta	Apparition of dark green to black biofilms after restoration	[56]
Sandstone	La Galea Fortress (Spain)	*Trentepohlia* algae	Reddish biofilm, material disintegration, erosion, discoloration	[57]
Limestone	Chaalis Abbey (France)	Alphaproteobacteria, Actinobacteria, Cyanobacteria, Bacteroidetes, Betaproteobacteria, Deinococcus, Acidobacteria, etc.	Biocorrosion, discoloration, detachment of mineral grains, salt crystallization	[58]
Mortar	Casa Godoy (Porto Alegre, Brazil)	Fungal species: *A. niger*; *T. atroviride*; *T. harzianum*; *Trichoderma* sp.; *C. sphaerospermum*; *Cladosporium* sp.; *Lecanicillium* sp.; *Penicillium oxalicum*; and *Purpureocillium lilacinum*	Chemical alterations in mortar substrates, physical damages due to the growth of filamentous structures	[59]
Tuff and limestone blocks, mortar and plasters, frescoes	Casa della caccia antica (Pompeii, Italy)	Twenty-two lichen species (the most encountered being *Dirina massiliensis*, *Verrucaria macrostoma* and *Lepraria lobificans*)	Physical or chemical interaction with the substrate: hyphal penetration, expansion and contraction of thalli, secretion of metabolites with acidic and chelating functions endolithic growth of other lithobiotic microorganisms	[60]

The literature is much more focused on the identification of the microorganisms affecting the masonry materials than the proposal of new alternative treatments. As there are no substances particularly developed for cultural heritage, the biocidal substances used were typically those developed for other applications (such as commercially available pesticides, based on active ingredients as glyphosate, benzalkonium chloride, *N*-octyl-isothiazolinone, usnic acid, etc.) [61] or natural materials, such as natural extracts and essential oils [62,63] or lipopeptides [64].

Another potential approach is represented by the physical decontamination methods (such as the mechanical cleaning, the use of ionizing or UV-radiation) [65]. These latter methods possess a series of disadvantages (the mechanical cleaning could damage the substrata, UV and gamma radiation can induce color changes). However, with the identification of the potential hazard to human health and to the environment of those methods, the need for dedicated pesticides became evident. Among the first solutions proposed were the natural alternatives (plant extracts, essential oils, etc.), their use being recently reviewed by Fidanza and Caneva [66]; although the approach has some advantages (such as the good efficiency, or a potential eco-friendly character), in our opinion, the lack of supplementary data, regarding the interaction with the material itself, as well as regarding the behavior over longer period of times, makes the solution of natural biocides inapplicable at this time in the field of cultural heritage.

3.2.2. Nanotechnological Approaches

Considering the shortcomings of the classical methods, a viable alternative is represented by the application of nanotechnology. Nowadays, nanotechnology emerged as a research field with successful application in the cultural heritage domain. As our group previously presented [67], the application of nanotechnology for the development of antimicrobial coatings represents an emerging field, which could offer valuable resources for specialists in restoration/conservation. In spite of the wide-spread use of nanomaterials, their application as biocidal agents in cultural heritage stone conservation represents the subject of a surprisingly low number of articles (details presented in Table 4).

Usually, the use of nanomaterials in the field of antimicrobial protection of stone artifacts harvests the known potential of some metallic or metal oxide nanoparticles (such as silver, a wide known antimicrobial, ZnO, TiO_2, CuO, Cu, etc.) [68–72]. Among those examples, the hydrophobic film developed by Ruffolo et al. [68], incorporating a photocatalytic agent (TiO_2) and an antimicrobial agent (Ag), showed very good antifouling properties for application on underwater marble artifacts. The procedure also proved to be reversible, after 20 months no trace of protective film being identified, suggesting a repetition of the treatment every 12–24 months. With a similar approach, Becerra et al. [73] used silver nanoparticles and Ag/TiO_2 nanocomposites as antimicrobial agents on limestone. By using two different synthesis procedures for silver nanoparticles—AgNPs (citrate and sodium borohydride reduction), the authors observed a direct correlation between the antimicrobial effect of the silver nanoparticles/silver nanocomposites and the hydrodynamic diameter. More than that, the AgNPs and Ag/TiO_2 nanocomposites obtained by the citrate method led to superior results regarding the biofouling reduction, even compared with a commercial biocide (>70%, compared with 53% for Biotin T) without significantly altering the aesthetic properties of the limestone (particularly AgNPs). The silver nanoparticles alone were also proven to be an efficient antimicrobial agent against bacteria and fungi developed on different materials (stucco, calcite and basalt), inhibiting the colonization of the stones (0.16%–3.6% colonization, compared with the untreated samples—8%–28% colonization, depending on the material) [74]. The authors observed a dependency on the AgNPs dose, and less on the NPs size (as is the case for the in vitro antimicrobial properties of the nanoparticles) [75,76].

Another potential application of the nanotechnology is represented by the use of nanocapsules or nanoparticles for the controlled release of the biocidal agents. For example, Dresler et al. [77] proposed the use of pristine and functionalized silica (with amino or carboxylic groups) for the controlled release of the widely used biocides New Des 50 and Biotin T. The authors tested the efficiency of the proposed material both in vitro (against Gram-positive and Gram-negative bacteria—*Kokuria rhizophila*, *Staphylococcus aureus* and *Escherichia coli*). The proposed materials were tested by immersing in the solution a stone fragment (not defined) from a fountain located in Diamantina, Minas-Gerais, Brazil. The long-term effect was evaluated by determining the total viable bacterial counts after 1, 6 and 12 months (registering a 98.4% inhibition in bacterial counts after 12 months, compared with an untreated sample). This approach seems to be the most successful for future research works, as it harvests the nanotechnological advantages, together with the proven biocidal effect of commercial products. More than that, the method could be applied for the incorporation and controlled release of other types of biocides (such as, for example, the essential oils), which, without such delivery vehicles, hardly finds application in cultural heritage conservation. Another important aspect related to the potential use of nanoparticles is related to their potential harmful effects. The toxicity of nanoparticles represents to this date a subject of research. However, considering the relatively low levels necessary for the achievement of biocidal effect, the nanomaterials can be considered relatively safe for use [78]. In our opinion, future studies presenting the application of nanomaterials in the cultural heritage area should be accompanied by thorough toxicological studies.

Table 4. Nanomaterials applied as biocidal agents in cultural heritage conservation (references presented in chronological order).

Nanomaterial	Nanomaterial Characteristics	Application	Treated Material	Ref.
Functionalized carbon nanofibers and nanotubes	80–150 nm/1.2–1.4 nm diameter, commercially available	Surface treatment (removal of black and gray patina), finishing cleaning method	Marble	[79]
$Ca(OH)_2$ mixed with ZnO/TiO_2	500/10–30/<50 nm	Antimicrobial (against *Penicillium oxalicum* and *Aspergillus niger*)	Limestone	[80]
Ag nanopowder/ silane/siloxane emulsions	<100 nm, PVP coated, commercially available	Surface treatment emulsion for facades (against algae and cyanobacteria biofouling	Mortar	[81]
TiO_2/SiO_2 nanocomposites	Theoretical proposal, no studies performed	Preventing biodeterioration	Mortar	[56]
Ag nanoparticles	Phytosynthesized, 39 to >100 nm	Surface treatment (against *Pectobacterium carotovorum* and *Alternaria alternate*)	Stucco (pozzolanic material), calcite and basalt	[74]
TiO_2	4 nm, commercially available	Surface treatment (antifouling, against *Chlorella* cf. *mirabilis* Andreeva and *Chroococcidiopsis fissurarum*)	Fired bricks	[82]
TiO_2, TiO_2/Ag, TiO_2/Cu nanoparticles	TiO_2 – 40–50 nm	Surface treatment, spraying in three layers (against different algal species)	Travertine	[83]
TiO_2, ZnO and Ag nanoparticles dispersed in melted siloxane wax	Particles mean diameter 100 nm, commercially available	Antifouling agent for underwater stone materials (against epilitic and endolithic micro-organisms)	Marble	[68]
Pristine and functionalized silica (MCM41)	Commercially available	Controlled release of commercially available biocides New Des 50 and Biotin T.	Stone	[77]
ZnO and Ag nanoparticles	30/25 nm, commercially available	Dip-coated mortar disks (against *B. cereus* and *E. coli*)	Mortar	[71]
Si nanocapsules	148 nm	Controlled release of an eco-friendly biocidal agent for antifouling coatings	Proposed for cultural heritage applications	[84]
Si nanocapsules and nanoparticles	128/39 nm, with entrapped active ingredient	Controlled release of a commercial biocidal agent	Proposed for cultural heritage applications	[85]
Ag nanoparticles and Ag/TiO_2 nanocomposites	36/72/94 nm hydrodynamic diameter, depending on the synthesis pathway	Surface treatment (against multiple Chlorophyta and cyanobacteria)	Limestone	[72]

3.3. Restoration/Conservation of Masonry Materials against Abiotic Factors

3.3.1. Deterioration of Masonry Materials by Abiotic Factors—General Considerations

The alteration of stone (either natural or man-made) is mainly related to two types of abiotic factors [86,87]:

- Intrinsic characteristics of the materials:
    - Chemical and mineralogical composition (species solubility and their variation, presence of oxidable species, surface and ionic phenomena);
    - Structure and texture (mainly the pore distribution, resulting in gelifraction and salt crystallization resistance, water absorption and drying rates).
- Extrinsic factors:
    - Water presence;
    - Presence of foreign substances altering the pH or the composition;
    - Pressure and wind;
    - Thermal variations;
    - Anthropogenic abiotic factors (mainly related to pollution products).

The water (in all its forms—solid, liquid or vapors) represents one of the most important factors affecting the integrity of stones: it can interact with the substrate (dissolution, hydrolysis, oxidation-reduction), it can transport other substances (for example sulfates or other pollutants), it represents a medium for chemical reaction (and for the development of microorganisms) or (in case of temperature variation) can produce microcracks in the materials (in its solid form). Closely related to the presence of water, the soluble salts can damage the materials through two pathways (crystallization and hydration).

The main types of damages induced in stone materials are (as classified by the International Council on Monuments and Sites—ICOMOS [87]):

- Cracks (including fracture, star cracks, hair cracks, craquele and splitting) and deformation;
- Detachment (blistering, bursting and delamination);
- Material loss (alveolization, erosion, mechanical damage);
- Discoloration and deposits (crusts, coloration, bleaching, staining, efflorescence and encrustation).

The processes necessary for preserving damaged stone materials usually involves three steps [86]:

- Cleaning, often performed mechanically or with dedicated gentle solutions;
- Consolidation (in order to increase the resistance of the material);
- Protection (generally focused on the use of water repellant solutions, as water represents one of the main factors involved in the degradation, as previously presented).

Some classical and modern materials used for these applications are presented in Table 5, while some representative examples are detailed in the following paragraphs.

3.3.2. Cleaning Agents

Cleaning of stone artifacts is usually performed by mechanical (brushing, projection) [88] or chemical methods (using different solvents, such as methylene, acetone, acids, alkali or even commercial mixtures) [89,90]. More recently, the use of lasers was proposed for a wide variety of stone types (marble, sandstone, etc.) [91]. Removal of biofilms is usually performed using the same techniques, followed by a biocidal treatment (presented in Section 3.1). Regardless of the chosen technique, great care should be paid to not provoke damages to the original material; the processes should be gradual, selective and economically feasible [92].

Among the new materials used for cleaning purposes, the most encountered are the TiO_2 nanoparticles, which, due to their photocatalytic properties, can be used in self-cleaning protective layers. For example, La Russa et al. [93] proposed the use of this property of anatase-form nanoTiO_2 by incorporation in three types of commercial coatings (acrylic polymer in organic solvent—Paraloid B72, fluorinated polymer in an alcoholic solvent—Akeogard P, compared with a commercial aqueous suspension of TiO_2 and an acrylic polymer—Fosbuild). The poorest results were obtained for the material using the nanoparticles/Paraloid composition (intense alteration of the surface, poor photo-degradation effect), while the best results were obtained for the commercial formulation (Fosbuild). The composition based on fluorinated polymers also led to good results, with significant photo-degradation and water repellency. A similar approach was adopted by Quagliarini et al. [94], combining the hydrophilic and photocatalytic photo-induced properties of the nanoparticles into a coating that decreased the water adsorption by 50%. Other examples regarding the use of nano-TiO_2 as self-cleaning materials are provided in Table 5.

A particular and very important area of cleaning procedures is dedicated to the graffiti removing methods. This can be achieved by chemical or mechanical methods, laser cleaning [92] or biocleaning (using, for example, sulfate-reducing bacteria or enzymes) [95]. A preventive action (protective) is represented by the anti-graffiti coatings, based on organic or inorganic agents (either temporary—waxes, silicones, or permanent—polyurethanes, fluorocarbon, alkyl alkoxy silanes) [96].

3.3.3. Consolidation and Protection Agents

Consolidation represents the treatment applied in order to restore its mechanical properties, affected by weathering [86]. At the border between cleaning and consolidation, desalinization is often necessary; the removal of soluble salts is usually made by applying wet poultices consisting of clays or cellulosic mixtures [97,98], the alternative treatments proposed being represented by the application of ohmic technologies [99] and electrochemical methods [98], limewater (calcium hydroxide solution [100], crystallization modifiers (ferrocyanides, borax, etc. [101,102], or diammonium hydrogenphosphate [103].

As it emerges from the literature review, most of the authors treat the desalinization process as a secondary process (accompanying the main consolidation procedure), thus usually the traditional, well-established procedure being followed. This, in turn, leaves serious room for improving, by the development of new materials.

At this time, on the market are available a wide range of both organic and inorganic consolidants [104,105] with proven efficiency in consolidating different types of masonry materials. The stone consolidants can be divided in three main classes: (i) organic products (alkoxysilanes, recently reviewed by Xu et al. [106]); (ii) organic-inorganic mixtures and (iii) purely inorganic products (usually apatitic materials), relevant examples being provided in Table 5.

A good example regarding the application of organic products for the consolidation of stone materials is represented by the study of Liu and Liu [107]. The authors proposed the use of a composite polymeric material (tetraethoxysilane with additives as hydroxyl-terminated polydimethylsiloxane and cetyl trimethyl ammonium bromide) for the consolidation of sandstone. After treatment, the sandstone showed crack-free surface homogeneity, acid resistance, as well as salt crystallization resistance, the polymeric layer also exhibiting very good hydrophobic properties (demonstrated by a water contact angle of 110°). Generally speaking, the organic products (as well as many of the organic/inorganic composites) used as consolidants also possess very good hydrophobicity, which also makes them very good protective compounds. A particularly interesting study was recently published by Kapridaki et al. [108]. In a three-layer treatment, the authors offered a complex conservation solution for stone monuments, incorporating a self-cleaning (based on TiO_2 nanoparticles), consolidation (based on calcium oxalate nanoparticles) and a protective hydrophobic layer. The approach was successfully applied on different types of masonry materials (limestones of different porosity, ceramic materials and mortars).

The use of in situ formed hydroxyapatite represents a very good alternative to other methods. It is achieved by the reaction of a phosphate salt and the substrate (marble, limestone, sandstone, sulfated stone, gypsum stucco, concrete, etc.). The topic was recently reviewed by Sassoni [109], so a very thorough presentation of the method would be redundant. We have chosen to discuss only a modification of the method, proposed by Pesce et al. [110]. The in situ formation of a hydroxyapatite consolidating layer was achieved using aqueous solution of diammonium phosphate and two types of calcium nanosuspensions, calcium hydroxide and calcite (calcium carbonate), on limestone and sandstone. The authors observed an improvement of the compactness of the stones, accompanied by a risk of incompatibility (proven by the substantial reduction of water sorption, especially for sandstone). The authors also proposed the effective order of reactants deposition on the stone (the phosphate followed by the calcium source) and drew attention to a possible drawback of the method, respectively an elevated risk of yellowing on the surface. A particular approach was developed by our group, regarding the application of synthesized hydroxyapatite and apatitic materials, especially for the protection of limestone, but also for antimicrobial purposes [111–114]. However, due to the significant color changes recorded, the optimization of these recipes still represents a subject for future research.

The incorporation of basalt fibers (chopped fibers, continuous filaments or milled fibers) into mortars (prepared using natural hydraulic lime, dry premix and inert aggregates, respectively dry premix and inert aggregates with crushed bricks and tiles—*cocciopesto*) was proposed by Santarelli et al. [115]. The authors observed that the fibers addition increased the compressive properties of the mortars, while the chopped fibers imparted post-peak stress of the hydraulic lime mortar. For all the proposed materials, was also observed a decrease in the capillary water adsorption coefficient. Similar approaches were published by Moropoulou et al. [116] (using several pozzolanic additives), Andrejkovičová et al. [117] (using palygorskite and metakaolin), Ventolà et al. [118] (using commercial phase changing materials), Rosato et al. [119] (using commercial cellulose nano-fibrils), Gour et al. [120] (using natural polymers) or Pavlík et al. [121] (using crushed lava granulates). However, regarding the reconstruction/consolidation mortars, the best approach, in our opinion, is the one presented by Stefanidou et al. [122], respectively designing the mortars according to the nature of the natural stone (in the cases presented by the authors marl limestone, nummulitic limestone, marble, biogenic calcitic sandstones), and as, often as possible, reclaiming local materials.

A particular case is represented by the earth (unfired) masonry materials (such as earth-blocks—cob, adobe, mud-bricks or mud mortars). In those cases, considering the limited viability of the materials, the best approach is their replacement/grouting with materials as similar as possible, or, at least, compatible [123,124].

As already stated, many of the polymeric composites previously presented possess hydrophobic properties, thus having a protective role for the masonry materials. The usually applied conservation materials are primarily represented by siloxanes [125] and elastomers [126], with proven efficiency over a large variety of masonry materials. More interesting, the use of hybrid nanomaterial/polymeric coatings was proposed by some authors. Corcione et al. [127] proposed a mixture containing commercially available micrometric hydroxyapatite and multiple polymeric components (trimethylolpropane trimethacrylate, trimethoxypropyl silane methacrylate monomer, vinyl terminated polydimethylsiloxane and 3-mercaptopropyltriethoxysilane). The mixture was applied by brushing on two calcarenitic stones, with different porosity and photo-cured by UV-lamp. The coatings led to a surface hydrophobic character of the treated material (demonstrated by the contact angle—129°–136°, depending on hydroxyapatite amount, compared with the untreated sample—96°). Considering the hydrophobicity results and the observed color changes, the authors proposed an upper limit of 5% hydroxyapatite filler for future applications. Cappelletti et al. [128] incorporated nano-titania in a commercial silane resin (Alpha®® SI30). The hybrid mixture was airbrushed on the surface of different types of stones (marble, dolomite), obtaining superior values of hydrophobicity, compared with the pure commercial product. In the case of marble, was even achieved a superhydrophobicity character (contact angle > 150°). The same approach was used by Aslanidou et al. [129]. Using commercially available silica nanoparticles dispersed in commercial alkoxy silanes and organic fluoropolymer emulsion obtained superhydrophobic and superoleophobic coatings, successfully applied for the protection of masonry (marble, sandstone) and other materials (concrete, paper, silk), proving a good versatility of the method. The use of hydrophobic components (such as calcium stearate or silane/stearate) was also proposed Falchi et al. [130] as a viable alternative in order to develop restoration mortars with hydrophobic properties (thus, protection action). The authors introduced the water-repellent admixtures into pozzolana lime-mortar (0.5%–1.5%), obtaining materials with reduced water vapor permeability, without significantly affecting the mechanical properties of the mortar.

When developing functional coatings for masonry materials, particular attention should be payed to the possible formation of a coating surface which could seal in potential degradation agents and interfere with normal wet/dry cycle [70,131].

Table 5. Materials for the treatment of stones used in the vernacular constructions (references presented in chronological order).

Procedure (Effect)	Material	Characteristics and Application	Stone Type	Ref.
Cleaning	TiO_2 nanoparticles	18 nm, aqueous solution, applied by spraying	Travertine	[132]
	TiO_2 nanoparticles	10–20 nm obtained by sol-gel and hydrothermal method, applied by spray coating	Travertine	[94]
	TiO_2/poly(carbonate urethane) nanocomposite	31 nm, commercially available, aqueous dispersion; with associated protective role	-	[133]
	TiO_2 nanoparticles	Commercially available nanoparticles (25 nm), incorporated in different commercial coatings	Marble, calcarenite	[93]
	TiO_2 nanoparticles	5–6 nm, dispersed in water and ethylene glycol, applied by brush	Marble, calcarenite	[134]
	TiO_2 nanoparticles	Commercially available nanoparticles (30 nm), incorporated in different mortars	Lime-, cement- and lime/cement-based mortars	[135]
	TiO_2—tetraethoxysilane-polydimethylsiloxane	25 nm, commercially available, applied by brush	Modica Stone (limestone)	[136]
	TiO_2 nanoparticles	10–40 nm, commercially available, aqueous solution, applied by spraying	Sandstone, concrete slabs	[137]
	TiO_2 nanoparticles	External layer in a multi-purpose solution, with oxalic acid in the interface with environment; surface application, by brush	biomicritic limestone, travertine, calcitic sandstone, ceramic materials, mortars	[108]
Consolidation	Different inorganic additives	Earth of Milos, brick powder, crushed brick, used as pozzolanic additives for lime mortars	Mortar	[116]
	Inorganic additives	Palygorskite and metakaolin, used as pozzolanic additives for lime mortars	Mortar	[117]
	Organic additive	Commercial product (consisting of n-heptadecane core and polymethyl-methacrylate shell, PCM DS 5001 Micronal®®), incorporated in lime mortar	Mortar	[118]
	Basalt fibers	Incorporation in different composition for development of restoration mortars	Mortar	[115]

Table 5. *Cont.*

Procedure (Effect)	Material	Characteristics and Application	Stone Type	Ref.
Consolidation	Silicic acid esters (tetraethyl orthosilicate, dioctyltin dilaurate)	Polymeric coating, commercially available (Tegovakon®® V100), surface application (by brush/drop-by-drop)	Bioclastic calcarenite, chert	[104]
	Ethyl silicate hybrid binder (hydrolyzate)	Polymeric coating, commercially available (Wacker®® Tes 40 WN), surface application (by brush/drop-by-drop)	Bioclastic calcarenite, chert	[105]
	Nano SiO_2	Nanoparticles suspension (<20 nm), commercially available (NanoEstel), surface application (by brush/drop-by-drop)	Bioclastic calcarenite, chert	[104,105]
	Nano $Ca(OH)_2$	Nanoparticles suspension in isopropyl alcohol (Nanorestore®®), surface application (by brush/drop-by-drop)	Bioclastic calcarenite, chert	[104]
	Polymeric composite	Tetraethoxysilane having as additives hydroxyl-terminated polydimethylsiloxane and cetyl trimethyl ammonium bromide; application by immersion	Sandstone	[107]
	SiO_2/polymer	13.5–24 nm, SiO_2 pristine/hydrophobized (methylated or octylated), incorporated in ethoxysilanes mixture; surface application, by pipetting	Sandstone	[138]
	Hydroxyapatite (formed in situ)	Using diammonium phosphate; application by brushing and immersion	Limestone	[100]
	$Ca(OH)_2$	Water solution, limewater poultice for desalinization	Limestone	[100]
	Acrylic resin	Polymeric coating, commercially available (Paraloid®® B72), surface application (drop-by-drop)	Chert	[139]
	Cellulose fibers	Nano-fibrils, commercially available, incorporated in lime mortar	Mortar	[119]
	$Ca(OH)_2$/polymer	7–15 nm, amorphous calcium hydroxide monohydrate nanoparticles incorporated in tetraethoxysilane; first layer in in a multi-purpose solution; surface application, by brush	biomicritic limestone, travertine, calcitic sandstone, ceramic materials, mortars	[108]
	Natural polymer	Areca nut (natural polymer) incorporated in lime mortar	Mortar	[120]
	Diammonium hydrogenphosphate	Water solution, with cellulose pulp, poultice for desalinization	Limestone	[103]
	$Ca(OH)_2$	Commercially available (CaLoSiL®® E25), known as nanolime; surface application (by syringe) to saturation of the sample	Clunch, ooidal limestones (Bath, Barnack, Portland), coarse-grained shelly limestone (Ham), magnesian limestone	[140]

Table 5. *Cont.*

Procedure (Effect)	Material	Characteristics and Application	Stone Type	Ref.
Consolidation	TiO_2 and alkoxysilane	Tetraethyl-orthosilicate and alkyl-trialkoxysilane doped with synthesized (5–40 nm method not disclosed); application by capillary suction	Limestone, sandstone	[141]
	Hydroxyapatite (formed *in situ*)	Using two types of nanomaterials—$Ca(OH)_2$ and $CaCO_3$, and diammonium phosphate; application by capillary suction	Limestone, sandstone	[110]
	Crushed lava granulates	Used as sand replacement in hydrated lime, natural hydraulic lime, or cement-lime binder	Mortar	[111]
	Ternary composition	Commercial SiO_2 nanoparticles (25 nm), $Ca(OH)_2$ nanoparticles (200 nm), hydroxypropyl cellulose, in hydroalcoholic desertion; immersion treatment	Adobe	[124]
Protection	Organosilicons	Long chain polymerized siloxane, short chain polymerized siloxane, alkyl potassium silicate; surface application	Sandstone, dolomite, marble, granite	[125]
	Hydroxyapatite/siloxane-methacrylic formulations	Commercial micrometric hydroxyapatite added in siloxane-modified mixture; application by brush followed by photo-curing	Calcarenitic stones	[127]
	Stearate/silane	Incorporation of calcium stearate and silane/stearate (Silres A®®) in pozzolana-lime binders	Mortar	[130]
	Nano TiO_2/silane resin	TiO_2 nanoparticles solution mixed in a commercial silane resin (Alpha®® SI30); application by airbrush	Marble, dolomite	[128]
	Polymer hybrid coating	Trimethylpropane trimethylacrylate, trimethoxypropyl silane methacrylate, poly(dimethylsiloxane)-terminated vinyl, alkoxy-silane, bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide, 2-hydroxy-2-methyl-1-phenyl-1-propanone; applied by brushing	Calcarenitic stone	[142]
	Neat and nanomodified coatings	Protective coatings (linseed oil, silane/siloxane, alkosiloxane) neat or with silica nanoparticles (14 nm); applied by full immersion on fired bricks	Fired bricks	[143]
	Boehmite/polymers	Incorporation of organic-modified boehmite mineral in a series of commercially available protective coatings; application by brushing	Calcarenitic stones	[144]

Table 5. *Cont.*

Procedure (Effect)	Material	Characteristics and Application	Stone Type	Ref.
Protection	Oligoamides	Partially fluorinated oligoadipamide, ethylenediamide and hexamethylenediamide, solutions in propanol; adsorption into the stone materials.	Limestone, marble	[126]
	Silanes	Tetraethoxysilane/polydimethylsiloxane composite, intermediate layer in in a multi-purpose solution; surface application, by brush	biomicritic limestone, travertine, calcitic sandstone, ceramic materials, mortars	[108]
	Poly(hydroxyalkanoate)s	Poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate co-4-hydroxyvalerate), compared with silane and siloxane commercial formulations—Idrosil®® and Antipluviol®®; applied by dip-coating, poultice, spray.	Sandstone, limestone, marble	[145]
	Siloxanes	Oligomeric ethoxysilane, hydroxyl-terminated polydimethylsiloxane in aqueous n-octylamine solution (original solution proposed by the authors), compared with the commercial product BS290 (Wacker); application by spraying	Limestone	[146]
	SiO_2/polymer	Commercially available SiO_2 nanoparticles (7 nm) dispersed in commercially available emulsion of alkoxy silanes and organic fluoropolymer (Silres BS29A); applied by spraying	Marble, sandstone, concrete	[129]

4. Current Limitations and Future Perspectives

The main goal regarding cultural heritage objects is their preservation (conservation). Restoration appears often necessary, but should always be the subject of professional restorer's decision. As any restorer knows, all the recipes used for the restoration/conservation of cultural heritage objects should meet several critical conditions, among which two are of particular interest: the reversible character of the treatment and authenticity preservation [147]. The specialists working in this area find significant differences between clearly defined terms used (such as *protection*, *preservation*, *conservation*, *consolidation*, *restoration*, *reconstruction* or *anastylosis*) [147]. These terms are not, at this moment, thoroughly integrated in the vocabulary of the researchers working in the field of materials science (from which comes the large majority of the solutions presented in the current review). This represents a sign of a major (and probably the most important) drawback of the current approach, worldwide. Most researchers perform laboratory (or even in situ) experiments without the assistance (or collaboration) from a conservative/restorer. Although with scientific value for sure, this approach could lead to possibly insignificant results for the restorers. The main goal of materials science researchers should be, in our opinion, to provide the necessary tools and the scientific support for the specialists that have the authority and the knowledge to practically perform the interventions on the cultural heritage objects. Thus, closer collaboration should be established between the two types of scientists, as well as the development of a common criteria preferences regarding the materials/treatments, as some studies pointed out the major differences regarding the selection of materials for the protection of heritage objects [148].

Additionally, as a general remark, the wide spread of nanomaterials in their pure state (without incorporation in polymeric matrixes) can, in some instances, violate the reversibility criteria. This could, on the other hand, be explained by its relative wide criticism from conservationists, that consider it a "dubious principle", "chimera", "myth" or "Utopian idea" [149].

From the point of view of materials science, it appears surprising the lack of original materials, implemented at least at laboratory level. As researchers could obtain nanoparticles or nanomaterials (such as, for example, TiO_2, SiO_2, hydroxyapatite, etc.) with the desired morphological characteristics, they should use such synthesized materials instead of commercially available ones. There are a large number of metallic or metal oxide nanoparticles that could exhibit photocatalytic activity (for self-cleaning purposes) or antimicrobial properties. Additionally, the exploration of antimicrobial properties of phytosynthesized nanoparticles could offer new recipes with potential application in this area [78]. The same observations can be made regarding the use of hydroxyapatite/other apatitic materials (which could be tuned for multiple applications). These materials could be incorporated in polymeric films, in order to ensure the previously-stated reversible character.

Especially when talking about materials for cultural heritage buildings, the treatments should also meet some supplementary criteria (easy and deep penetration, resistant to attack, prevention of humidity penetration, allowing exiting of water, no modification alteration, uniform contraction and expansion with the substrate, inexpensive, non-corrosive, non-reactive, lasting properties, easily applicable, resistance to acid and alkaline attack, etc.) [150], which should be all presented by the authors reporting the evaluation of new materials.

Another important aspect for the restoration/conservation of traditional buildings is represented by the engineering assessment of the construction, including the differentiation between the structural and the decorative materials, which opens different treatment routes. For example, in the case of structural materials, the recovery of the material's functionality is mandatory, while for decorative materials, is only necessary the maintaining of their integrity [3,113,151]. If this is not possible, the natural stones can be replaced with natural stones with the same characteristics, or with cast stones, designed to replicate the natural ones [152].

Finally, the current developments in the materials science field in general allows us to envisage a continuous increase of the quality and properties of the materials offered to the specialists working as conservatives of the cultural heritage objects.

5. Conclusions

The present review paper summarizes different aspects related to the recent progress in the field of restoration/conservation of traditional building materials (wooden and masonry elements), including materials used for biocidal interventions, restoration/conservation of materials against abiotic factors, cleaning agents and consolidation and protection agents. This critical review can be considered a starting point for further transdisciplinary studies and experiments, with application in the cultural heritage domain. In this respect, new perspectives have emerged and development of new materials and methods based on classical restoration/conservation approaches will lead to preserving cultural heritage for future generations.

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