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Current and future chemical treatments to fight biodeterioration of outdoor building materials and associated biofilms: moving away from ecotoxic and towards efficient, sustainable solutions

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1 **Current and future chemical treatments to fight biodeterioration of outdoor**
2 **building materials and associated biofilms: moving away from ecotoxic and**
3 **towards efficient, sustainable solutions.**

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15

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18

Abbreviations

AHL: acyl-homoserine lactone – AOP: advanced oxidation process – ATMAC: alkyl trimethylammonium compounds – BAC: benzalkonium chloride – BIT: 1,2-benzisothiazol-3(2H)-one – BPR: Biocidal Products Regulation – CMC: critical micelle concentrations – CMIT: 5- 5-chloro-2-methyl-2H-isothiazol-3-one – DB: benzalkonium bromide – DCOIT: 4,5-dichloro-2-octyl-2H-isothiazol-3-one – DDMAC: didecyldimethylammonium chloride – DMSO: dimethyl sulfoxide – ECHA: European Chemicals Agency – ENT: eye nose throat – EO: essential oil – EU: European Union – FDA: Food and Drug Administration – FHWA: Federal Highway Administration – ILs: ionic liquids – IT: isothiazolinone – MIC: microbial induced corrosion – MIT: 2-methyl-2H-isothiazol-3-one – *MRSA*: Methicillin-resistant *Staphylococcus aureus* – MVOC: microbial volatile organic compounds – NACE: National Association of Corrosion Engineers – OEO: oregano essential oil – OIT: 2-octyl-2H-isothiazol-3-one – PAMAM: quaternary ammonium functionalized polyamidoamine – PT: product type – QAC: quaternary ammonium compound – QS: quorum sensing – ROS: reactive oxygen species – SAILs: surface active ionic liquids – TiO₂: titanium dioxide – ZnO: zinc oxide.

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83 **Abstract**

84 All types of building materials are rapidly colonized by microorganisms, initially through
85 an invisible and then later a visible biofilm that leads to their biodeterioration. Over centuries,
86 this natural phenomenon has been managed using mechanical procedures, oils, or even wax. In
87 modern history, many treatments such as high-pressure cleaners, biocides (mainly
88 isothiazolinones and quaternary ammonium compounds) are commercially available, as well
89 as preventive ones, such as the use of water-repellent coatings in the fabrication process. While
90 all these cleaning techniques offer excellent cost-benefit ratios, their limitations are numerous.
91 Indeed, building materials are often quickly recolonized after application, and microorganisms
92 are increasingly reported as resistant to chemical treatments. Furthermore, many antifouling

93 compounds are ecotoxic, harmful to human health and the environment, and new regulations
94 tend to limit their use and constrain their commercialization. The current state-of-the-art
95 highlights an urgent need to develop innovative antifouling strategies and the widespread use
96 of safe and eco-friendly solutions to biodeterioration. Interestingly, innovative approaches and
97 compounds have recently been identified, including the use of photocatalysts or natural
98 compounds such as essential oils or quorum sensing inhibitors. Most of these solutions
99 developed in laboratory settings appear very promising, although their efficiency and
100 ecotoxicological features remain to be further tested before being widely marketed. This review
101 highlights the complexity of choosing the adequate antifouling compounds when fighting
102 biodeterioration and proposes developing case-to-case innovative strategies to raise this
103 challenge, relying on integrative and multidisciplinary approaches.

104

105 **Keywords**

106 biodeterioration, building materials, cleaning procedures, biocides, water-repellents, natural
107 compounds

108

109 **1. Introduction**

110 Biodeterioration of mineral building materials (*i.e.*, stone, ceramics, cement, concrete) is a
111 global and expensive problem for manufacturers and building owners (Romani et al., 2019;
112 Saiz-Jimenez, 2001; Warscheid and Braams, 2000). Biodeterioration consists of the natural
113 degradation of these materials by (micro)organisms (Guiamet et al., 2013; Warscheid and
114 Braams, 2000), which grow as multispecies biofilms that develop on all types of surfaces (Di
115 Martino, 2016; Romani et al., 2019). Such biofilms are usually composed of multiple
116 interacting microorganisms (bacteria, fungi, algae) (Krakova et al., 2015) embedded in a

117 protective and very resistant polymeric matrix (Figure 1) (Flemming and Wingender, 2010).
118 Vital microbial activities, such as cell division, biofilm formation, acid production, and redox
119 activities, lead to the long-term degradation of materials (Guiamet et al., 2013). This
120 phenomenon is also known as microbiologically-influenced or microbially-induced corrosion
121 (MIC) (Enning and Garrelfs, 2014). Biofilms that grow on building materials are initially
122 invisible but turn visible with time, as their development leads to thick and pigmented
123 structures. Finally, the last step of biodeterioration implicates the colonization of such a mature
124 biofilm by mosses or higher plants, especially on stones (Coutinho et al., 2015; Gulotta et al.,
125 2018; Li et al., 2018; Q. Li et al., 2016; Norma Italiana UNI 11182, 2006).

126 According to the building materials industry, the first problem with microbial colonization
127 is its unsightly aspect (Coutinho et al., 2015; Di Martino, 2016). Indeed, the biofilm that
128 develops on the materials is often pigmented, which forms unaesthetic dark or green streaks or
129 spots (Di Martino, 2016), which is undesirable since customers expect their product to stay
130 stable over time (The Brick Industry Association, 2018). The unaesthetic aspect of the
131 darkening of buildings and other materials is also an essential aspect of historic monument
132 conservation (Di Martino, 2016; Grabek-Lejko et al., 2017; Saiz-Jimenez, 2001). Therefore,
133 manufacturers of building materials invest massively in strategies to prevent their products to
134 rapidly turn green or black, and building owners face significant expenses to clean and restore
135 materials that have deteriorated over time. Thus, in addition to the unsightly appearance,
136 biodeterioration causes less visible but more significant damages, including the modification or
137 loss of physical properties of many types of materials (Coutinho et al., 2015). Indeed, as the
138 biofilm grows, surface and deep cracks increasing the porosity of materials are observed
139 (Berdahl et al., 2008; Coutinho et al., 2015). In addition, this increased porosity facilitates the
140 colonization of materials by other microorganisms and promotes their growth. Furthermore,
141 many colonizing microorganisms accelerate deterioration due to the metabolites they produce,

142 such as organic acids (Dubosc, 2000). Overall, the weakening of materials caused by biofilms
143 development leads to faster decay by accelerating the effects of rain or freeze/thaw events
144 (Berdahl et al., 2008; Gladis and Schumann, 2011; Joseph, 2021). Finally, advanced
145 biodeterioration results in the loss of the structural or thermal insulation, drainage, or solar
146 reflectance (proportion of light reflected from the surface of a material) of the materials
147 (Berdahl et al., 2008; Pena-Poza et al., 2018).

148 Because of the aesthetic issues they cause and their impact on the durability of materials
149 described above, biofilms colonizing building materials must be regularly eliminated (Tiano,
150 2016). Cleaning techniques have been developed over centuries (Cappitelli et al., 2020;
151 Sanmartín et al., 2018), and some were even reported and documented in antiquity (Plinius
152 Secundus, 77AD; Vitruvius Pollio, 27BC). Such mechanical cleaning strategies are still widely
153 used even though they slowly disappear nowadays to favor low-cost and efficient chemical
154 compounds. However, these latest treatments have a high environmental and economic cost
155 due to their intensive (Scheerer et al., 2009). For example, biocides applied on façades and roofs
156 runoff in soils and are frequently persistent in the environment. Many (like terbutryn or
157 isoproturon) are poorly biodegradable and lead to long-term soil and water pollution (Bollmann
158 et al., 2017; Chand et al., 2018). Also, the degradation products issued from these biocides
159 remain poorly understood and are suspected to be extremely ecotoxic (Paijens et al., 2020).
160 Finally, these marketed broad-spectrum and harsh biocides cause human health issues for
161 customers, especially when used without basic personal protections (Garcia-hidalgo et al.,
162 2016; Wieck et al., 2018, 2016).

163 The ecotoxicity of commercial large-spectrum and aggressive biocides is a significant factor
164 associated with their use on outdoor building materials, and the regulations concerning these
165 compounds are increasingly restrictive (Scheerer et al., 2009; Tiano, 2016; Warscheid and
166 Braams, 2000). The biocidal products that can be used for preventive or curative treatments of

167 outdoor building materials are classified in product type (PT) 2 of main group 1 corresponding
168 to disinfectants, and PT 10 of main group 2 corresponding to preservatives in annex V to the
169 Biocidal Products Regulation (BPR), Regulation (EU) 528/2012 (Commission Européenne,
170 2012). All these products target both microbial and algal organisms. While the costs of the fight
171 against biodeterioration are challenging to evaluate, they will undoubtedly rise in the future
172 since it will include not only the cost of treatments (i.e., biocides, paints) but also the costs
173 associated with their application in safe conditions for customers and likely the costs associated
174 with their environmental impact (Gaylarde et al., 2003; Guézennec, 2017).

175 This review aims to provide a comprehensive understanding of the different commercially
176 available methods to clean outdoor building materials, focusing on chemical treatment
177 strategies as well as their environmental and health impacts. We will discuss the potential of
178 future and more eco-friendly solutions leading to “greener” and sustainable antifouling
179 compounds and strategies, even though most of these upcoming solutions still require a wider
180 efficacy and more thorough ecotoxicological evaluations. Overall, our primary goal is to
181 provide a case-by-case analysis of chemical control strategies against biodeterioration of
182 outdoor building materials based on multidisciplinary approaches combining the viewpoint of
183 microbiologists, eco-toxicologists, chemists, and material engineers.

184

185 **2. Mechanical cleaning approaches**

186 Building materials have always biodeteriorated over time, and over centuries humankind
187 has tried to prevent or limit this phenomenon. For example, the famous French architect Viollet-
188 le-Duc reported on the preoccupation with tile colonization since the 10th century. Also, he
189 pointed out that as early as the 11th century that the shape of the tiles in the North of France
190 (plain) was different from that of the South (barrel) to limit the development of "mosses and
191 vegetation" (Viollet-le-Duc, 1854).

192 Mechanical cleaning has been, since, the first type of treatment applied to building materials
193 to remove the deteriorating biofilm and is currently often conducted before chemical treatments
194 (Table 1). The utilization of water pressure and steam systems is the widest spread and easy to
195 employ. They have shown their efficacy on various types of microorganisms, such as
196 *Apatococcus lobatus* (Sanmartín et al., 2020). However, if these methods are efficient in the
197 short term on superficial biofilms, they can also spread the microorganisms on the substrate
198 (Favero-Longo and Viles, 2020). In addition, a difficulty associated with these strategies is to
199 correctly adjust the water pressure, which must be sufficient to remove the biofilm but not too
200 high and leading to the degradation of the materials (Slaton and Normandin, 2005). Abrasive
201 systems are another mechanical strategy employed to clean the materials through abrasion,
202 roughening, or erosion (Table 1). For example, sandblasting methods have shown their
203 efficiency on lichens as *Diploschistes scruposus* (Pozo-Antonio et al., 2021). Unfortunately,
204 these methods also damage building materials: high-pressure sand or grit blasting are no longer
205 used to restore historic buildings because of their induced severe damages (Slaton and
206 Normandin, 2005). For the cleaning of historical monuments, other mechanical methods based
207 on lasers are sometimes applied (Di Martino, 2016). These devices operate by applying a laser
208 in a pulse frequency while the output power is controlled (Slaton and Normandin, 2005). The
209 use of these lasers on objects and monuments has shown promise (Table 1). For instance, laser
210 cleaning is efficient on black removal, including *Desulfovibrio desulfuricans* (Elhagrassy et al.,
211 2018); *Verrucaria nigrescens* (Speranza et al., 2013), *Circinaria hoffmanniana* (Pozo-Antonio
212 et al., 2019). However, their large-scale application has so far been minimal, partly due to the
213 high costs (Di Martino, 2016; Slaton and Normandin, 2005). Their use has other drawbacks
214 since it does not eliminate the encrusted part of the biofilm. Even worse, laser treatment can
215 increase the porosity of materials such as tiles, facilitating their recolonization (Barberousse et
216 al., 2006; Di Martino, 2016).

217

218 **3. The extensive use of wide-spectrum biocides.**

219 According to the BPR, Regulation (EU) 528/2012, biocidal products are substances or
220 mixtures used to destroy, prevent the action of, or exert a controlling effect on harmful
221 organisms by a mechanism that is not purely physical or mechanical (Commission Européenne,
222 2012). In this review, biocides will be defined as chemical molecules that are widely and
223 commonly used to kill and remove macro- and microorganisms on the surfaces of building
224 materials. As described below, it is worth noting that the same families of biocides are used in
225 a wide variety of industrial fields and also in the household (*i.e.*, cosmetic, medical care, food
226 industry, metalworking fluids, building cleaning, etc.). The market for these antiseptics and
227 disinfectants never ceases to grow, and customer demand is continuously increasing. For
228 instance, it was expected in 2016 that this market will increase by more than 6 % (Merchel
229 Piovesan Pereira and Tagkopoulos, 2019) and will generate more than US\$8.1 billion by 2021
230 (Zion Market Research, 2016). However, the use of biocides is also increasingly being
231 questioned, as more and more research and publications are demonstrating their toxic effects
232 on humans and the environment.

233 3.1 Isothiazolinones

234 • 3.1.1 Nature and commercially available compounds

235 The isothiazolinones (ITs) constitute a major class of antifouling and biocides compounds
236 used to treat biofilms growing on building materials chemically (Table 1). ITs are sometimes
237 used as reference biocides to test the efficacy of new antimicrobials for the treatment of
238 biodeteriorated stones (Boccalon et al., 2021). ITs are heterocyclic organic compounds
239 containing vicinal sulfur and nitrogen atoms. The four most commonly used molecules in these
240 products are 2-methyl-2H-isothiazol-3-one (MIT, CAS: 2682-20-04), 5- 5-chloro-2-methyl-
241 2H-isothiazol-3-one (CMIT, CAS: 26172-55-4), 1,2-benzisothiazol-3(2H)-one (BIT, CAS:

242 2634-33-5) and 2-octyl-2H-isothiazol-3-one (OIT, CAS: 26530-20-1) (Table 2) (Garcia-
243 hidalgo et al., 2016). These compounds are found in common commercially available products
244 to treat and prevent biodeterioration, such as Biotin R (CTS) or Algicid-Plus (Keim).

245 • 3.1.2 Historical and current use

246 ITs have been marketed since the 1970s as cleaning chemicals for home or professional
247 usage, as well as preservatives, and these applications are still ubiquitous (Schwensen and
248 Johansen, 2018). ITs can be used directly for their biocide effects as in household products
249 (laundry, detergents) and marine antifouling paints (Amara et al., 2018; Batista-Andrade et al.,
250 2018; Callow and Callow, 2011; Soroldoni et al., 2017), but also as preservatives in products
251 containing water such as cosmetics and personal care products (i.e., shower gels, soaps, creams,
252 infant products) (Garcia-hidalgo et al., 2016; Wieck et al., 2018). This domestic application is
253 responsible for a large part of releasing these compounds into the environment and the
254 environmental impact (Wieck et al., 2018).

255 Finally, ITs are very frequently used to prevent the biodeterioration of buildings, roofs,
256 stones, and facades. For example, ITs and especially OIT and its derivative the 4,5-dichloro-2-
257 octyl-2H-isothiazol-3-one (DCOIT, CAS: 64359-81-5) are utilized in paints that are sold to
258 protect house facades (Vermeirssen et al., 2018), such as Lichenicida 468 (Bresciani) (Favero-
259 Longo et al., 2017) or Algi 201 (Algimouss Pro, ITs concentration 0.45%). They can be
260 employed alone or combined with other antifouling compounds, such as quaternary ammonium
261 compounds (see below).

262 • 3.1.3 Efficacy

263 ITs are wide-spectrum biocidal molecules, particularly effective in combating the
264 biodeterioration of building materials. They are typically reported as more bioactive when
265 compared to quaternary ammoniums (benzalkonium chloride), especially at low (<5%)
266 concentration ranges (Favero-Longo et al., 2018). The biocidal efficiency of ITs is based on

267 their electrophilic nature. They are transported into cells by active transport, where they
268 interfere with many cell processes (Williams, 2007). In particular, ITs block O₂ consumption
269 of cells, and consequently, all aerobic processes cease; energy production (ATP) is reduced,
270 slowing down metabolism and growth (Williams, 2007). ITs also inhibit several types of
271 enzymes, including dehydrogenases (*i.e.*, pyruvate, NADH-, lactate dehydrogenase) as well as
272 the adenosine triphosphatase. The inhibition of these enzymes interrupts the TCA cycle, thus
273 perturbing the entire cell metabolism (Williams, 2007). Besides, ITs also oxidizes thiol-
274 containing cytoplasmic and membrane-bound molecules, including those in numerous
275 enzymes' active sites (Williams, 2007). These oxidations also lead to inhibition of metabolism
276 (Favero-Longo et al., 2018). Collectively, all these effects induced by ITs actively damage cells,
277 leading to the production of many free radicals or reactive oxygen species (ROS), which,
278 combined with the inhibition of cell repair mechanisms, quickly leads to the death of
279 (micro)organisms (Williams, 2007).

280 • 3.1.4 Advantages and drawbacks

281 One of the major advantages of ITs is that they act on a wide range of (micro)organisms
282 (*i.e.*, bacteria, fungi, lichens, algae) over a wide pH range (pH 1 to 11) (Favero-Longo et al.,
283 2017; Garcia-hidalgo et al., 2016; Silva et al., 2020). Thus, these compounds can attack very
284 diverse types of multispecies biofilms under numerous environmental conditions. For example,
285 ITs are efficient on filamentous fungi such as *Cladosporium* sp., *Penicillium* sp., and *Fusarium*
286 sp.; but ITs are not effective on cyanobacteria (Table 1) (Barrionuevo and Gaylarde, 2011). As
287 preservatives, the MIT/CMIT combination is one of the most cost-effective solutions currently
288 known (Karsa and Ashworth, 2007). However, some commercial products containing ITs may
289 cause alterations to stone, especially limestone and granite surfaces, after application (Tirado
290 Hernández et al. 2015; Sanmartín et al. 2020). Moreover, the safety of these products has now
291 been questioned by different studies (Thomsen et al., 2018; Wieck et al., 2016). ITs are known

292 to be responsible for contact allergies, called contact dermatitis (Garcia-hidalgo et al., 2016).
293 Humankind is increasingly affected by ITs but understanding this impact remains challenging
294 to estimate due to the diversity of exposure sources (Garcia-hidalgo et al., 2016; Wieck et al.,
295 2018, 2016). For instance, occupational sources of exposure remain difficult to determine due
296 to the lack of information on the composition of marketed products (Garcia-Hidalgo et al.,
297 2018; Ripert et al., 2012).

298 Though, the safety of these molecules must be reassessed and challenged with the
299 deployment of wider ecotoxicological testings. However, the current state of affairs suggests
300 that their usage will be reduced in the future (Wieck et al., 2016). Since 2016 the European
301 Union (EU) and Swiss legislations are quite restrictive for cosmetics use. Commission
302 Regulation (EU) 2017/1224 of 6 July 2017 limits the usage of MIT at 0,0015% (15 ppm) in
303 rinse-off products and prohibits its use in leave-on products; BIT and OIT are now totally
304 forbidden (European Commission, 2017a; Garcia-Hidalgo et al., 2018). Further, ITs are
305 considered as "Dangerous Substances" by the EU Ecolabel criteria [EU. Substances Rendering
306 Goods Ineligible for EU Ecolabel, Art. 6(6), Reg. 66/2010/EC, L 27/1, 30 January 2010 (T. 3
307 of Anx VI to CLP; Candidate List of SVHCs)]. For example, the EU Ecolabel criteria for hard
308 surface cleaning products limit MIT and BIT concentrations at 0,0050% and CMIT at 0,0015%
309 weight by weight (Commission Decision (EU) 2017/1217 of 23 June 2017) (European
310 Commission, 2017b). Contrastingly, currently, there are no regulations for using ITs to prevent
311 building biodeterioration, and the estimated employed concentrations are higher than 0,5% (5
312 000 ppm) in most commercially available products (Garcia-Hidalgo et al., 2018). Moreover,
313 ecotoxicological evaluations have recently reported the high toxicity of OIT and DCOIT against
314 environmental bacteria leaching from facade paints, demonstrating potential deleterious effects
315 on biodiversity and ecosystems (Vermeirssen et al., 2018). In addition, photodegradation
316 products of ITs were found more toxic than ITs themselves in a few studies (Varga et al., 2020),

317 which is very concerning given their extensive applications on outdoor building materials
318 (Vermeirssen et al., 2018). However, ecotoxicity studies concerning degradation products
319 available today are scarce, and further investigations should be conducted to better characterize
320 the potential cytotoxic effects of ITs.

321 • 3.1.5 Future and perspectives

322 The 2016 changes in EU cosmetic legislation seemed to stabilize the occurrence of contact
323 allergic reactions to MIT and CMIT (Garcia-Hidalgo et al., 2018; Wieck et al., 2018).
324 Nevertheless, the widespread use of OIT and the lesser-studied DCOIT by the chemical
325 industry could lead to a new contact dermatitis outbreak (Herman et al., 2019). Moreover, cross-
326 reactions between MIT and OIT may occur (*i.e.*, exposure to OIT may induce allergic reactions
327 to MIT that would not occur without this sensitization) (Aerts et al., 2017). Therefore, new
328 regulations to limit the usage of ITs as anti-biodeterioration agents are expected in a near future,
329 and this risk has to be considered by the industry before expanding the commercialization of
330 these products. To address these concerns, the concentrations of these compounds should also
331 be reduced in marketed products, for example, by the combined use with other less toxic
332 biocides. Such modifications are essential for manufacturers to anticipate and adapt their
333 industrial processes for potential upcoming legislative changes and develop greener and
334 sustainable industrial processes and compounds. In the same vein, more studies evaluating the
335 ecotoxicological risks of these molecules are needed, and recommendations towards using
336 adapted protective devices when spraying such products on buildings have also to be reinforced
337 to protect customer's health.

338 3.2 Quaternary ammonium compounds

339 • 3.2.1 Nature and commercially available compounds

340 Quaternary ammonium compounds (QACs) are the most commonly used biocides after ITs
341 (Table 1). QACs are composed of a quaternary nitrogen atom surrounded by four organic

342 functional groups, so the nitrogen is permanently positively charged (Mulder et al., 2017). An
343 anion balances this charge, usually a chloride or bromide ion, and therefore, QACs exist in the
344 form of water-soluble salts (Mulder et al., 2017; Nuñez et al., 2004). The functional groups (R)
345 include at least one long-chain alkyl group, while the others are methyl, benzyl, or ester groups
346 (Tezel and Pavlostathis, 2011). The most commonly employed biocide QACs are
347 benzalkonium chloride (BAC, CAS: 121-54-0) (Gadea et al., 2017a; Mulder et al., 2017; Nuñez
348 et al., 2004); benzalkonium bromide (DB, CAS: 91080-29-4) (Gadea et al., 2017a),
349 didecyldimethylammonium chloride (DDMAC, CAS: 7173-51-5) (Nuñez et al., 2004), alkyl
350 dimethylbenzyl ammonium chloride (ADMAC, CAS: 8001-54-5), and alkyl
351 trimethylammonium compounds (ATMAC, CAS: 61789-18-2) (Table 2) (Mulder et al., 2017;
352 Nuñez et al., 2004). In BAC-homolog compounds, the nitrogen atom is surrounded by a benzyl
353 group, two methyl groups, and an alkyl chain of variable length (C8 to C18). The highest
354 biocidal activity is associated with C12-C14 homologs, which are the main components of
355 disinfection products (Mulder et al., 2017). The most commonly consumed BACs are C12-
356 BAC, C14-BAC, and C16-BAC. Each homolog has different biocidal ranges. Indeed, C12-
357 BAC has been demonstrated to be effective against yeasts and fungi, while C14-BAC against
358 Gram-positive bacteria and C16-BAC targets Gram-negative bacteria (Nuñez et al., 2004).

359 • 3.2.2 Historical and current use

360 BACs were introduced in 1935 by Gerhard Domagk as zephiran chlorides (Price, 1950).
361 Since they were first commercialized, their use has continuously grown, and their applications
362 diversified. Today, BACs are widely used for domestic applications (softeners, conditioners, or
363 medication for the ENT (eye, nose, throat) therapy); and as disinfectants for industrial,
364 agricultural, and clinical areas (Merchel Piovesan Pereira and Tagkopoulos, 2019; Zhang et al.,
365 2015). Finally, BACs are applied to building materials (walls, floors, roofs, pools, woods) to
366 prevent their biodeterioration (Merchel Piovesan Pereira and Tagkopoulos, 2019). Thus,

367 protocols using DDMAC are effective for the preventive and curative control of the greening
368 of historic building materials (Nowicka-Krawczyk et al., 2019). DDMAC associated with OIT
369 in ROCIMA™ 103 (Dow®) induces in-depth killing of fouling microorganisms and prevents
370 most biological recolonization of sandstone and marble tombs surfaces for a period of five years
371 after treatment (Mascalchi et al., 2020). The effectiveness of benzalkonium chloride treatment
372 in preventing bacterial recolonization of stone was also observed after the treatment of the
373 granite walls of the San Martiño Pinario Monastery in Santiago de Compostela (NW Spain)
374 (Sanmartín and Carballeira, 2021). QACs are components of several cleaning and disinfection
375 solutions such as Algicid-Plus (Keim, DDMAC 0.36% and OIT 0.081%), Preventol® RI50 and
376 R180 (Lanxess), Organcide QC50 (formerly Vitalub QC50, France Organo Chimique,
377 ADMAC 50%, used in solution between 3 and 5%), Algidal (Algimouss Pro, CAQ C12-C16
378 20%), Sikagard® Stop Algues Pro (Sika®), and Dalep PE (Dalep®).

379 • 3.2.3 Efficacy

380 The biocidal effects of QACs rely on their ability to lyse cells by disrupting lipid bilayers.
381 The cationic nitrogen interacts with the phospholipid head *via* ionic interactions, while the alkyl
382 chain of quaternary ammonium integrates into the hydrophobic tails of phospholipids through
383 hydrophobic interactions (Heerklotz, 2008). Such interplays increase surface pressure in the
384 exposed part of the membrane and decrease its fluidity. Thus, the cell membrane is rapidly
385 disintegrated (Tezel and Pavlostathis, 2011). Even when QACs are present at non-lytic or sub-
386 inhibitory concentrations in the environment (*i.e.*, below the minimum inhibitory
387 concentration), they are reported to disrupt microorganisms by inhibiting specific membrane
388 processes such as solute transport and cell wall biosynthesis (Tezel and Pavlostathis, 2011).
389 However, at these low concentrations, QACs can also increase biofilm formation and induce
390 oxidative stress, amplifying genetic variation in some microorganisms that may lead to

391 microbial resistance (Gadea et al., 2017a; Houari and Di Martino, 2007; Tezel and Pavlostathis,
392 2015).

393 • **3.2.4 Advantages and drawbacks**

394 The success of QACs relies on their multiple biological targets and their wide range of
395 applications. They also have shown efficiency on numerous microorganisms, like fungi as
396 *Aspergillus* sp., *Penicillium* sp., *Chaetomium* sp. (Isquith et al., 1972), and lichens as
397 *Diploschistes actinostomus*, *Parmelia conspersa*, *Parmelia ioxodes* (Table 1) (Pinna et al.,
398 2012). Their multiple usages and low production cost make these molecules the best-selling
399 biocides along with ITs (Merchel Piovesan Pereira and Tagkopoulos, 2019; Tezel and
400 Pavlostathis, 2011). As they are widely consumed, they are also released in large amounts into
401 the environment during their production and use. It is estimated that approximately 25% of the
402 QACs are directly discharged into the environment as a result of their multiple usages (Tezel
403 and Pavlostathis, 2011). For example, QACs are released into nature at high concentrations (5
404 to 30 mg.L⁻¹) from roof runoffs, even after several months after tiles' treatment (Gromaire et
405 al., 2015). Their long-term effects on ecosystems and human health are still poorly understood
406 (Zhang et al., 2015). Nevertheless, it has been shown that their accumulation in the environment
407 leads to the development of drug-resistant microorganisms (Merchel Piovesan Pereira and
408 Tagkopoulos, 2019; Mulder et al., 2017). The main mechanisms of microbial adaptation to
409 QACs are the same as those responsible for antibiotic resistance, such as modification of
410 membrane structure and composition, improvement of biofilm formation (which protects
411 microorganisms), lateral acquisition of genes coding various types of efflux pumps, and
412 overexpression of these efflux pump systems (Gadea et al., 2017a; Slipski et al., 2017; Tezel
413 and Pavlostathis, 2015). Consequently, the development of bacterial populations resistant to
414 QACs also potentially increases antibiotic resistance in ecosystems (Gadea et al., 2017a; Kim
415 et al., 2018). It has already been shown that some nosocomial outbreaks were due to resistant

416 pathogens to antiseptics or contaminated disinfectants, especially those based on QACs and
417 those using BACs as major active compounds (Weber et al., 2007). Microorganisms on building
418 materials exposed to QACs can adapt and thus promote biodeterioration by resisting current
419 treatments (Gadea et al., 2017a; Tezel and Pavlostathis, 2015). The effectiveness of quaternary
420 ammoniums is influenced by the chemical composition and the physical properties of the
421 material to which they are applied (Favero-Longo et al., 2017). The application of solutions
422 containing QACs to porous materials like sandstone can lead to their penetration and their
423 gradual release, resulting in the exposure of microorganisms and other algae to low
424 concentrations of biocides over a relatively long period (Favero-Longo et al., 2017). This
425 process may facilitate the induction of a decrease in the sensitivity of the target organisms to
426 the biocides. Finally, QACs are considered one of the most toxic products among biocides with
427 ITs and antifouling products (Roy, 2020). BACs are responsible, for instance, for skin and
428 respiratory irritations, and they are considered to be skin sensitizers (Merchel Piovesan Pereira
429 and Tagkopoulos, 2019). As with ITs, the application of commercial products containing QACs
430 can lead to alterations in the stone material (Sanmartín et al., 2020; Tirado Hernández et al.,
431 2015).

432 • 3.2.5 Future and perspectives

433 As with ITs, the use of QACs will be increasingly regulated in a near future. For example,
434 since 2016, the EU has drastically reduced the number of BACs allowed in food products and
435 has banned them in antiseptic hand and body soaps. Similarly, the US Food and Drug
436 Administration (FDA) is considering banning BACs in these same products (Merchel Piovesan
437 Pereira and Tagkopoulos, 2019). Moreover, CAQs have been reported to be toxic to various
438 aquatic organisms, such as *Daphnia magna* and *Criodaphnia dubia*, where they are highly
439 poisonous at lower concentrations (0.4 to 4 ng.L⁻¹) than those found in the environment (on the
440 order of mg.L⁻¹) (Lavorgna et al., 2016). The long-term effects of CAQs are also of serious

441 concern due to their ecotoxicity, bioavailability, and possible interactions with other chemicals
442 (Lavorgna et al., 2016; U.S. Environmental Protection Agency (EPA), 2006).

443 Consequently, the proven toxicity of QACs for the environment and especially aquatic
444 ecosystems (Di Nica et al., 2017; Merchel Piovesan Pereira and Tagkopoulos, 2019) may lead
445 authorities to limit their application on outdoor surfaces in the coming years. As for IT's, such
446 ecotoxicological effects have to be considered before widespread commercialization and launch
447 of new products. The use of adapted personal protection devices has to be strongly
448 recommended to avoid impact on users' health. Decreasing the usage of QAC's, reducing their
449 concentrations at their minimum, and combining QACs products with less toxic biocides is
450 essential before considering any use of these products. Finally, more ecotoxicological studies
451 should be conducted to better precise the effects of these widely marketed products on health
452 and the environments

453 3.3 Other types of widely-used biocides

454 Many other chemical products are commercialized to prevent biodeterioration. They are all
455 employed as wide-spectrum biocides, but they are less commonly used than ITs and QACs
456 (Tezel and Pavlostathis, 2011). Their mode of action, their potentially hazardous effects on
457 health and the environment are also much less documented.

458 • 3.3.1 Sodium hypochlorite

459 Among those other types of broad-spectrum biocides utilized to clean building materials is
460 sodium hypochlorite (CAS: 7681-52-9) (Table 2), also known as bleach (Table 1). This
461 compound is, for example, commercialized under the names Clorox® or 30 seconds® outdoor
462 cleaner. Sodium hypochlorite is cheap and rapidly efficient on a wide range of microorganisms
463 (Fukuzaki, 2006). For instance, sodium hypochlorite is effective on filamentous green algae
464 and cyanobacteria (Pozo-Antonio et al., 2017). However, this application could have
465 deleterious effects on metals or stones, as its degradation can lead to the formation of

466 chlorinated compounds that are toxic to aquatic organisms (Fukuzaki, 2006). Bleach may also
467 affect energy metabolism and damage DNA (Emmanuel et al., 2004). Besides, sodium
468 hypochlorite is a harmful compound responsible for mucosal irritations (Fukuzaki, 2006).

469 • **3.3.2 Acid compounds**

470 Some other biocides, like Biorox®, commercialized to clean natural stones are based on
471 oleic acid activity (CAS: 112-80-1) (Table 2). These molecules were first employed as
472 herbicides in agriculture. The most common oleic acid is the nonanoic acid (also named
473 pelargonic acid, CAS: 112-05-0), and is included in many commercialized products like
474 Natria® (Bayer), Premiumgreen total (Finalsan plus) mixed with maleic hydrazide by CTS, or
475 Dalep eco (Dalep®). The use of pelargonic acid seems to be efficient in preventing
476 biodeterioration of building materials, and this molecule is quickly degraded in soils (Marin et
477 al., 2016), limiting its ecotoxicity. Norstictic (CAS: 571-67-5) and usnic (CAS: 7562-61-0)
478 acids, which are lichen secondary metabolites, have also shown efficiency and low toxicity on
479 various microorganisms as cyanobacteria (*Chroococcus minutus*) and fungi (*Coniosporium*
480 *perforans*, *Phaeococcomyces chersonesos*) (Table 1) (Fidanza and Caneva, 2019; Gazzano et
481 al., 2013) However, there are few available studies on these compounds, and more research is
482 needed to confirm these preliminary observations. As with QACs (especially BACs),
483 pelargonic acid causes slow onset irritancy, erythema and is an irritant compound (Frosch and
484 John, 2011). Other families of acids are employed and commercialized to prevent
485 biodeterioration like lactic acid (CAS: 50-21-5) as MossKade® supplied by HortiPro. However,
486 some studies have also highlighted the effects of lactic acid on human health, which has been
487 shown to be responsible for erythema and stinging when used at 5% in water (Frosch and John,
488 2011). For this reason, the supplier recommends that customers wear gloves and eye protection
489 to avoid its potential hazards (Hortipro B.V., 2014).

490 • **3.3.3 Chlorinated phenol compounds**

491 Besides, some biocides containing chlorinated phenol compounds are also commercialized
492 to prevent biodeterioration, such as Atagol sodique from CTS containing *p*-chlorocresol (4-
493 chloro-3-méthylphenol, CAS: 59-50-7) and Panacide® containing dichlorophen (2,2'-
494 Methylenebis(4-chlorophenol), CAS: 97-23-4) (Table 2) (Rosado et al., 2017). For example,
495 Panacide® has shown to be efficient on filamentous fungi as *Aspergillus* sp., *Cladosporium* sp.,
496 and *Penicillium* sp. (Table 1) (Rosado et al., 2017). However, as the other biocides, they are
497 also mentioned as an irritant if not used with personal protection gear (Frosch and John, 2011),
498 and in 2019 government of Canada has assessed *p*-chlorocresol as posing a risk to human health
499 and has recommended a reduction in its usage (Government of Canada, 2019).

500 • **3.3.4 Other compounds broad-spectrum biocides**

501 Finally, among the other biocides used to prevent biodeterioration, disodium metasilicate
502 (CAS: 229-912-9) has been commercialized as in AlgiClean (Algimouss pro), and dimethyl
503 sulfoxide (DMSO, CAS: 67-68-5) can be found in "Solvent Gels" utilized to restore historical
504 monuments (Table 2) (Toreno et al., 2018). However, both molecules are noted for their toxicity
505 and corrosive effects, and personal protection gears (gloves and goggles) are recommended
506 when handling these compounds (Frosch and John, 2011).

507 **3.4 Innovative use of biocides**

508 Among innovative biocidal compounds are gemini surfactants (Table 1). These are
509 amphiphilic compounds composed of two conventional surfactant molecules covalently
510 bonded together by a spacer. Geminis are characterized by very low critical micelle
511 concentrations (CMC), low surface tension (γ), anti-adhesive activities, and low minimal
512 inhibitory concentrations as compared to the related monomeric surfactants. For these reasons,
513 such compounds are very attractive as biocides in materials science, especially when they
514 expose ammoniums as polar groups (Brycki et al., 2017; Tyagi and Tyagi, 2009). For instance,
515 the antifungal activity of cationic gemini surfactants has been recently demonstrated against

516 *Aspergillus brasiliensis* by measuring the content of ergosterol, a method used to estimate the
517 level of mold infestation in buildings (Koziróg et al., 2018). Additionally, it has been shown
518 that the antimicrobial efficiency of these compounds depends on the length and type of spacer
519 as well as their hydrophobic counterpart. As expected, diquatery ammonium geminis of
520 structure $[C_{12}H_{25}N^+(CH_3)_2CH_2CONH]_2Y \cdot 2Cl^-]$ where $Y = -(CH_2)_4$ or $-(CH_2)_2SS(CH_2)_2-$ were
521 shown to exhibit a higher antimicrobial activity against gram-positive/negative organisms and
522 *Candida albicans* than "plain" hexadecyltrimethyl ammonium bromide (Diz et al., 1994). Also,
523 Winnicki *et al.* showed the anti-algal activity of pentylene-1,5-bis(dimethyl dodecylammonium
524 bromide) against *Chlorella*, single-celled green freshwater algae also known to foul industrial
525 cooling systems and building facades (Table 1) (Winnicki et al., 2021).

526 Another way to expose antimicrobial moieties is to derive the end groups of dendrimers
527 (Table 1). Once functionalized with quaternary ammonium salts, these highly branched and
528 star-shaped globular macromolecules exert a more potent biocidal activity than their small-
529 molecule counterparts (Chen and Cooper, 2000; Karthikeyan et al., 2016). Chen *et al.*
530 demonstrated that dimethyl dodecylammonium chloride functionalized poly-(propylene imine)
531 dendrimers were over two orders of magnitude more potent than their mono-functional
532 counterparts against *E. coli* (Chen et al., 1999). Another dendrimer scaffold based on quaternary
533 ammonium functionalized polyamidoamine (PAMAM) has been successfully used against a
534 group of common Gram-negative and Gram-positive bacteria (Zainul Abid et al., 2016) and
535 *Staphylococcus aureus* as a coating on textile fabrics (Ghosh et al., 2010). However, to the best
536 of our knowledge, such promising architectures have never been applied yet to prevent the
537 biodeterioration of building materials.

538 3.5 Conclusions about the usage of biocides to prevent biodeterioration of building materials

539 To conclude, it is essential to note that the composition of marketed biocidal products used
540 to control the biodeterioration of building materials is unclear and difficult to obtain. Moreover,

541 many commercialized products mix several families of molecules such as Biotin T (CTS),
542 Algicid-Plus (Keim), which are mixtures of OIT and QACs, or Net 9 Anti-Lichen (Dalep®),
543 which is a mixture of sodium hypochlorite with other compounds. Many, if not all, of these
544 compounds are now recognized by many research as harmful to human and environmental
545 health. In the future, regulations for many biocidal molecules could follow the same path as ITs
546 and QACs. For instance, this is already the case for *p*-chlorocresol, as the EU and Canada have
547 limited their use in cosmetics (Government of Canada, 2019). Even in the case of ITs and
548 CAQs, their effect remains to be better understood, and multidisciplinary efforts (combining
549 expertise in microbiology, building materials, chemistry, ecotoxicology, medicine) remain to
550 be conducted in order to evaluate their usage and effects. Environmental and legal risks have
551 to be considered by major industries commercializing these products to maintain their economic
552 profitability and by customers to limit their environmental footprint. In this perspective,
553 massive investments in research and development of more sustainable and environmentally-
554 friendly antifouling compounds appear to be an urgent need and a promising economic strategy.
555 After comparative studies of the effectiveness of commercial biocidal solutions to control
556 outdoor colonization of stone in historical monuments and consider their toxicity, some authors
557 recommend water-based treatments and brushing to remove the colonizing biomass (Sanmartín
558 et al., 2020). There remains the problem of controlling microbial regrowth and recolonization
559 of the substrate after cleaning.

560

561 **4. Water-repellent compounds and surfaces offer interesting antifouling** 562 **properties.**

563 Throughout the ages, the biodeterioration of building materials, especially stone, has been
564 of significant concern to builders. Over time and civilizations, many different treatments have

565 been developed and used, such as oils, waxes, or sacrificial layers (Charola, 2001; Rossi-
566 Manaresi, 1996). Sacrificial layers are paints, renders, or plasters deposited on building
567 materials to protect them from weather and the time effects (Charola, 1995). For instance, Pliny
568 the Elder explained that the Carthaginian pitch-coated their walls made of tuff, a stone highly
569 sensitive to biodeterioration (Plinius Secundus, 77AD; Rossi-Manaresi, 1996). Vitruvius also
570 described that Roman coated their walls with three layers of plaster and two layers of stucco to
571 protect fragile materials (limestone and tuff) from biodeterioration and to mimic at the same
572 time more precious stones like marble (Rossi-Manaresi, 1996; Vitruvius Pollio, 27BC). It has
573 also been reported that water repellent coatings such as wax or oils have been used in ancient
574 times (Rossi-Manaresi, 1996), and to date, waterproofing strategies are still widely employed
575 alone or in combination with biocidal treatments (Moreau et al., 2008; Pinna et al., 2012; Urzi
576 and De Leo, 2007). The development of innovative superhydrophobic materials remains a
577 major industrial challenge.

578 4.1 Conventional water-repellent treatments

579 • 4.1.1 Nature and commercially available compounds

580 Different water-repellents are available on the market, but the most popular ones are all
581 silicone derivatives (Table 1) (Roos et al., 2008). These compounds consist of an inorganic
582 network of Si-O-Si bonds with an organic pendant group bearing by silicon atoms. In
583 antifouling applications and water-repellent treatments, organic pendant groups are usually
584 alkyl chains or aromatic groups due to their intrinsic hydrophobic character. Whatever the
585 precursors used in antifouling or water-repellent treatments, the chemistry involved in the
586 production of silicone derivatives remains the same and is the sol-gel chemistry implying
587 hydrolysis and condensation reactions (Brinker and Scherer, 2013; Iler, 1979). Thus, silicone
588 derivatives could be produced starting with organosilanes, siloxanes, and/or siliconates.
589 Organosilanes are monomeric species containing at least one hydrolytically sensitive group,

590 mainly chloride atom or alkoxy group (OR), which could undergo hydrolysis (formation of
591 reactive silanol Si-OH) and condensation reactions allowing the growth of Si-O-Si backbone
592 and/or covalent bonding on a substrate. Organosilanes also possess one or more organic
593 substitutions linked to a silicon atom with a hydrolytically stable Si-C bond, silicon atom being
594 tetravalent. Siliconates are their basic salts, and siloxanes correspond to their oligomeric or
595 polymeric forms.

596 Regarding antifouling of building materials, alkyltrialkoxysilanes such as
597 triethoxyisobutylsilane (CAS: 17980-47-1), *N*-octyltriethoxysilane (CAS: 2943-75-1), and iso-
598 octyltriethoxysilanes (CAS: 35435-21-3) are the most utilized compounds (Table 2) (Roos et
599 al., 2008). Interestingly, when the alkyl chain is long (C12-C16), the resistance of these
600 molecules to alkalis is more important, making them able to penetrate deeply into a substrate
601 such as concrete (Roos et al., 2008; Urzi and De Leo, 2007). In comparison, siloxanes have a
602 much more complex structure due to their oligomeric or polymeric state (Roos et al., 2008).
603 Siloxanes, which are liquid due to their low intermolecular forces, have better thermal stability
604 than silanes. Still, they cannot penetrate a substrate as deeply as monomeric silanes because of
605 a steric hindrance (Roos et al., 2008). As they are also alkali-resistant, they can be used on
606 concrete. However, they are much better suited to porous substrates such as ceramics (i.e.,
607 bricks, ceramic roof tiles) and stone (Roos et al., 2008; Urzi and De Leo, 2007). Organo-
608 modified siloxanes are mainly used for building material protection, as their methyl groups
609 around the silicon atom are replaced by other organic groups (Roos et al., 2008). Finally,
610 siliconates are smaller molecules than silanes and siloxanes; therefore, they provide the deepest
611 penetration (Urzi and De Leo, 2007). They also present no water sensitivity, unlike
612 organosilane and siloxane species, and they are water-soluble, meaning that they are fully
613 compatible with water-based processes and less expensive. Commercially available water-
614 repellents include the following molecules: alkyl alkoxy silane (Hydrophase superfici supplied

615 by Phase), alkyltrialkoxysilane (Hydrophase malta PH91503, Phase) (Urzi and De Leo, 2007),
616 trimethoxy-(2,4,4-trimethylpentyl)silane (CAS: 34396-03-7) (Sikaguard® Roof Protection,
617 Sika), polydimethylsiloxane (Rhodorsil RC80, Phase) (Urzi and De Leo, 2007), or potassium
618 methylsiliconate (or potassium methylsilanetriolate, CAS: 031795-24-1) (Table 2) (SILRES®
619 BS 16, Wacker).

620 In addition to silicon derivatives, fluoropolymer coatings are also marketed for their water-
621 repellent properties. For example, some of them have lowered biofilm formation by some
622 bacteria, such as *Bacillus subtilis* (Table 1) (Bao et al., 2017). However, they also have shown
623 high toxicity for both human health and the environment. Consequently, these compounds will
624 not be described in this review, as their use is not recommended on building materials (Daubert
625 et al., 2009; Hekster et al., 2003; Sznajder-Katarzyńska et al., 2019).

626 • 4.1.2 Historical and current use

627 To protect building materials, the most popular water-repellents are alkyl-silicone products
628 like alkyl-silanes, alkyl-siliconates (Charola, 2001), oligomeric and polymeric siloxanes
629 (Khoshnevis et al., 2020; Roos et al., 2008). These products are derivatives of ethyl-silicate
630 (CAS: 78-10-4) (Table 2), discovered by the French chemist Ebelmen in 1845 (Charola, 2001;
631 Ebelmen, 1855). Shortly after this discovery, in 1861, tetraethoxysilane (developed by
632 Ebelmen in 1846) (Ebelmen, 1855) was suggested by W. von Hoffman as a protectant to the
633 House of Parliament in London. However, it was not until the 1920s that the use of ethyl-silicate
634 as a stone treatment was revived with the work of A.P. Laurie (Laurie, 1926a, 1926b, 1926c,
635 1925, 1923; Wheeler, 2005). It was only in the 1950s that silicone-based solutions gained
636 popularity, and their applications were multiplied for both industry and consumers (Noll, 1954).
637 For instance, these silicone-based solutions have been used to protect building materials, as
638 shown in the patent by Bayard R. Brick, for the treatment with a non-aqueous solution of
639 organo-siloxane resins (Bayard R. Brick, 1951). Until the late 1980s, water-repellents were

640 solvent-based, but due to environmental concerns, their composition was modified to a water-
641 based emulsion form (Charola, 2001; Roos et al., 2008). Today, silicones are widely used in
642 the preservation of building materials, as well as in domestic applications (shampoos,
643 conditioners) (Roos et al., 2008).

644 • 4.1.3 Efficacy

645 Water-repellent coatings consist of depositing a hydrophobic substance on targeted
646 materials to prevent liquid water penetration (Charola, 2001; Fassier, 2009). The goal is to
647 obtain a contact angle between 90° and 150° on the treated surface. Hydrophobic substances
648 increase the solid-liquid interfacial tension and thus limit wetting and liquid water penetration
649 into the material (Fassier, 2009) necessary for biofilm establishment and growth. The extent of
650 water-repellency depends on the substrate (Roos et al., 2008) and the nature of the alkyl
651 group(s) attached to the silicon atom (Charola, 2001).

652 • 4.1.4 Advantages and drawbacks

653 Water-repellents reduce water availability for microorganisms, thus slowing down their
654 growth and, in turn, the biodeterioration of building materials (Fassier, 2009; Urzi and De Leo,
655 2007). For example, silanes and siloxanes efficiently reduce building material colonization by
656 photosynthetic microorganisms, such as filamentous *Nostoc*-like cyanobacteria (Urzi and De
657 Leo, 2007), and *Stichococcus bacillaris* (Romani et al., 2021b). Potassium methyl silicate
658 has also shown *in vitro* effects on the growth of *Cladosporium cladosporioides* (Table 1)
659 (Romani et al., 2021b). Additionally, silicone-based water-repellents are insensitive to UV
660 radiations, making them particularly stable through time (Charola, 2001; Fort González et al.,
661 2000; Wendler, 1997). Water-based silicone formulations also offer adequate protection for
662 granites and low-porosity limestones, while siloxanes are mostly used for the treatment of
663 facades, despite their low affinity with alkali substrates and the fact that they exhibit a lesser
664 hydrophobicity in comparison with silanes (Bruchertseifer et al., 1995; Roos et al., 2008).

665 However, the use of water-repellents also has some drawbacks. Indeed, it has been reported
666 that they increase the sensitivity of some materials to freezing (Snethlage and Wendler, 1996)
667 and impact their surface rigidity (Sasse and Snethlage, 1997). These properties lead to a higher
668 erosion and biodegradation of the building materials over time (Charola, 2001). Moreover,
669 water-repellent treatments have a short lifespan since they are poorly resistant to decay and bad
670 weather (Fassier, 2009; Ferreira Pinto and Delgado Rodrigues, 2000; Pinna et al., 2012). They
671 are less effective than solvent-based formulations when facing many freeze-thaw periods. They
672 are also destabilized by salts in the material (Charola, 2001) and thus less efficient when used
673 on buildings constructed in coastal areas.

674 Evaluation of advantages and drawbacks of water repellents remains a complex task as there
675 is a gap between nature as well as the importance of biofilms' development and the type of
676 water-repellent treatments sprayed on the construction or the cultural heritage preservation
677 fields. The effectiveness of some of these water-repellents to prevent microbial colonization of
678 stone or mortars has been tested in various studies (Moreau et al., 2008; Pinna et al., 2012; Urzi
679 and De Leo, 2007). The main results of the work published by Urzi and De Leo pointed out that
680 applying a hydrophobic compound alone was not sufficient to stop the development of biofilm
681 over 15 months of exposure and that only the combined use of water-repellent and a biocidal
682 substance reduced the colonization of materials by algae and bacteria (Pozo-Antonio et al.,
683 2016; Urzi and De Leo, 2007). Moreover, they do not lower the colonization of materials by
684 "black" fungi such as *Alternaria* sp. or *Cladosporium* sp., which are the most resistant to
685 chemical treatments (Hallmann et al., 2011; Krause et al., 2006; Romani et al., 2021b; Urzi and
686 De Leo, 2007). Combining polysiloxane with copper nanoparticles reduces biocolonization and
687 blackening of marble surfaces (Pinna et al., 2012). When treating successively with a water
688 repellent and a biocide, the question of the order of application of each chemical arises (Moreau
689 et al., 2008). A water-repellent applied after a quaternary ammonium treatment loses

690 effectiveness. When the biocide is used after the water repellent, the surface hydrophobicity of
691 the stone is reduced, and the biocide penetrates little into the material. Treating a surface
692 previously treated with a water repellent with a quaternary ammonium compound can remove
693 the biofouling that has developed at a given time but cannot prevent recolonization in the longer
694 term (Moreau et al., 2008). Nevertheless, we have some clues about the efficiency of silicone-
695 based coatings towards the development of biofilms in marine fouling since they are
696 commercially used as fouling release coatings (Lejars et al., 2012).

697 Evaluating the ecotoxicity of water-repellents remains a major challenge, and more research
698 and assessment are urgently needed. On the one hand, coating building surfaces with water
699 repellents reduced microbial growth and protected materials. Thus, the use of water-repellent
700 coatings leads to a reduction in the use of biocides compounds. On the other hand, water
701 repellent molecules also present ecotoxicological effects, as reported in a few studies, and their
702 runoff with time could damage humans and environmental health. Again, multidisciplinary
703 studies would be required to fully address these yet unsolved questions.

704 • 4.1.5 Future and perspectives

705 The use of water-repellents is widespread in the construction industry, which has
706 successfully adapted to environmental concerns to propose safer products (Charola, 2001; Roos
707 et al., 2008). However, to properly apply water-repellents and avoid risk for the materials
708 (Sauder, 1999), a "holistic approach" is needed. This means that it is necessary to consider the
709 treatment, application, and the substrate for successful waterproofing (Charola, 2001, 1995).
710 Otherwise, an innovative approach consists of creating superhydrophobic surfaces on the
711 building materials (see below). In this regard, some silicones are promising, such as
712 poly(dimethylsiloxane) (CAS: 70131-67-8) (Table 2) (Amara et al., 2018). From a regulation
713 and environmental point of view, since oligomeric-polymeric silicone derivatives could be

714 considered as microplastics, their release from substrates could be limited and even forbidden
715 in the future (ECHA, 2019).

716 4.2 The case of superhydrophobic materials

717 The abovementioned water-repellents offer hydrophobic properties to building materials,
718 which means that the resulting apparent contact angle is between 90° and 150°. In the case of
719 superhydrophobic compounds, the apparent contact angle is higher than 150° on material
720 surfaces with a low hysteresis or a low tilting angle (less than 10°) (Table 1) (Jeevahan et al.,
721 2018). Research on superhydrophobic materials is relatively recent and has rapidly grown over
722 the last ten years, from around 100 publications per year in 2009 to more than 700 in 2018
723 (Dalawai et al., 2020). This section of this review will mainly focus on silicones used to develop
724 this type of coating. As described above, water repellent compounds have been known for a
725 long time, have an excellent cost-benefit ratio, and are widely used. Other techniques exist to
726 develop superhydrophobic materials, but they are more complex and less developed, and at this
727 time, they remain promising research strategies that needed to be developed and widely tested
728 (Dalawai et al., 2020; Li et al., 2017).

729 • 4.2.1 Nature and commercially available compounds

730 The design of silicone-based superhydrophobic surfaces is generally achieved by two
731 different pathways: the top-down approach and the bottom-up strategy (Dalawai et al., 2020;
732 L. Li et al., 2016; Niu et al., 2020; Wang et al., 2020). The top-down allows the formation of
733 superhydrophobic surfaces by selective matter removal, while the bottom-up approach
734 corresponds to the assembly of precursors (monomeric, oligomeric, or polymeric chemical
735 species, nanoparticles, microparticles ...). The top-down approach is generally a two-step
736 procedure involving first surface etching (either physical or chemical) leading to a patterned
737 master and then forming a master negative replica with silicone derivatives. The second step
738 usually implies pouring silicone prepolymers over the master, followed by curing and peeling

739 off phases (Xia and Whitesides, 1998). Alternatively, some authors have directly modified
740 silicone rubbers by laser irradiation and/or chemical etching (Wang et al., 2020). Concerning
741 the second strategy, *i.e.*, the bottom-up approach, it generally involves the preparation of a
742 solution containing silicon precursors, solvents, particles and nanoparticles, and catalysts. This
743 solution is next deposited on the surface of the substrate, and evaporation of volatile species
744 (solvent) leads to the formation of the superhydrophobic surface by a multiscale component
745 assembly. A subsequent treatment (often thermal or UV curing) allows the stiffening of the
746 superhydrophobic coating. The deposition step could be achieved by dip-, spin- or spray-
747 coating. It appears thus that the bottom-up approach is much more convenient for treating
748 building materials since its synthesis procedure is fully compatible with outdoor treatments,
749 especially when spray-coating on large surfaces with commercial equipment is required
750 (Faustini et al., 2018). Several commercialized superhydrophobic paint are currently marketed,
751 such as SuperCN™ (NEI Corporation), NeverWet® anti-icing coating, HydroFoe™ (LotusLeaf
752 Coatings), Lotusan®, (Sto) (Sto, 2020). Today, in addition to building materials,
753 superhydrophobicity is under development for many applications such as photovoltaic devices,
754 fabrics, and textiles, anti-corrosion, anti-snow, and freeze and anti-reflective (Dalawai et al.,
755 2020).

756 • 4.2.2 Historical and current use

757 Superhydrophobicity was first studied in 1756 by the German physician Leidenfrost by
758 depositing a water drop on a hot solid surface (>200°C) and observing the drop flowing
759 everywhere. The water drop had an apparent contact angle of 180°, constituting what was then
760 named “the Leidenfrost effect” (Leidenfrost, 1756; Quéré and Reyssat, 2008). Also, the
761 superhydrophobic property of lotus (*Nelumbus* sp.) leaves is due to their unique nano-
762 structuration combined with the production of a hydrophobic coating (a wax made of various
763 non-polar methyl groups, such as nonacosane diols) (Ensikat et al., 2011; Sanchez, 2012;

764 Sanchez et al., 2010). The lotus “self-cleaning” phenomenon has been known in Asia for at
765 least 2000 years, where the lotus is a symbol of purity in many cultures (Cheng and Rodak,
766 2005). Nevertheless, it was not until the early 1970s that the lotus phenomenon was studied and
767 then luckily understood by the German botanist Barthlott after realizing that he did not need to
768 dust off the lotus leaves before observing them under a microscope, unlike other plants
769 (Barthlott and Neinhuis, 1997; Cheng and Rodak, 2005). This discovery led to the "Lotus-
770 Effekt" patent in cooperation with Sto, producer of the Lotusan® paint (Sto, 2020).

771 Thanks to 3.8 billion years of evolution, various organisms, such as lotus, have developed
772 non-wetting traits that protect them from microbial colonization and pathogenic agents. For
773 example, these properties were depicted in ramee leaves (contact angle 164°) or insects like
774 some Homoptera (*Meimuna opalifera*, contact angle 165°) (Wolfs et al., 2013). Researchers
775 and industrials aim to develop materials with superhydrophobic properties to allow their self-
776 cleaning and protect them against biodeterioration, following a modern and very promising
777 approach called biomimicry (Zhang et al., 2017). Indeed, observation of natural phenomena is
778 frequently recognized as a promising way of developing eco-friendly solutions (Scardino and
779 de Nys, 2011; Wolfs et al., 2013; Zhang et al., 2017).

780 • 4.2.3 Efficacy

781 To the best of our knowledge, no studies have evaluated the effectiveness of
782 superhydrophobic coatings in preventing long-term microbial colonization and biodeterioration
783 of building materials (Xiang et al., 2019). Again, integrative and multidisciplinary research is
784 needed to assess better the efficiency of these antifouling strategies, which, for the moment,
785 mostly rely on empirical observations and assessments.

786 • 4.2.4 Advantages and drawbacks

787 Superhydrophobic coatings under development provide amphiphobic properties to building
788 materials, which means that they prevent water (hydrophobic) and oil (oleophobic) uptakes

789 (Facio et al., 2017). Moreover, superhydrophobicity provides self-cleaning properties that avoid
790 microbial and dirt attachment, delaying building material biodeterioration (Dalawai et al., 2020;
791 Jeevahan et al., 2018). However, the real-world applications of superhydrophobic coatings are
792 minimal due to low durability, expensive and toxic reagents, and complex preparation processes
793 (Li et al., 2017). These coatings may also be toxic for the environment and human health due
794 to some of their components, such as methanol (Zulfiqar et al., 2017) or fluorinated molecules
795 (Arabzadeh et al., 2017; Facio et al., 2017; Guo et al., 2005). However, determining the toxicity
796 level of such compounds remains an open question, as previously discussed for conventional
797 water-repellents.

798 • 4.2.5 Future and perspectives

799 Superhydrophobic coatings appear to be promising by conferring self-cleaning properties
800 to building materials. However, their durability and environmental impacts remain to be
801 assessed. They appear at first sight as interesting alternatives to avoid applying biocides.
802 However, a few studies also report that the toxicity of such water repellents could cause health
803 or environmental issues (Arabzadeh et al., 2017; Facio et al., 2017; Guo et al., 2005; Zulfiqar
804 et al., 2017). To the best of our knowledge, these coatings have only been evaluated under
805 laboratory conditions (Zulfiqar et al., 2017), and comprehensive tests under various *in situ*
806 conditions are needed to evaluate the toxicity of these compounds (Arabzadeh et al., 2017;
807 Facio et al., 2017; Guo et al., 2005; Zulfiqar et al., 2017). This nature-inspired approach to
808 prevent biodeterioration is attractive and recent compared to the use of biocide or silicones.
809 Consequently, more research is needed to improve superhydrophobic coatings before
810 commercializing durable and eco-friendly products (Dalawai et al., 2020).

811

812 **5. The efficacy of the photocatalysis mechanisms**

813 A promising and eco-friendly way to develop self-cleaning building materials relies on
814 using the photocatalysis process (Table 1) (Wang et al., 2014). This approach was discovered
815 more than a century ago in Germany (Coronado et al., 2013; Eibner, 1911). Its principle relies
816 on an advanced oxidation process (AOP) based on the absorption of photons by a photocatalyst
817 and the subsequent production of ROS (Ameta et al., 2018). Thanks to the high stability of
818 photocatalysts, this AOP has many applications in different fields: from converting water to
819 hydrogen gas to disinfection and use in antifouling coatings (Ameta et al., 2018).

820 • **5.1. Nature and commercially available compounds**

821 Most of the employed photocatalysts are semiconductors, as they can conduct electricity in
822 the presence of light and at room temperature (Ameta et al., 2018; Wang et al., 2014).
823 Semiconductors are defined by their bandgap comprised between 1.5 and 3.0 eV (the bandgap
824 is the energy difference between the valence band and the conduction band (Ameta et al., 2018).
825 For the photocatalysis-induced AOP, the semiconductor can simultaneously drive reduction
826 and oxidation of the substrate when the redox level of the substrate is lower than the conduction
827 band and higher than the valence band (Ameta et al., 2018; Wang et al., 2014). The most
828 commonly commercialized semiconductors are binary oxides such as titanium dioxides (TiO₂,
829 CAS: 13463-67-7) or zinc oxides (ZnO, CAS: 1314-13-2) (Chen et al., 2010). For example,
830 270 patents registered for ceramic roof tiles include the use of binary oxides for photocatalysis
831 (Ranogajec and Radeka, 2013). For example, this is the case with Erlus Lotus air® tiles, which
832 are coated with TiO₂ to reduce nitrogen oxide pollution (“Erlus Lotus Air®,” n.d.).

833 • **5.2 Historical and current use**

834 Photocatalysis was first mentioned in 1911 by German chemist Eibner, who studied the
835 effect of illumination of ZnO on the bleaching of Prussian blue, a dark blue pigment (Coronado
836 et al., 2013; Eibner, 1911). However, it was not until 1938 that Goodeve and Kitchener
837 discovered the photocatalytic effect of TiO₂ (Goodeve and Kitchener, 1938). These authors

838 provided the first description of ROS production induced by UV absorption and leading to
839 photooxidation (Coronado et al., 2013). Today, photocatalysis is employed in many different
840 fields (*i.e.*, wastewater treatment (Cantiello et al., 2020), air purification (“Erlus Lotus Air®,”
841 n.d.), antifouling coatings (Gladis et al., 2010)).

842 • 5.3 Efficacy

843 The efficiency of photocatalysts relied on ROS production coupled with the oxidation and
844 reduction process. These photochemical properties are intrinsic to semiconductors like TiO₂ or
845 ZnO (Ameta et al., 2018; Carretero-Genevri er et al., 2012; Coronado et al., 2013). The
846 interesting property which is exploited in the context of the present review is that ROS produced
847 during photocatalysis have deleterious effects on many types of microorganisms by degrading
848 coenzyme A or disrupting the cell wall membranes. For that reason, photocatalysts are also
849 used as antifouling or in disinfection treatments (Ganguly et al., 2018). The use of TiO₂ and
850 ZnO to prevent the biodeterioration of buildings and heritage monuments has been recently
851 reviewed (Ganguli and Chaudhuri, 2021). For instance, ZnO has shown better efficiency than
852 TiO₂ to prevent the biodeterioration of building materials, mainly by fungal growth, even
853 without light exposure (Loh et al., 2018). Moreover, higher efficiency of photocatalysts has
854 been shown when they are combined with metallic nanoparticles as silver (Becerra et al., 2020,
855 2018; Fellahi et al., 2013; Goffredo et al., 2019, 2017). Such TiO₂ association with Ag can be
856 used as coatings for outdoor treatment of limestone fa ades to prevent microalgal fouling
857 (Becerra et al., 2020). When a TiO₂ treatment is applied after a biocide treatment on stone, there
858 is a reduction in recolonization of the treated area (Ruffolo et al., 2017).

859 • 5.4 Advantages and drawbacks

860 One of the significant advantages of photocatalysts, compared to biocides or water-
861 repellents, is that they resist the firing along with the industrial production of building materials
862 (*i.e.*, around 1,000 C for ceramic roof tiles). Thus, they can be added during the manufacturing

863 process, and their usage does not need an additional coating step at the end of fabrication
864 (Gladis et al., 2010; Gladis and Schumann, 2011; Ranogajec and Radeka, 2013), facilitating the
865 industrialization of antifouling solutions based on photocatalysts. Moreover, photocatalysts and
866 especially TiO₂, are very stable over time (Hashimoto et al., 2005) and thus have shown suitable
867 antimicrobial activity and prevent biodeterioration over a long time (Dyshlyuk et al., 2020). For
868 example, photocatalysts are efficient on lichens, such as *Diploschistes actinostomus*, *Parmelia*
869 *conspersa*, *Parmelia ioxodes* (Table 1) (Pinna et al., 2012). However, TiO₂ is a white powder
870 that can alter building material color over time (Hashimoto et al., 2005). Photocatalysts also
871 increase the hydrophilicity of building materials, promoting microbial colonization due to a higher
872 water uptake level of the materials (Ranogajec and Radeka, 2013). The effectiveness of TiO₂
873 coatings is highly dependent on the substrate material and, in particular, its porosity and
874 roughness. However, many stone materials in historic buildings are very porous and rough
875 (Gladis and Schumann, 2011; Graziani et al., 2016, 2014; Quagliarini et al., 2018).

876 On the negative side, some studies revealed that some photocatalysts applied to prevent
877 building biodeterioration (especially facades) were detected at significant concentrations in the
878 aquatic environments where they are potentially harmful to many organisms (Kaegi et al.,
879 2008). Also, as pointed out by a few studies, the photocatalysts' size and nature could constitute
880 a serious issue for both human health and the environment (Remzova et al., 2019). The risks of
881 photocatalysts used as TiO₂ or ZnO nanoparticles in cosmetics to human health have been
882 pointed out, especially when inhaled (Dréno et al., 2019; Subramaniam et al., 2019). Regarding
883 the risks associated with their inhalation, some studies suggested a potential link between
884 exposure to TiO₂ nanoparticles and certain pulmonary and cardiovascular conditions in workers
885 exposed to these nanoparticles (Dréno et al., 2019; Pelclova et al., 2018, 2015; Rossnerova et
886 al., 2020).

887 • 5.5 Future and perspectives

888 Photocatalysis is clearly an up-and-coming solution for air-purification and self-cleaning of
889 building materials to prevent their colonization and biodeterioration (Loh et al., 2018; Nath et
890 al., 2016). The choice of photocatalysts, their size, and how they are incorporated in the process
891 of manufacturing materials remain to this day a matter of debate. Photocatalytic small
892 (nano)particles appear as the most efficient; however, the smaller the particles are, the higher
893 the risk that they will be inhaled during the industrial process, which may be harmful to the
894 health of operators (Remzova et al., 2019; Tobaldi et al., 2017). Nevertheless, the
895 ecotoxicological risks of nanoparticles remain a large subject of debate, and clearly, much more
896 scientific studies to evaluate their potentially hazardous effects remain to be conducted.
897 Moreover, managing the durability and efficiency of photocatalytic building materials is still
898 challenging since it depends on the main microbial colonizers, nature of the substrate, and
899 environmental conditions (Boonen et al., 2016; Goffredo et al., 2017). Finally, it is essential to
900 note that further studies are really needed to develop innovative and more efficient
901 photocatalytic building materials at supportable costs for this industry.

902

903 **6. Ionic liquids: promising eco-friendly synthetic molecules**

904 Lo Schiavo *et al.* recently underlined that ionic liquids could be valid alternatives to
905 conventional biocides for stone-built cultural heritage (Table 1) (Lo Schiavo et al., 2020). Ionic
906 liquids (ILs) are salts with a melting point $<100^{\circ}\text{C}$ comprising organic cations (imidazolium,
907 ammonium, pyrrolidinium, etc.) associated with inorganic anions (Cl^- , AlCl_4^- , PF_6^- , BF_4^- , NTf_2^- ,
908 , etc.) or organic anions (CH_3COO^- , CH_3SO_3^- , etc.) which are liquid around room temperature.
909 Their structure can be tuned to access physicochemical properties such as wide electrochemical
910 window, high thermal stability, and null vapor pressure. Due to their structural analogies with
911 conventional amphiphilic quaternary ammonium (QACs) species, ILs have an intense
912 antimicrobial activity since the cation is responsible for the primary electrostatic interactions

913 with cell walls (Pendleton and Gilmore, 2015). Consequently, ILs have been successfully
914 applied to clean calcium crust (CaCO_3 , CaSO_4 , CaC_2O_4) from stained glasses (Machado et al.,
915 2011) as well as from synthetic and natural varnishes (Pacheco et al., 2013). Phosphonium-
916 based ILs were also tested for corrosion crust removal from medieval glasses (Delgado et al.,
917 2017). For instance, it has been recently demonstrated that surface active ionic liquids (SAILs),
918 based on cholinium and dodecylbenzenesulfonate, have been tested to prevent the
919 biodeterioration of stone-built cultural heritage (Table 1). These SAILs have shown
920 antimicrobial activity on pure Gram-positive (*Micrococcus luteus*) and Gram-negative
921 (*Stenotrophomonas maltophilia*) bacteria, yeasts (*Cladosporium* sp.), hyphomycetes
922 (*Aureobasidium* sp.), and algae (*Chlorella* sp.) (De Leo et al., 2021).

923 Polyoxometalates (POMs) are also being considered as biocidal agents. POMs are a large
924 group of anionic polynuclear metal–oxo clusters with discrete and chemically modifiable
925 structures (Gumerova and Rompel, 2020; Miras et al., 2012). Generally based on group 6
926 transition metals (Mo, W), and sometimes group 5 (V, Nb, Ta), these closed 3-dimensional
927 frameworks are characterized by a wide and versatile range of physicochemical properties that
928 can be specifically tailored at a molecular level. Their polyanionic feature allows them to form
929 complexes with many proteins or peptides containing cationic residues through ionic bonds.
930 For these reasons, many reports have reported both a direct antibacterial activity and a
931 synergistic one with conventional antibiotics (Bijelic et al., 2018). For instance,
932 polyoxotungstates have been shown to exhibit antibacterial activities against *Helicobacter*
933 *pylori* (Inoue et al., 2005). Moreover, Gumerova *et al.* demonstrated that of the 29 different
934 POMS tested, the polyoxotungstate $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ showed the highest activity against
935 *Moraxella catarrhalis* (Gumerova et al., 2018). However, most of the inorganic POMs do not
936 exhibit biocidal activities strong enough to be exploited yet as coatings for building materials.
937 It is also worthy of mention that attempts have been made to combine the properties of

938 polyoxametalated anions and the organic cations coming from ionic liquids. In this way,
939 silicotungstate and phosphotungstate-based POM-ILs fused with long-chain quaternary
940 alkylammonium cations have been shown to exhibit an enhanced antifungal activity on
941 historical bricks (Rajkowska et al., 2020). Another study demonstrated that hydrophobic
942 polyoxotungstate POM-ILs could be used as suitable anti-corrosion and antibacterial coatings
943 for natural stones (Misra et al., 2018).

944

945 **7. “Natural compounds”: on the path to the discovery of sustainable** 946 **antifouling?**

947 We explained above that Nature is a source of inspiration for manufacturers and researchers,
948 particularly through the design of biomimetic materials like, for example, those imitating the
949 “lotus effect”. The natural environment is also a source of antifouling compounds, and more
950 especially plants and algae that are naturally resistant to microbial damage. Thus, naturalist
951 observations also inspire another type of biomimetic approach to discover efficient antifouling
952 compounds: observing nature to identify bioactive compounds before producing them at the
953 industrial scale. “Natural compounds”, *i.e.*, compounds that are not molecules purely
954 synthesized by industrial processes but primarily by natural organisms, are hypothesized to be
955 less toxic than purely synthetic alternatives. They thus appear as promising molecules to fight
956 biodeterioration. The scientific literature on natural biocides that can be used against
957 biodeterioration of stone cultural heritage is extensive (Fidanza and Caneva, 2019). More than
958 sixty natural substances, mainly essential oils and substances of plant origin, have been the
959 subject of published scientific evaluations for this type of application. However, in most cases,
960 their substantial cost of production makes them, for the moment, non-adapted to fight
961 biodeterioration at large scales.

962 7.1 Plants and essential oils

963 • 7.1.1 Nature and commercially available compounds

964 Many plants have shown antimicrobial properties, such as Chili peppers, Eucalyptus
965 globulus, *Melaleuca alternifolia* (tea tree), or *Thymus vulgaris* (Jeong et al., 2018; Omolo et
966 al., 2014; Palla et al., 2020) (Table 1). For peppers and especially species related to the genus
967 *Capsicum*, the active molecule has been identified and is called capsaicin (8-Methyl-N-vanillyl-
968 trans-6-nonenamide, CAS: 404-86-4) (Table 2) (Omolo et al., 2014). This compound has shown
969 antibacterial activities against many pathogens, such as *Vibrio cholerae* and *Staphylococcus*
970 *aureus* (Mokhtar et al., 2017; Omolo et al., 2014), and also antifungal properties (Martini et al.,
971 2014). Often, the active molecule produced by plants is available through the use of essential
972 oils (EOs) or purified secondary metabolites such as thymol (2-isopropyl-5-methylphenol,
973 CAS: 89-83-8), eugenol (2-Methoxy-4-(2-propenyl)phenol, CAS Number: 97-53-0) or
974 cinnamaldehyde (3-Phenylprop-2-enal, CAS: 104-55-2) (Table 2) (Jesus et al., 2015; Marchese
975 et al., 2016; Palla et al., 2020; Veneranda et al., 2018). EOs and secondary metabolites are
976 readily available commercially or from specialized chemical companies (e.g., Sigma-Aldrich).
977 The capsaicin and its synthetic equivalent, the N-vanillynonanamide (CAS: 2444-46-4), are
978 also easily purchased (Table 2).

979 • 7.1.2 Historical and current use

980 Plants and their derivatives as EOs have been employed for centuries for their natural
981 antimicrobial properties (Algburi et al., 2017; Nazzaro et al., 2013). The earliest documented
982 traces of the medicinal application of plants date back 5,000 years (Petrovska, 2012). Today, in
983 addition to being used in the pharmaceutical and aromatherapy industries, EOs are also applied
984 in the food industry (Gadea et al., 2017b; Palla et al., 2020). EOs and their component
985 (secondary plant metabolites) are also tested in conservation due to the need for new cleaning
986 procedures using less harmful molecules for both human health and cultural heritage

987 preservation (Fidanza and Caneva, 2019; Palla et al., 2020; Sasso et al., 2016; Veneranda et al.,
988 2018).

989 • **7.1.3 Efficacy**

990 Some EOs and plant secondary metabolites are very effective against bacteria, algae, and
991 fungi at low concentrations (Gómez de Saravia et al., 2018; Nazzaro et al., 2013; Owen and
992 Laird, 2018; Sasso et al., 2016; Veneranda et al., 2018). For instance, only 0,4 mg.mL⁻¹ of
993 oregano essential oil (OEO) is sufficient to inhibit the bacterial growth of methicillin-resistant
994 *Staphylococcus aureus* (*MRSA*) (Cui et al., 2019). Moreover, EOs have shown synergistic
995 interactions with antibiotics reducing drug resistance (Owen and Laird, 2018). However, their
996 action mechanisms remain poorly understood due to their high chemical variability and broad-
997 spectrum activities (Algburi et al., 2017; Owen and Laird, 2018). For example, OEO has been
998 demonstrated to affect cell membrane permeability, respiratory metabolism, energy
999 metabolism, and gene expression of *MRSA* (Cui et al., 2019). Essential oils are complex
1000 mixtures of active substances whose antimicrobial activities vary from one substance to
1001 another. OEO and its components, carvacrol (5-Isopropyl-2-methylphenol, CAS number 499-
1002 75-2) and thymol, are also described as putative efflux-pump blockers (Table 2) (Cirino et al.,
1003 2015). Finally, some EOs as of *Eucalyptus* sp. are quorum sensing (QS) inhibitors, and QS is a
1004 key bacterial mechanism involved in biofilm formation (more details below) (Algburi et al.,
1005 2017; Nazzaro et al., 2013; Szabó et al., 2010).

1006 • **7.1.4 Advantages and drawbacks**

1007 Due to their wide range of targets, EOs are promising in many different applications to
1008 avoid the use of antibiotics and biocides, such as cultural heritage preservation (Algburi et al.,
1009 2017; Fidanza and Caneva, 2019; Gadea et al., 2017b; Owen and Laird, 2018; Veneranda et al.,
1010 2018). Some EOs appear very efficient, even at low concentrations as described above (Nazzaro
1011 et al., 2013; Owen and Laird, 2018). Some of EOs or plant extracts such as Lavandin oil (CAS:

1012 91722-69-9) and geraniol (CAS: 106-24-1) are already included in the European Biocidal
1013 Products Regulation list (Article 95 of the Biocidal Products Regulation (BPR), as amended by
1014 Regulation (EU) No 334/2014 of 11 March 2014) (European Chemicals Agency, 2014;
1015 Veneranda et al., 2018). The most recently added biocidal plant compound was garlic extract
1016 (CAS: 8008-99-9) in April 2020 (European Chemicals Agency, 2020). These additions to the
1017 BPR list also highlight the interest of private companies in the development of new natural
1018 biocidal products. Many EOs have shown antimicrobial properties against various types of
1019 microorganisms, like cyanobacteria as *Nostoc* sp. and *Gloeocapsa* sp. (Table 1) (Bartolini and
1020 Pietrini, 2016; Cuzman, 2009; Devreux et al., 2015). For example, EO from *Melaleuca*
1021 *alternifolia* had been efficient against bacteria like *Micrococcus luteus* and *Bacillus subtilis*;
1022 and against fungi as *Aspergillus* sp. and *Cladosporium* sp. (Fidanza and Caneva, 2019;
1023 Mansour, 2013; Rotolo et al., 2016). In addition, EO from *Thymus vulgare* has also shown anti-
1024 algal effect on *Chlorella* sp. and *Aptacoccus* sp. (Bartolini and Pietrini, 2016; Fidanza and
1025 Caneva, 2019).

1026 Despite their enormous potential, the safety of EOs must be assessed. Especially in the
1027 medical field, where EO-antibiotic combinations need to be more closely studied and their
1028 potential toxicity measured before further development (Algburi et al., 2017; Owen and Laird,
1029 2018). For building materials, most of the studies were carried out *in-vitro* (Gómez de Saravia
1030 et al., 2018; Veneranda et al., 2018). Therefore, it is necessary to explore the possible
1031 interactions between EOs and building materials before considering their usage at larger scales.
1032 Finally, some natural products are pointed to their deleterious effects on human health. For
1033 example, while capsaicin and chili peppers derivatives are very efficient as antimicrobials or
1034 pain relievers (Martini et al., 2014; Omolo et al., 2014); but they are also very irritant, as shown
1035 by their use in pepper sprays (Oliveira Junior et al., 2020; Omolo et al., 2014). This is also the
1036 case of Geraniol (3,7-dimethylocta-trans-2,6-dien-1-ol, CAS: 106-24-1), which is one of the

1037 most important molecules in cosmetic industries for its antimicrobial activities (Chen and
1038 Viljoen, 2010) and can induce allergic reactions such as irritant contact dermatitis (Johansen et
1039 al., 2020).

1040 • **7.1.5 Future and perspectives**

1041 If we suppose low toxicity of EOs, and the use of these compounds does not induce
1042 deleterious effects on building materials, these substances may represent an up-and-coming
1043 alternative to purely synthetic compounds to prevent building biodeterioration due to their
1044 broad spectrum of activities and targets. However, a major obstacle to use this type of natural
1045 compound is their substantial cost to manufacturers, which is much higher than the cost of the
1046 conventional biocides currently in use. For example, natural products like geraniol are sold
1047 between 1 and 5€ per gram and EOs in between 50 and 100€ per kilogram, while solutions
1048 based on quaternary ammonium compounds (like Organcide QC50) are sold between 10 and
1049 20€ per kilogram.

1050 **7.2 “Natural” compounds: conclusions**

1051 Natural compounds are highly effective against a large number of targets (bacteria, fungi,
1052 algae) through a wide diversity of action mechanisms (QS inhibition, modification of cell
1053 permeability, or energy metabolism), and they can bypass the resistance of some bacteria to
1054 biocides (efflux pump inhibition). Consequently, they appear very promising to prevent the
1055 biodeterioration of building materials. They also could be mixed with conventional biocide as
1056 on temples in Angkor Vat (Cambodia), where they have shown excellent results (Charola and
1057 Salvadori, 2011). The “Mélange d’Angkor” is made of thymol, quaternary ammonium
1058 compounds, borax, copper-complex, Mergal S90, and S88, Zn-Omadine, Algophase (PHASE,
1059 Firenze, Italy), Parmetol DF 12 (Schülke & Mayr, Norderstedt, Germany). In the latter, the
1060 "Mélange d’Angkor" was applied in the field, and the cleaning effect lasted up to 10 years,
1061 depending on the site and time of treatment. However, the effectiveness of natural compounds

1062 has so far mainly been demonstrated *in-vitro*, and their potentially deleterious effects on
1063 materials remain unknown, as well as the cost of their application on industrial scales.

1064

1065 **8. Future research and development strategies to develop “green” and** 1066 **sustainable antifouling for building materials?**

1067 Throughout this review, an apparent contradiction exists in the challenge we discuss: On
1068 the one hand, antifouling compounds should present a very strong biocidal activity to prevent
1069 the development of very diverse microorganisms forming multispecies biofilms including
1070 various types of eukaryotes and prokaryotes. On the other hand, sustainable antifouling should
1071 ideally be compounds that have a low impact on health and the environment, thus, *a priori*, low
1072 biological activity. Thus, the goal of current research and development strategies is to find
1073 solutions to address this *a priori* unsolvable paradox (Lami, 2019). This analysis highlights the
1074 reason why the antifouling “miracle” compounds, which are advertised on the market from
1075 time-to-time, cannot completely solve the problem of biodeterioration on building materials.
1076 One potential solution is to target specific biological mechanisms that control biofilm
1077 development without killing the microbial cells, *i.e.*, inhibiting specific microbial functions (in
1078 other words, *antibiofilm* solutions that are not *biocide*).

1079 In this perspective, the development of quorum quenching compounds (QQ) appears
1080 extremely promising (Lami, 2019). The biofilm that grows on building materials promotes
1081 bacterial interactions, in particular by facilitating chemical communication between
1082 microorganisms; among those, one common type is named quorum sensing (QS) (Romani et
1083 al., 2021a; Xavier and Foster, 2007). QS is a coordinated response of the microbial community
1084 from a certain cell density (quorum), which involves the production of extracellular chemical
1085 signals (sensing) (Henke and Bassler, 2004). These signals accumulate in the immediate

1086 environment until they reach the level necessary to activate the transcription of specific genes
1087 (Whiteley et al., 2017). QS was first demonstrated in the marine model *Vibrio fischeri*, which
1088 emits bioluminescence when the cell concentration in the environment is sufficient (Whiteley
1089 et al., 2017). However, QS is involved in a wide range of bacterial mechanisms, including,
1090 among others, biofilm formation (Girard et al., 2019; Kalia, 2018). Therefore, inhibiting this
1091 key bacterial mechanism seems particularly promising in the fight against environmental
1092 biofilms (Algburi et al., 2017; Kalia, 2018), as QQs are not biocides but inhibit cell mechanisms
1093 involved in biofilm formation. Consequently, such compounds hold the promise to solve the
1094 paradox we raise previously, targeting the biofilm without presenting high cytotoxicity. Also,
1095 the resistance of microorganisms to these compounds is suspected of appearing at lower rates
1096 compared to that against biocides substances (Rémy et al., 2018).

1097 Interestingly, these bioactive compounds are frequently discovered, setting up biomimetic
1098 approaches (Scardino and de Nys, 2011), after an attentive observation of antifouling traits
1099 among natural species and in combination with an in-depth analysis of their microbiota
1100 (Tourneroché et al., 2019; Vallet et al., 2020). In addition to the EOs described above, some
1101 organisms are capable of producing anti-QS molecules (quorum quenchers), such as bacteria
1102 as *Bacillus* sp., *Pseudomonas* sp., *Rhodococcus* sp., and *Streptomyces* sp. or fungi as
1103 *Cladosporium cladosporioides*, and algae as *Stichococcus bacillaris*, which, interestingly, were
1104 also previously identified on building materials (Coutinho et al., 2015; Di Martino, 2016; Paul
1105 et al., 2018; Romani et al., 2021a, 2019; Urzì et al., 2010). This is also the case of the
1106 halogenated furanones discovered in *Delisea pulchra* (Manefield et al., 1999) or of the
1107 butyrolactones identified in the microbiota of the brown macroalga *Saccharina latissima*
1108 (Vallet et al., 2020). The best-known quorum quenchers are enzymes AHL-lactonases that
1109 hydrolyze QS compounds (the acyl-homoserine lactones) by cleaving the ester bond of their
1110 lactone ring (Paul et al., 2018). Despite these advances, more research and development efforts

1111 are needed to better understand the mechanisms of action of these promising compounds and
1112 their effective innocuity on health and the environment (Lami, 2019). Thus, the development
1113 of these new treatments will require more investment, and even if this research strategy appears
1114 promising, the road remains long before the commercialization of such products at large scales.
1115 Nevertheless, the challenge has been taken by a few startups, in partnership with academic
1116 research labs, like Green&GeneTK at the IHU Marseille, France, a consortium specialized in
1117 the production of anti-QS enzymes.

1118 Another promising strategy that has already produced interesting results in the field is the
1119 use of microorganisms capable of removing corrosive substances, especially on metal surfaces
1120 where aerobic biofilms have been shown to protect against corrosion by reactive oxygen species
1121 (Kip and Van Veen, 2015). For example, *Bacillus* sp. presented anti-corrosion activities related
1122 to the production of two enzymes, a catalase and a peroxidase. By contrast, strains that produced
1123 little or no catalase tended to induce the corrosion process (Karn et al., 2017). Certain non-
1124 corrosive microorganisms can also form a protective layer on materials (De Muynck et al.,
1125 2010). This method is used to prevent corrosion of stone, limestone, and concrete and is based
1126 on microbial carbonate precipitation (Kip and Van Veen, 2015). The carbonate precipitates
1127 (mainly calcium carbonate) produced by bacteria are similar to concrete and mortar, attach to
1128 them and thus strengthen the material, and can even fill and repair small cracks (Jonkers et al.,
1129 2010). For example, *Bacillus subtilis*, which has been identified on many building materials
1130 (Coutinho et al., 2015; Di Martino, 2016), can produce calcium carbonates. It has also been
1131 shown that the use of bacterial fractions containing their cell walls alone is sufficient to induce
1132 the production of calcium carbonates, thus avoiding the inoculation of living microorganisms
1133 on the materials (Perito et al., 2014).

1134

1135 **9. Conclusions: A toolbox and methodology for the development of**
1136 **innovative, efficient, and eco-friendly solutions: case by case analysis,**
1137 **multidisciplinary, integrative, and pragmatic approaches.**

1138 When considering the list of compounds and solutions reviewed here, it appears that no
1139 “gold standard” methodology against biodeterioration has been yet established. Such a
1140 reference approach would have to combine high efficiency against biofilms growth and their
1141 induced building biodeterioration, low production cost, and high ecological standards. While
1142 in the present state of scientific knowledge, the combination of these criteria appears too
1143 paradoxical to be solved (Figure 2). Some interesting, innovative research strategies presented
1144 in this review are currently being developed in research labs and might pave the way for the
1145 future. Furthermore, the recent development of "omics" approaches combining metagenomics,
1146 metatranscriptomics, metabolomics, and metaproteomics will also contribute to this quest in
1147 the near future (Stien et al., 2020, 2019). Indeed, such a multi-omics approach will help to point
1148 out novel and unsuspected metabolic pathways and mechanisms to serve as targets in the design
1149 of innovative solutions.

1150 In the present situation, since no “gold standard methodology” has yet been established, our
1151 recommendation would be to address the problem of biodeterioration on a case-by-case basis,
1152 adopting a multidisciplinary research strategy, associating the skills of biologists, chemists, and
1153 material designers. Such an approach enables to draw solutions adapted to each particular
1154 situation and type of biodeterioration (Liu et al., 2020). For example, this process of work was
1155 used to treat temples in Angkor Vat (Cambodia) (Warscheid and Leisen, 2011) and ruins of the
1156 archeological site of Milet (Turkey), where the black microbial biofilm needed to be removed
1157 as it enhanced the heating effect leading to a microcracking of the marble (Charola and

1158 Salvadori, 2011). On both sites, innovative case-by-case solutions were successfully designed
1159 without mechanical impact.

1160 The design of innovative solutions should systematically rely on a very detailed analysis of
1161 biofilm composition and activities, which consist of an in-depth analysis of the bacterial, algal,
1162 and fungal diversities (and functions) forming the deteriorating multispecies biofilms,
1163 combining the state of the art of culture-dependent and culture-independent methodologies
1164 (Romani et al., 2021a, 2019). From this precise assessment, different possible solutions can be
1165 considered and likely combined in a specific fashion for each specific case. For example, a pre-
1166 treatment with water-repellent coatings helps to lower the required concentrations of various
1167 types of biocides, which is a first step in the design of more ecologically friendly solutions
1168 (Romani et al., 2021b). Also, an in-depth analysis of the microbial composition colonizing
1169 building materials is essential to select the best biocide or coating to use, thus avoiding the use
1170 of non-essential compounds and their release in the environment. In this logic, targeting
1171 pioneering bacteria and pioneering biofilms, which can develop even on unexposed materials
1172 (Romani et al., 2019), appears to be one of the most promising strategies to lower the amount
1173 and concentrations of the applied antifouling compounds.

1174 In addition to the choice of chemicals, it is important to optimize their application to the
1175 materials. Thus, the development of adapted protocols for biocides has a significant impact on
1176 their effectiveness (Favero-Longo et al., 2020). For example, the effectiveness of different
1177 biocides is higher if the lichen thalli are hydrated before their use and if the biocidal substance
1178 is applied with a cellulose poultice. Similarly, when a hydrogel is used to apply a biocide
1179 solution to a polymicrobial patina, a high percentage of water loading is essential to ensure a
1180 deep antimicrobial action (Boccalon et al., 2021). The application of hydrogels delivering
1181 biocides has shown great results on stone (Gabriele et al., 2021); however, their use on highly

1182 porous stones is not recommended, as antimicrobial action remains superficial in such cases
1183 (Favero-Longo et al., 2020).

1184 As shown in this paper, fundamental scientific knowledge is necessary to prevent the
1185 biodeterioration of outdoor building materials efficiently. Today, all biocidal products used for
1186 building preservation are registered as preservatives or disinfectants in annex V of the BPR,
1187 EU 528/2012, which means that they are tested only on human pathogens. Also, the usage
1188 concentrations of these biocidal products are determined on the basis of such tests conducted
1189 on non-environmentally relevant microbial models. Such observation highlights the urgent
1190 need to isolate more representative microbial models from the environment and to test the
1191 effectiveness of current and future solutions in suitable biotests which rely on their culture
1192 rather than on representative human pathogens. Such effort will lead to better adapt current
1193 regulations and will allow the industry to improve the marketed solutions for the control of
1194 outdoor building materials biodeterioration.

1195 Collectively, all these observations reinforce the necessity to establish strong links between
1196 academic research labs and building materials manufacturers, to transfer the multidisciplinary
1197 scientific knowledge and tools, and to custom solutions to the end-user needs (Figure 2). Some
1198 countries develop governmental programs to favor the establishment of these academy-industry
1199 links. For example, the French government offers specific funding like the Ph.D. CIFRE
1200 program (which is leading the Ph.D. student to work at the interface in between academic labs
1201 and companies), or through the “Crédit Impôt Recherche”, which gives many financial
1202 advantages to the companies that invest in research in partnership with the academic labs (tax
1203 reduction). The creation of deep tech startups is also encouraged and allows public financial
1204 support.

1205 The development of innovative and sustainable solutions will rely on a significant
1206 investment throughout the entire production chain: in fundamental research to develop

1207 alternative and lower toxic compounds, in applied research to select the best solutions, in
1208 production systems to industrialize at large scales the innovative solutions, in
1209 commercialization and marketing to raise end-user awareness to the health and environmental
1210 challenges and undoubtedly to increase customer tolerance to biodeterioration.

1211

1212 **Credit authorship contribution statement**

1213 This review was built according to the guidelines of the Transparent Reporting of
1214 Systematic Reviews and Meta-Analysis extension for scoping reviews (PRISMA-Scr).
1215 Electronic sources were Medline (via Pubmed), Scopus (Elsevier: Amsterdam, The
1216 Netherlands), and Web of Science (Clarivate Analytics: Philadelphia, PA, USA). Papers were
1217 retrieved using the following keywords: biodeterioration + building material (or stone or
1218 ceramic) + cleaning procedures, biodeterioration + building material (or stone or ceramic) +
1219 type of biocide, biodeterioration + building material (or stone or ceramic) + water repellent,
1220 biodeterioration + building material (or stone or ceramic) + natural compounds. Research
1221 excluded from this analysis were articles related to indoor materials and articles related to
1222 human health.

1223

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1231

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2045 **Figures**

2046 Figure 1: Biofilm formation pattern. (a) Bacterial adhesion, (b) pioneering biofilm
2047 formation embedded in the extracellular matrix, and then (c) pigmented mature biofilm
2048 development. During all these stages, many microbial functions are expressed as
2049 communication (quorum sensing), cooperation (nitrification, microbial consortia),
2050 biodeterioration processes (extracellular enzymes, acids, hyphae), competition (antimicrobial
2051 and quorum quenching compounds), and resistance and tolerance to antifouling treatments
2052 (inhibited diffusion, sublethal concentrations, tolerance forms, resistance genes).

2053 Figure 2: Targets (bacteria, algae, fungi), mechanisms of action (cell membrane
2054 modification, metabolism modification, ROS production, adhesion inhibition, quorum sensing
2055 inhibition), commercial interests (efficiency, lixiviation, duration, cost, commercial

2056 availability), and side-effects of antifouling molecules (human health, environment, building
2057 materials); (a) biocides, (b), water-repellents, (c) superhydrophobic materials, (d)
2058 photocatalysts, and (e) natural compounds.

2059