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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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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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 – TiO_2: titanium dioxide – ZnO: zinc oxide.

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Abstract

All types of building materials are rapidly colonized by microorganisms, initially through an invisible and then later a visible biofilm that leads to their biodeterioration. Over centuries, this natural phenomenon has been managed using mechanical procedures, oils, or even wax. In modern history, many treatments such as high-pressure cleaners, biocides (mainly isothiazolinones and quaternary ammonium compounds) are commercially available, as well as preventive ones, such as the use of water-repellent coatings in the fabrication process. While all these cleaning techniques offer excellent cost-benefit ratios, their limitations are numerous. Indeed, building materials are often quickly recolonized after application, and microorganisms are increasingly reported as resistant to chemical treatments. Furthermore, many antifouling compounds are ecotoxic, harmful to human health and the environment, and new regulations tend to limit their use and constrain their commercialization. The current state-of-the-art highlights an urgent need to develop innovative antifouling strategies and the widespread use of safe and eco-friendly solutions to biodeterioration. Interestingly, innovative approaches and compounds have recently been identified, including the use of photocatalysts or natural compounds such as essential oils or quorum sensing inhibitors. Most of these solutions developed in laboratory settings appear very promising, although their efficiency and ecotoxicological features remain to be further tested before being widely marketed. This review highlights the complexity of choosing the adequate antifouling compounds when fighting biodeterioration and proposes developing case-to-case innovative strategies to raise this challenge, relying on integrative and multidisciplinary approaches.

Keywords

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

1. Introduction

Biodeterioration of mineral building materials (*i.e.*, stone, ceramics, cement, concrete) is a global and expensive problem for manufacturers and building owners (Romani et al., 2019; Saiz-Jimenez, 2001; Warscheid and Braams, 2000). Biodeterioration consists of the natural degradation of these materials by (micro)organisms (Guiamet et al., 2013; Warscheid and Braams, 2000), which grow as multispecies biofilms that develop on all types of surfaces (Di Martino, 2016; Romani et al., 2019). Such biofilms are usually composed of multiple interacting microorganisms (bacteria, fungi, algae) (Krakova et al., 2015) embedded in a protective and very resistant polymeric matrix (Figure 1) (Flemming and Wingender, 2010). Vital microbial activities, such as cell division, biofilm formation, acid production, and redox activities, lead to the long-term degradation of materials (Guiamet et al., 2013). This phenomenon is also known as microbiologically-influenced or microbially-induced corrosion (MIC) (Enning and Garrelfs, 2014). Biofilms that grow on building materials are initially invisible but turn visible with time, as their development leads to thick and pigmented structures. Finally, the last step of biodeterioration implicates the colonization of such a mature biofilm by mosses or higher plants, especially on stones (Coutinho et al., 2015; Gulotta et al., 2018; Li et al., 2018; Q. Li et al., 2016; Norma Italiana UNI 11182, 2006).

According to the building materials industry, the first problem with microbial colonization is its unsightly aspect (Coutinho et al., 2015; Di Martino, 2016). Indeed, the biofilm that develops on the materials is often pigmented, which forms unaesthetic dark or green streaks or spots (Di Martino, 2016), which is undesirable since customers expect their product to stay stable over time (The Brick Industry Association, 2018). The unaesthetic aspect of the darkening of buildings and other materials is also an essential aspect of historic monument conservation (Di Martino, 2016; Grabek-Lejko et al., 2017; Saiz-Jimenez, 2001). Therefore, manufacturers of building materials invest massively in strategies to prevent their products to rapidly turn green or black, and building owners face significant expenses to clean and restore materials that have deteriorated over time. Thus, in addition to the unsightly appearance, biodeterioration causes less visible but more significant damages, including the modification or loss of physical properties of many types of materials (Coutinho et al., 2015). Indeed, as the biofilm grows, surface and deep cracks increasing the porosity of materials are observed (Berdahl et al., 2008; Coutinho et al., 2015). In addition, this increased porosity facilitates the colonization of materials by other microorganisms and promotes their growth. Furthermore, many colonizing microorganisms accelerate deterioration due to the metabolites they produce, such as organic acids (Dubosc, 2000). Overall, the weakening of materials caused by biofilms development leads to faster decay by accelerating the effects of rain or freeze/thaw events (Berdahl et al., 2008; Gladis and Schumann, 2011; Joseph, 2021). Finally, advanced biodeterioration results in the loss of the structural or thermal insulation, drainage, or solar reflectance (proportion of light reflected from the surface of a material) of the materials (Berdahl et al., 2008; Pena-Poza et al., 2018).

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

The ecotoxicity of commercial large-spectrum and aggressive biocides is a significant factor associated with their use on outdoor building materials, and the regulations concerning these compounds are increasingly restrictive (Scheerer et al., 2009; Tiano, 2016; Warscheid and Braams, 2000). The biocidal products that can be used for preventive or curative treatments of outdoor building materials are classified in product type (PT) 2 of main group 1 corresponding to disinfectants, and PT 10 of main group 2 corresponding to preservatives in annex V to the Biocidal Products Regulation (BPR), Regulation (EU) 528/2012 (Commission Européenne, 2012). All these products target both microbial and algal organisms. While the costs of the fight against biodeterioration are challenging to evaluate, they will undoubtedly rise in the future since it will include not only the cost of treatments (i.e., biocides, paints) but also the costs associated with their application in safe conditions for customers and likely the costs associated with their environmental impact (Gaylarde et al., 2003; Guézennec, 2017).

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

2. Mechanical cleaning approaches

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

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

3. The extensive use of wide-spectrum biocides.

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

3.1 Isothiazolinones

- #### 3.1.1 Nature and commercially available compounds

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

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

- 3.1.2 Historical and current use

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

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

- 3.1.3 Efficacy

ITs are wide-spectrum biocidal molecules, particularly effective in combating the biodeterioration of building materials. They are typically reported as more bioactive when compared to quaternary ammoniums (benzalkonium chloride), especially at low (<5%) concentration ranges (Favero-Longo et al., 2018). The biocidal efficiency of ITs is based on their electrophilic nature. They are transported into cells by active transport, where they interfere with many cell processes (Williams, 2007). In particular, ITs block O_2 consumption of cells, and consequently, all aerobic processes cease; energy production (ATP) is reduced, slowing down metabolism and growth (Williams, 2007). ITs also inhibit several types of enzymes, including dehydrogenases (*i.e.*, pyruvate, NADH-, lactate dehydrogenase) as well as the adenosine triphosphatase. The inhibition of these enzymes interrupts the TCA cycle, thus perturbating the entire cell metabolism (Williams, 2007). Besides, ITs also oxidizes thiol-containing cytoplasmic and membrane-bound molecules, including those in numerous enzymes' active sites (Williams, 2007). These oxidations also lead to inhibition of metabolism (Favero-Longo et al., 2018). Collectively, all these effects induced by ITs actively damage cells, leading to the production of many free radicals or reactive oxygen species (ROS), which, combined with the inhibition of cell repair mechanisms, quickly leads to the death of (micro)organisms (Williams, 2007).

- #### 3.1.4 Advantages and drawbacks

One of the major advantages of ITs is that they act on a wide range of (micro)organisms (*i.e.,* bacteria, fungi, lichens, algae) over a wide pH range (pH 1 to 11) (Favero-Longo et al., 2017; Garcia-hidalgo et al., 2016; Silva et al., 2020). Thus, these compounds can attack very diverse types of multispecies biofilms under numerous environmental conditions. For example, ITs are efficient on filamentous fungi such as *Cladosporium* sp., *Penicillium* sp., and *Fusarium* sp.; but ITs are not effective on cyanobacteria (Table 1) (Barrionuevo and Gaylarde, 2011). As preservatives, the MIT/CMIT combination is one of the most cost-effective solutions currently known (Karsa and Ashworth, 2007). However, some commercial products containing ITs may cause alterations to stone, especially limestone and granite surfaces, after application (Tirado Hernández et al. 2015; Sanmartín et al. 2020). Moreover, the safety of these products has now been questioned by different studies (Thomsen et al., 2018; Wieck et al., 2016). ITs are known to be responsible for contact allergies, called contact dermatitis (Garcia-hidalgo et al., 2016). Humankind is increasingly affected by ITs but understanding this impact remains challenging to estimate due to the diversity of exposure sources (Garcia-hidalgo et al., 2016; Wieck et al., 2018, 2016). For instance, occupational sources of exposure remain difficult to determine due to the lack of information on the composition of marketed products (Garcia-Hidalgo et al., 2018; Ripert et al., 2012).

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

- 3.1.5 Future and perspectives

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

3.2 Quaternary ammonium compounds

- 3.2.1 Nature and commercially available compounds

Quaternary ammonium compounds (QACs) are the most commonly used biocides after ITs (Table 1). QACs are composed of a quaternary nitrogen atom surrounded by four organic functional groups, so the nitrogen is permanently positively charged (Mulder et al., 2017). An anion balances this charge, usually a chloride or bromide ion, and therefore, QACs exist in the form of water-soluble salts (Mulder et al., 2017; Nuńez et al., 2004). The functional groups (R) include at least one long-chain alkyl group, while the others are methyl, benzyl, or ester groups (Tezel and Pavlostathis, 2011). The most commonly employed biocide QACs are benzalkonium chloride (BAC, CAS: 121-54-0) (Gadea et al., 2017a; Mulder et al., 2017; Nuńez et al., 2004); benzalkonium bromide (DB, CAS: 91080-29-4) (Gadea et al., 2017a), didecyldimethylammonium chloride (DDMAC, CAS: 7173-51-5) (Nuńez et al., 2004), alkyl dimethylbenzyl ammonium chloride (ADMAC, CAS: 8001-54-5), and alkyl trimethylammonium compounds (ATMAC, CAS: 61789-18-2) (Table 2) (Mulder et al., 2017; Nuńez et al., 2004). In BAC-homolog compounds, the nitrogen atom is surrounded by a benzyl group, two methyl groups, and an alkyl chain of variable length (C8 to C18). The highest biocidal activity is associated with C12-C14 homologs, which are the main components of disinfection products (Mulder et al., 2017). The most commonly consumed BACs are C12-BAC, C14-BAC, and C16-BAC. Each homolog has different biocidal ranges. Indeed, C12-BAC has been demonstrated to be effective against yeasts and fungi, while C14-BAC against Gram-positive bacteria and C16-BAC targets Gram-negative bacteria (Nuńez et al., 2004).

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BACs were introduced in 1935 by Gerhard Domagk as zephiran chlorides (Price, 1950). Since they were first commercialized, their use has continuously grown, and their applications diversified. Today, BACs are widely used for domestic applications (softeners, conditioners, or medication for the ENT (eye, nose, throat) therapy); and as disinfectants for industrial, agricultural, and clinical areas (Merchel Piovesan Pereira and Tagkopoulos, 2019; Zhang et al., 2015). Finally, BACs are applied to building materials (walls, floors, roofs, pools, woods) to prevent their biodeterioration (Merchel Piovesan Pereira and Tagkopoulos, 2019). Thus, protocols using DDMAC are effective for the preventive and curative control of the greening of historic building materials (Nowicka-Krawczyk et al., 2019). DDMAC associated with OIT in ROCIMA™ 103 (Dow®) induces in-depth killing of fouling microorganisms and prevents most biological recolonization of sandstone and marble tombs surfaces for a period of five years after treatment (Mascalchi et al., 2020). The effectiveness of benzalkonium chloride treatment in preventing bacterial recolonization of stone was also observed after the treatment of the granite walls of the San Martiño Pinario Monastery in Santiago de Compostela (NW Spain) (Sanmartín and Carballeira, 2021). QACs are components of several cleaning and disinfection solutions such as Algicid-Plus (Keim, DDMAC 0.36% and OIT 0.081%), Preventol® RI50 and R180 (Lanxess), Organcide QC50 (formerly Vitalub QC50, France Organo Chimique, ADMAC 50%, used in solution between 3 and 5%), Algidal (Algimouss Pro, CAQ C12-C16 20%), Sikagard® Stop Algues Pro (Sika®), and Dalep PE (Dalep®).

3.2.3 Efficacy

The biocidal effects of QACs rely on their ability to lyse cells by disrupting lipid bilayers. The cationic nitrogen interacts with the phospholipid head *via* ionic interactions, while the alkyl chain of quaternary ammonium integrates into the hydrophobic tails of phospholipids through hydrophobic interactions (Heerklotz, 2008). Such interplays increase surface pressure in the exposed part of the membrane and decrease its fluidity. Thus, the cell membrane is rapidly disintegrated (Tezel and Pavlostathis, 2011). Even when QACs are present at non-lytic or sub-inhibitory concentrations in the environment (*i.e.,* below the minimum inhibitory concentration), they are reported to disrupt microorganisms by inhibiting specific membrane processes such as solute transport and cell wall biosynthesis (Tezel and Pavlostathis, 2011). However, at these low concentrations, QACs can also increase biofilm formation and induce oxidative stress, amplifying genetic variation in some microorganisms that may lead to microbial resistance (Gadea et al., 2017a; Houari and Di Martino, 2007; Tezel and Pavlostathis, 2015).

- 3.2.4 Advantages and drawbacks

The success of QACs relies on their multiple biological targets and their wide range of applications. They also have shown efficiency on numerous microorganisms, like fungi as *Aspergillus* sp., *Penicillium* sp., *Chaetomium* sp. (Isquith et al., 1972), and lichens as *Diploschistes actinostomus*, *Parmelia conspersa*, *Parmelia ioxodes* (Table 1) (Pinna et al., 2012). Their multiple usages and low production cost make these molecules the best-selling biocides along with ITs (Merchel Piovesan Pereira and Tagkopoulos, 2019; Tezel and Pavlostathis, 2011). As they are widely consumed, they are also released in large amounts into the environment during their production and use. It is estimated that approximately 25% of the QACs are directly discharged into the environment as a result of their multiple usages (Tezel and Pavlostathis, 2011). For example, QACs are released into nature at high concentrations (5 to 30 $mg.L^{-1}$) from roof runoffs, even after several months after tiles' treatment (Gromaire et al., 2015). Their long-term effects on ecosystems and human health are still poorly understood (Zhang et al., 2015). Nevertheless, it has been shown that their accumulation in the environment leads to the development of drug-resistant microorganisms (Merchel Piovesan Pereira and Tagkopoulos, 2019; Mulder et al., 2017). The main mechanisms of microbial adaptation to QACs are the same as those responsible for antibiotic resistance, such as modification of membrane structure and composition, improvement of biofilm formation (which protects microorganisms), lateral acquisition of genes coding various types of efflux pumps, and overexpression of these efflux pump systems (Gadea et al., 2017a; Slipski et al., 2017; Tezel and Pavlostathis, 2015). Consequently, the development of bacterial populations resistant to QACs also potentially increases antibiotic resistance in ecosystems (Gadea et al., 2017a; Kim et al., 2018). It has already been shown that some nosocomial outbreaks were due to resistant pathogens to antiseptics or contaminated disinfectants, especially those based on QACs and those using BACs as major active compounds (Weber et al., 2007). Microorganisms on building materials exposed to QACs can adapt and thus promote biodeterioration by resisting current treatments (Gadea et al., 2017a; Tezel and Pavlostathis, 2015). The effectiveness of quaternary ammoniums is influenced by the chemical composition and the physical properties of the material to which they are applied (Favero-Longo et al., 2017). The application of solutions containing QACs to porous materials like sandstone can lead to their penetration and their gradual release, resulting in the exposure of microorganisms and other algae to low concentrations of biocides over a relatively long period (Favero-Longo et al., 2017). This process may facilitate the induction of a decrease in the sensitivity of the target organisms to the biocides. Finally, QACs are considered one of the most toxic products among biocides with ITs and antifouling products (Roy, 2020). BACs are responsible, for instance, for skin and respiratory irritations, and they are considered to be skin sensitizers (Merchel Piovesan Pereira and Tagkopoulos, 2019). As with ITs, the application of commercial products containing QACs can lead to alterations in the stone material (Sanmartín et al., 2020; Tirado Hernández et al., 2015).

- 3.2.5 Future and perspectives

As with ITs, the use of QACs will be increasingly regulated in a near future. For example, since 2016, the EU has drastically reduced the number of BACs allowed in food products and has banned them in antiseptic hand and body soaps. Similarly, the US Food and Drug Administration (FDA) is considering banning BACs in these same products (Merchel Piovesan Pereira and Tagkopoulos, 2019). Moreover, CAQs have been reported to be toxic to various aquatic organisms, such as *Daphnia magna* and *Criodaphnia dubia*, where they are highly poisonous at lower concentrations (0.4 to 4 $ng.L^{-1}$) than those found in the environment (on the order of $mg.L^{-1}$) (Lavorgna et al., 2016). The long-term effects of CAQs are also of serious concern due to their ecotoxicity, bioavailability, and possible interactions with other chemicals (Lavorgna et al., 2016; U.S. Environmental Protection Agency (EPA), 2006).

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

3.3 Other types of widely-used biocides

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

• 3.3.1 Sodium hypochlorite

Among those other types of broad-spectrum biocides utilized to clean building materials is sodium hypochlorite (CAS: 7681-52-9) (Table 2), also known as bleach (Table 1). This compound is, for example, commercialized under the names Clorox® or 30 seconds® outdoor cleaner. Sodium hypochlorite is cheap and rapidly efficient on a wide range of microorganisms (Fukuzaki, 2006). For instance, sodium hypochlorite is effective on filamentous green algae and cyanobacteria (Pozo-Antonio et al., 2017). However, this application could have deleterious effects on metals or stones, as its degradation can lead to the formation of chlorinated compounds that are toxic to aquatic organisms (Fukuzaki, 2006). Bleach may also affect energy metabolism and damage DNA (Emmanuel et al., 2004). Besides, sodium hypochlorite is a harmful compound responsible for mucosal irritations (Fukuzaki, 2006).

- 3.3.2 Acid compounds

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

- 3.3.3 Chlorinated phenol compounds

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

- 3.3.4 Other compounds broad-spectrum biocides

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

3.4 Innovative use of biocides

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

Aspergillus brasiliensis by measuring the content of ergosterol, a method used to estimate the level of mold infestation in buildings (Koziróg et al., 2018). Additionally, it has been shown that the antimicrobial efficiency of these compounds depends on the length and type of spacer as well as their hydrophobic counterpart. As expected, diquaternary ammonium geminis of 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 shown to exhibit a higher antimicrobial activity against gram-positive/negative organisms and *Candida albicans* than "plain" hexadecyltrimethyl ammonium bromide (Diz et al., 1994). Also, Winnicki *et al*. showed the anti-algal activity of pentylene-1,5-bis(dimethyl dodecylammonium bromide) against *Chlorella*, single-celled green freshwater algae also known to foul industrial cooling systems and building facades (Table 1) (Winnicki et al., 2021).

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

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

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

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

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

4.1 Conventional water-repellent treatments

- ### 4.1.1 Nature and commercially available compounds

Different water-repellents are available on the market, but the most popular ones are all silicone derivatives (Table 1) (Roos et al., 2008). These compounds consist of an inorganic network of Si-O-Si bonds with an organic pendant group bearing by silicon atoms. In antifouling applications and water-repellent treatments, organic pendant groups are usually alkyl chains or aromatic groups due to their intrinsic hydrophobic character. Whatever the precursors used in antifouling or water-repellent treatments, the chemistry involved in the production of silicone derivatives remains the same and is the sol-gel chemistry implying hydrolysis and condensation reactions (Brinker and Scherer, 2013; Iler, 1979). Thus, silicone derivatives could be produced starting with organosilanes, siloxanes, and/or siliconates. Organosilanes are monomeric species containing at least one hydrolytically sensitive group, mainly chloride atom or alkoxy group (OR), which could undergo hydrolysis (formation of reactive silanol Si-OH) and condensation reactions allowing the growth of Si-O-Si backbone and/or covalent bonding on a substrate. Organosilanes also possess one or more organic substitutions linked to a silicon atom with a hydrolytically stable Si-C bond, silicon atom being tetravalent. Siliconates are their basic salts, and siloxanes correspond to their oligomeric or polymeric forms.

Regarding antifouling of building materials, alkyltrialkoxysilanes such as triethoxyisobutylsilane (CAS: 17980-47-1), *N*-octyltriethoxysilane (CAS: 2943-75-1), and iso-octyltriethoxysilanes (CAS: 35435-21-3) are the most utilized compounds (Table 2) (Roos et al., 2008). Interestingly, when the alkyl chain is long (C12-C16), the resistance of these molecules to alkalis is more important, making them able to penetrate deeply into a substrate such as concrete (Roos et al., 2008; Urzì and De Leo, 2007). In comparison, siloxanes have a much more complex structure due to their oligomeric or polymeric state (Roos et al., 2008). Siloxanes, which are liquid due to their low intermolecular forces, have better thermal stability than silanes. Still, they cannot penetrate a substrate as deeply as monomeric silanes because of a steric hindrance (Roos et al., 2008). As they are also alkali-resistant, they can be used on concrete. However, they are much better suited to porous substrates such as ceramics (i.e., bricks, ceramic roof tiles) and stone (Roos et al., 2008; Urzì and De Leo, 2007). Organo-modified siloxanes are mainly used for building material protection, as their methyl groups around the silicon atom are replaced by other organic groups (Roos et al., 2008). Finally, siliconates are smaller molecules than silanes and siloxanes; therefore, they provide the deepest penetration (Urzì and De Leo, 2007). They also present no water sensitivity, unlike organosilane and siloxane species, and they are water-soluble, meaning that they are fully compatible with water-based processes and less expensive. Commercially available water-repellents include the following molecules: alkyl alkoxysilane (Hydrophase superfici supplied by Phase), alkyltrialkoxysilane (Hydrophase malta PH91503, Phase) (Urzì and De Leo, 2007), trimethoxy-(2,4,4-trimethylpentyl)silane (CAS: 34396-03-7) (Sikaguard® Roof Protection, Sika), polydimethylsiloxane (Rhodorsil RC80, Phase) (Urzì and De Leo, 2007), or potassium methylsiliconate (or potassium methylsilanetriolate, CAS: 031795-24-1) (Table 2) (SILRES® BS 16, Wacker).

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

- 4.1.2 Historical and current use

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

4.1.3 Efficacy

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

4.1.4 Advantages and drawbacks

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

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

Evaluation of advantages and drawbacks of water repellents remains a complex task as there is a gap between nature as well as the importance of biofilms' development and the type of water-repellent treatments sprayed on the construction or the cultural heritage preservation fields. The effectiveness of some of these water-repellents to prevent microbial colonization of stone or mortars has been tested in various studies (Moreau et al., 2008; Pinna et al., 2012; Urzì and De Leo, 2007). The main results of the work published by Urzì and De Leo pointed out that applying a hydrophobic compound alone was not sufficient to stop the development of biofilm over 15 months of exposure and that only the combined use of water-repellent and a biocidal substance reduced the colonization of materials by algae and bacteria (Pozo-Antonio et al., 2016; Urzì and De Leo, 2007). Moreover, they do not lower the colonization of materials by "black" fungi such as *Alternaria* sp. or *Cladosporium* sp., which are the most resistant to chemical treatments (Hallmann et al., 2011; Krause et al., 2006; Romani et al., 2021b; Urzì and De Leo, 2007). Combining polysiloxane with copper nanoparticles reduces biocolonization and blackening of marble surfaces (Pinna et al., 2012). When treating successively with a water repellent and a biocide, the question of the order of application of each chemical arises (Moreau et al., 2008). A water-repellent applied after a quaternary ammonium treatment loses effectiveness. When the biocide is used after the water repellent, the surface hydrophobicity of the stone is reduced, and the biocide penetrates little into the material. Treating a surface previously treated with a water repellent with a quaternary ammonium compound can remove the biofouling that has developed at a given time but cannot prevent recolonization in the longer term (Moreau et al., 2008). Nevertheless, we have some clues about the efficiency of silicone-based coatings towards the development of biofilms in marine fouling since they are commercially used as fouling release coatings (Lejars et al., 2012).

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

- 4.1.5 Future and perspectives

The use of water-repellents is widespread in the construction industry, which has successfully adapted to environmental concerns to propose safer products (Charola, 2001; Roos et al., 2008). However, to properly apply water-repellents and avoid risk for the materials (Sauder, 1999), a "holistic approach" is needed. This means that it is necessary to consider the treatment, application, and the substrate for successful waterproofing (Charola, 2001, 1995). Otherwise, an innovative approach consists of creating superhydrophobic surfaces on the building materials (see below). In this regard, some silicones are promising, such as poly(dimethylsiloxane) (CAS: 70131-67-8) (Table 2) (Amara et al., 2018). From a regulation and environmental point of view, since oligomeric-polymeric silicone derivatives could be considered as microplastics, their release from substrates could be limited and even forbidden in the future (ECHA, 2019).

4.2 The case of superhydrophobic materials

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

4.2.1 Nature and commercially available compounds

The design of silicone-based superhydrophobic surfaces is generally achieved by two different pathways: the top-down approach and the bottom-up strategy (Dalawai et al., 2020; L. Li et al., 2016; Niu et al., 2020; Wang et al., 2020). The top-down allows the formation of superhydrophobic surfaces by selective matter removal, while the bottom-up approach corresponds to the assembly of precursors (monomeric, oligomeric, or polymeric chemical species, nanoparticles, microparticles …). The top-down approach is generally a two-step procedure involving first surface etching (either physical or chemical) leading to a patterned master and then forming a master negative replica with silicone derivatives. The second step usually implies pouring silicone prepolymers over the master, followed by curing and peeling off phases (Xia and Whitesides, 1998). Alternatively, some authors have directly modified silicone rubbers by laser irradiation and/or chemical etching (Wang et al., 2020). Concerning the second strategy, *i.e.,* the bottom-up approach, it generally involves the preparation of a solution containing silicon precursors, solvents, particles and nanoparticles, and catalysts. This solution is next deposited on the surface of the substrate, and evaporation of volatile species (solvent) leads to the formation of the superhydrophobic surface by a multiscale component assembly. A subsequent treatment (often thermal or UV curing) allows the stiffening of the superhydrophobic coating. The deposition step could be achieved by dip-, spin- or spray-coating. It appears thus that the bottom-up approach is much more convenient for treating building materials since its synthesis procedure is fully compatible with outdoor treatments, especially when spray-coating on large surfaces with commercial equipment is required (Faustini et al., 2018). Several commercialized superhydrophobic paint are currently marketed, such as SuperCN™ (NEI Corporation), NeverWet® anti-icing coating, HydroFoe™ (LotusLeaf Coatings), Lotusan®, (Sto) (Sto, 2020). Today, in addition to building materials, superhydrophobicity is under development for many applications such as photovoltaic devices, fabrics, and textiles, anti-corrosion, anti-snow, and freeze and anti-reflective (Dalawai et al., 2020).

- #### 4.2.2 Historical and current use

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

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

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

- 4.2.3 Efficacy

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

- 4.2.4 Advantages and drawbacks

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

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

- 4.2.5 Future and perspectives

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

5. The efficacy of the photocatalysis mechanisms

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

• 5.1. Nature and commercially available compounds

Most of the employed photocatalysts are semiconductors, as they can conduct electricity in the presence of light and at room temperature (Ameta et al., 2018; Wang et al., 2014). Semiconductors are defined by their bandgap comprised between 1.5 and 3.0 eV (the bandgap is the energy difference between the valence band and the conduction band (Ameta et al., 2018). For the photocatalysis-induced AOP, the semiconductor can simultaneously drive reduction and oxidation of the substrate when the redox level of the substrate is lower than the conduction band and higher than the valence band (Ameta et al., 2018; Wang et al., 2014). The most commonly commercialized semiconductors are binary oxides such as titanium dioxides (TiO_2, CAS: 13463-67-7) or zinc oxides (ZnO, CAS: 1314-13-2) (Chen et al., 2010). For example, 270 patents registered for ceramic roof tiles include the use of binary oxides for photocatalysis (Ranogajec and Radeka, 2013). For example, this is the case with Erlus Lotus air® tiles, which are coated with TiO_2 to reduce nitrogen oxide pollution (“Erlus Lotus Air®,” n.d.).

• 5.2 Historical and current use

Photocatalysis was first mentioned in 1911 by German chemist Eibner, who studied the effect of illumination of ZnO on the bleaching of Prussian blue, a dark blue pigment (Coronado et al., 2013; Eibner, 1911). However, it was not until 1938 that Goodeve and Kitchener discovered the photocatalytic effect of TiO_2 (Goodeve and Kitchener, 1938). These authors provided the first description of ROS production induced by UV absorption and leading to photooxidation (Coronado et al., 2013). Today, photocatalysis is employed in many different fields (*i.e.,* wastewater treatment (Cantiello et al., 2020), air purification ("Erlus Lotus Air®," n.d.), antifouling coatings (Gladis et al., 2010)).

- ### 5.3 Efficacy

The efficiency of photocatalysts relied on ROS production coupled with the oxidation and reduction process. These photochemical properties are intrinsic to semiconductors like TiO_2 or ZnO (Ameta et al., 2018; Carretero-Genevrier et al., 2012; Coronado et al., 2013). The interesting property which is exploited in the context of the present review is that ROS produced during photocatalysis have deleterious effects on many types of microorganisms by degrading coenzyme A or disrupting the cell wall membranes. For that reason, photocatalysts are also used as antifouling or in disinfection treatments (Ganguly et al., 2018). The use of TiO_2 and ZnO to prevent the biodeterioration of buildings and heritage monuments has been recently reviewed (Ganguli and Chaudhuri, 2021). For instance, ZnO has shown better efficiency than TiO_2 to prevent the biodeterioration of building materials, mainly by fungal growth, even without light exposure (Loh et al., 2018). Moreover, higher efficiency of photocatalysts has been shown when they are combined with metallic nanoparticles as silver (Becerra et al., 2020, 2018; Fellahi et al., 2013; Goffredo et al., 2019, 2017). Such TiO_2 association with Ag can be used as coatings for outdoor treatment of limestone façades to prevent microalgal fouling (Becerra et al., 2020). When a TiO_2 treatment is applied after a biocide treatment on stone, there is a reduction in recolonization of the treated area (Ruffolo et al., 2017).

- ### 5.4 Advantages and drawbacks

One of the significant advantages of photocatalysts, compared to biocides or water-repellents, is that they resist the firing along with the industrial production of building materials (*i.e.,* around 1,000°C for ceramic roof tiles). Thus, they can be added during the manufacturing process, and their usage does not need an additional coating step at the end of fabrication (Gladis et al., 2010; Gladis and Schumann, 2011; Ranogajec and Radeka, 2013), facilitating the industrialization of antifouling solutions based on photocatalysts. Moreover, photocatalysts and especially TiO_2, are very stable over time (Hashimoto et al., 2005) and thus have shown suitable antimicrobial activity and prevent biodeterioration over a long time (Dyshlyuk et al., 2020). For example, photocatalysts are efficient on lichens, such as *Diploschistes actinostomus*, *Parmelia conspersa*, *Parmelia ioxodes* (Table 1) (Pinna et al., 2012). However, TiO_2 is a white powder that can alter building material color over time (Hashimoto et al., 2005). Photocatalysts also increase the hydrophily of building materials, promoting microbial colonization due to a higher water uptake level of the materials (Ranogajec and Radeka, 2013). The effectiveness of TiO_2 coatings is highly dependent on the substrate material and, in particular, its porosity and roughness. However, many stone materials in historic buildings are very porous and rough (Gladis and Schumann, 2011; Graziani et al., 2016, 2014; Quagliarini et al., 2018).

On the negative side, some studies revealed that some photocatalysts applied to prevent building biodeterioration (especially facades) were detected at significant concentrations in the aquatic environments where they are potentially harmful to many organisms (Kaegi et al., 2008). Also, as pointed out by a few studies, the photocatalysts' size and nature could constitute a serious issue for both human health and the environment (Remzova et al., 2019). The risks of photocatalysts used as TiO_2 or ZnO nanoparticles in cosmetics to human health have been pointed out, especially when inhaled (Dréno et al., 2019; Subramaniam et al., 2019). Regarding the risks associated with their inhalation, some studies suggested a potential link between exposure to TiO_2 nanoparticles and certain pulmonary and cardiovascular conditions in workers exposed to these nanoparticles (Dréno et al., 2019; Pelclova et al., 2018, 2015; Rossnerova et al., 2020).

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

6. Ionic liquids: promising eco-friendly synthetic molecules

Lo Schiavo *et al.* recently underlined that ionic liquids could be valid alternatives to conventional biocides for stone-built cultural heritage (Table 1) (Lo Schiavo et al., 2020). Ionic liquids (ILs) are salts with a melting point <100°C comprising organic cations (imidazolium, ammonium, pyrrolidinium, etc.) associated with inorganic anions (Cl^-, $AlCl^{4-}$, PF^{6-}, BF^{4-}, NTf^{2-}, etc.) or organic anions (CH_3COO^-, $CH_3SO_3^-$, etc.) which are liquid around room temperature. Their structure can be tuned to access physicochemical properties such as wide electrochemical window, high thermal stability, and null vapor pressure. Due to their structural analogies with conventional amphiphilic quaternary ammonium (QACs) species, ILs have an intense antimicrobial activity since the cation is responsible for the primary electrostatic interactions with cell walls (Pendleton and Gilmore, 2015). Consequently, ILs have been successfully applied to clean calcium crust ($CaCO_3$, $CaSO_4$, CaC_2O_4) from stained glasses (Machado et al., 2011) as well as from synthetic and natural varnishes (Pacheco et al., 2013). Phosphonium-based ILs were also tested for corrosion crust removal from medieval glasses (Delgado et al., 2017). For instance, it has been recently demonstrated that surface active ionic liquids (SAILs), based on cholinium and dodecylbenzenesulfonate, have been tested to prevent the biodeterioration of stone-built cultural heritage (Table 1). These SAILs have shown antimicrobial activity on pure Gram-positive (Micrococcus luteus) and Gram-negative (*Stenotrophomonas maltophilia*) bacteria, yeasts (*Cladosporium* sp.), hyphomycetes (*Aureobasidium* sp.), and algae (*Chlorella* sp.) (De Leo et al., 2021).

Polyoxometalates (POMs) are also being considered as biocidal agents. POMs are a large group of anionic polynuclear metal–oxo clusters with discrete and chemically modifiable structures (Gumerova and Rompel, 2020; Miras et al., 2012). Generally based on group 6 transition metals (Mo, W), and sometimes group 5 (V, Nb, Ta), these closed 3-dimensional frameworks are characterized by a wide and versatile range of physicochemical properties that can be specifically tailored at a molecular level. Their polyanionic feature allows them to form complexes with many proteins or peptides containing cationic residues through ionic bonds. For these reasons, many reports have reported both a direct antibacterial activity and a synergistic one with conventional antibiotics (Bijelic et al., 2018). For instance, polyoxotungstates have been shown to exhibit antibacterial activities against *Helicobacter pylori* (Inoue et al., 2005). Moreover, Gumerova *et al.* demonstrated that of the 29 different POMS tested, the polyoxotungstate $[NaP_5W_{30}O_{110}]^{14-}$ showed the highest activity against *Moraxella catarrhalis* (Gumerova et al., 2018). However, most of the inorganic POMs do not exhibit biocidal activities strong enough to be exploited yet as coatings for building materials. It is also worthy of mention that attempts have been made to combine the properties of polyoxametalated anions and the organic cations coming from ionic liquids. In this way, silicotungstate and phosphotungstate-based POM-ILs fused with long-chain quaternary alkylammonium cations have been shown to exhibit an enhanced antifungal activity on historical bricks (Rajkowska et al., 2020). Another study demonstrated that hydrophobic polyoxotungstate POM-ILs could be used as suitable anti-corrosion and antibacterial coatings for natural stones (Misra et al., 2018).

7. "Natural compounds": on the path to the discovery of sustainable antifoulings?

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

7.1 Plants and essential oils

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

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Plants and their derivatives as EOs have been employed for centuries for their natural antimicrobial properties (Algburi et al., 2017; Nazzaro et al., 2013). The earliest documented traces of the medicinal application of plants date back 5,000 years (Petrovska, 2012). Today, in addition to being used in the pharmaceutical and aromatherapy industries, EOs are also applied in the food industry (Gadea et al., 2017b; Palla et al., 2020). EOs and their component (secondary plant metabolites) are also tested in conservation due to the need for new cleaning procedures using less harmful molecules for both human health and cultural heritage preservation (Fidanza and Caneva, 2019; Palla et al., 2020; Sasso et al., 2016; Veneranda et al., 2018).

- 7.1.3 Efficacy

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

- 7.1.4 Advantages and drawbacks

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

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

Despite their enormous potential, the safety of EOs must be assessed. Especially in the medical field, where EO-antibiotic combinations need to be more closely studied and their potential toxicity measured before further development (Algburi et al., 2017; Owen and Laird, 2018). For building materials, most of the studies were carried out *in-vitro* (Gómez de Saravia et al., 2018; Veneranda et al., 2018). Therefore, it is necessary to explore the possible interactions between EOs and building materials before considering their usage at larger scales. Finally, some natural products are pointed to their deleterious effects on human health. For example, while capsaicin and chili peppers derivatives are very efficient as antimicrobials or pain relievers (Martini et al., 2014; Omolo et al., 2014); but they are also very irritant, as shown by their use in pepper sprays (Oliveira Junior et al., 2020; Omolo et al., 2014). This is also the case of Geraniol (3,7-dimethylocta-trans-2,6-dien-1-ol, CAS: 106-24-1), which is one of the most important molecules in cosmetic industries for its antimicrobial activities (Chen and Viljoen, 2010) and can induce allergic reactions such as irritant contact dermatitis (Johansen et al., 2020).

- 7.1.5 Future and perspectives

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

7.2 “Natural” compounds: conclusions

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

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

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

In this perspective, the development of quorum quenching compounds (QQ) appears extremely promising (Lami, 2019). The biofilm that grows on building materials promotes bacterial interactions, in particular by facilitating chemical communication between microorganisms; among those, one common type is named quorum sensing (QS) (Romani et al., 2021a; Xavier and Foster, 2007). QS is a coordinated response of the microbial community from a certain cell density (quorum), which involves the production of extracellular chemical signals (sensing) (Henke and Bassler, 2004). These signals accumulate in the immediate environment until they reach the level necessary to activate the transcription of specific genes (Whiteley et al., 2017). QS was first demonstrated in the marine model *Vibrio fischeri*, which emits bioluminescence when the cell concentration in the environment is sufficient (Whiteley et al., 2017). However, QS is involved in a wide range of bacterial mechanisms, including, among others, biofilm formation (Girard et al., 2019; Kalia, 2018). Therefore, inhibiting this key bacterial mechanism seems particularly promising in the fight against environmental biofilms (Algburi et al., 2017; Kalia, 2018), as QQs are not biocides but inhibit cell mechanisms involved in biofilm formation. Consequently, such compounds hold the promise to solve the paradox we raise previously, targeting the biofilm without presenting high cytotoxicity. Also, the resistance of microorganisms to these compounds is suspected of appearing at lower rates compared to that against biocides substances (Rémy et al., 2018).

Interestingly, these bioactive compounds are frequently discovered, setting up biomimetic approaches (Scardino and de Nys, 2011), after an attentive observation of antifouling traits among natural species and in combination with an in-depth analysis of their microbiota (Tourneroche et al., 2019; Vallet et al., 2020). In addition to the EOs described above, some organisms are capable of producing anti-QS molecules (quorum quenchers), such as bacteria as *Bacillus* sp., *Pseudomonas* sp., *Rhodococcus* sp., and *Streptomyces* sp. or fungi as *Cladosporium cladosporioides*, and algae as *Stichococcus bacillaris*, which, interestingly, were also previously identified on building materials (Coutinho et al., 2015; Di Martino, 2016; Paul et al., 2018; Romani et al., 2021a, 2019; Urzì et al., 2010). This is also the case of the halogenated furanones discovered in *Delisea pulchra* (Manefield et al., 1999) or of the butyrolactones identified in the microbiota of the brown macroalga *Saccharina latissima* (Vallet et al., 2020). The best-known quorum quenchers are enzymes AHL-lactonases that hydrolyze QS compounds (the acyl-homoserine lactones) by cleaving the ester bond of their lactone ring (Paul et al., 2018). Despite these advances, more research and development efforts are needed to better understand the mechanisms of action of these promising compounds and their effective innocuity on health and the environment (Lami, 2019). Thus, the development of these new treatments will require more investment, and even if this research strategy appears promising, the road remains long before the commercialization of such products at large scales. Nevertheless, the challenge has been taken by a few startups, in partnership with academic research labs, like Green&GeneTK at the IHU Marseille, France, a consortium specialized in the production of anti-QS enzymes.

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

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

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

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

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

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

In addition to the choice of chemicals, it is important to optimize their application to the materials. Thus, the development of adapted protocols for biocides has a significant impact on their effectiveness (Favero-Longo et al., 2020). For example, the effectiveness of different biocides is higher if the lichen thalli are hydrated before their use and if the biocidal substance is applied with a cellulose poultice. Similarly, when a hydrogel is used to apply a biocide solution to a polymicrobial patina, a high percentage of water loading is essential to ensure a deep antimicrobial action (Boccalon et al., 2021). The application of hydrogels delivering biocides has shown great results on stone (Gabriele et al., 2021); however, their use on highly porous stones is not recommended, as antimicrobial action remains superficial in such cases (Favero-Longo et al., 2020).

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

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

The development of innovative and sustainable solutions will rely on a significant investment throughout the entire production chain: in fundamental research to develop alternative and lower toxic compounds, in applied research to select the best solutions, in production systems to industrialize at large scales the innovative solutions, in commercialization and marketing to raise end-user awareness to the health and environmental challenges and undoubtedly to increase customer tolerance to biodeterioration.

Credit authorship contribution statement

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

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Figures

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

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

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