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Review

Sustainable and Bio-Based Coatings as Actual or Potential Treatments to Protect and Preserve Concrete

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Abstract: The durability of reinforced concrete strongly depends on the environment in which it is located; in any case, the concrete and the reinforcing bars it contains are constantly subject to slow deterioration processes. The protection of concrete structures is, therefore, essential to increase their service life, reducing the costs for their repair and maintenance. The commercial widely used coatings are mainly based on petroleum derivatives (i.e., resins, solvents): increased sensitivity and attention to human health and the protection of the environment pressed research to find alternatives to synthetic products, identifying safer materials with a low environmental impact to employ as protective coatings. In this review, new sustainable products already used or potentially suitable to act as protective treatments for concrete were analyzed and presented. These are natural (bio-based) or waste materials, in which the use of synthetic resins and hazardous solvents, for humans and the environment, are minimized, exploiting waste materials or by-products of other processes, if possible. The main properties and characteristics of these new products are illustrated, highlighting the potential advantages over commercial products also in terms of performance.

Keywords: concrete; reinforcing bar; sustainable coating; bio-based coating; surface treatments; protective treatments

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1. Introduction

A surface coating is a thin film that acts as a physical obstacle to prevent harmful substances from penetrating the substrate. The use of a surface coating, or a surface treatment, to protect the underlying object is widespread in various fields, from cultural heritage (such as wood or stone [1]) to civil engineering (such as concrete [2]), from metal surfaces [3] to glasses [4].

Concrete is a porous, nonhomogeneous, and highly hydrophilic material that it is widely employed in the construction industry. It is, in fact, employed in many civil construction projects (such as buildings, beams, bridges, dams, tunnels, etc.); it consequently requires extremely reliable strength and durability. The deterioration of concrete is mainly due to its contact with the environment and external agents (i.e., chronic hazards), as well as to episodic (i.e., earthquake) risks [5]. Degradation over time leads to a lowering of its mechanical strength resulting in structural damage and, in turn, to huge costs to repair or even rebuild the structure. Hence, it is important to protect this material from environmental attacks. Since the action of external agents is more harmful when the porosity of the concrete is greater, to improve its compactness, the water/cement ratio can be reduced; this solution, on the other hand, leads to a concrete with poor workability. The inclusion in the concrete formulation of admixtures that are able to increase the workability of the paste while limiting the amount of water can lead to the formation of colloidal crystals [6,7], increasing the risks of failure after its hardening. Moreover, this strategy would not change the hydrophilic nature of the concrete, as water is the environmental agent that has the greatest influence on the durability of the concrete [8]. From these considerations, the necessity arises to develop effective methods to enhance the impermeability of the concrete, optimizing also the durability against the corrosion of reinforcing steel bars, and against freeze and thaw cycles. In recent decades, in fact, the application of surface treatments able to protect concrete has been widely investigated [9–12].

Environmental changes, the increase in pollutants, and the growing presence of aggressive chemicals in the atmosphere may severely affect the durability of concrete structures. As already mentioned, the main cause of concrete deterioration can be attributed to the presence of water acting as a vehicle for different substances, i.e., carbon dioxide, sulphur dioxide, chloride ion, and other water-soluble aggressive agents [13]. These substances, penetrating the concrete paste through any crack, can reach the steel bars and corrode them. Furthermore, the water in liquid or vapor forms can provoke chemical reactions and alterations, freeze-thaw cycles upon variations in external temperatures; all of these processes produce severe damages to the structure [14].

Generally speaking, durability is defined as the ability of a material to last for a long time without significant deterioration: therefore, durability is an important aspect to take into consideration in order to assure the quality of concrete structures [15]. Considering that cement is one of the most energy intensive materials for construction and one of the largest sources of CO_2 emissions, the premature deterioration of reinforced concrete leads to serious waste of resources and environmental issues. Thus, there is an urgent demand to make the reinforced concrete more durable. To achieve this goal, and extend the service life of concrete structures, various protection measures have been developed. It is generally recognized that the main properties of a well performing protective coating are:

- A waterproof behavior.
- Its chemical inertness against substrates.
- A good stability against acids, alkalis, UV radiations, heat, and oxidation.
- A suitable permeability to water vapor (the underlying concrete must still "breathe").
- An adequate adhesion to the substrate.
- Possibly a crack-bridging ability.
- The coating should be non-toxic and non-dangerous for the environment and human beings.

One of the first and most comprehensive reviews on this topic was published by Basheer et al. [16]. Coatings for concrete are typically divided into two groups according to their chemical composition, i.e., organic and inorganic surface treatments.

Organic coatings, applied on the surface of the concrete slab as films of about 0.1–1 mm thick, are the most popular since they are highly impermeable even though they have limited durability. In addition, these products have poor fire resistance and they do not allow the reversibility of the process: once they lose their protective characteristics, it is very difficult to remove and replace them [17–19]. Traditional polymer coatings are generally based on epoxy, polyurethane, or acrylic resins. During their application, volatile solvents or other compounds may release toxic vapors causing health issues and air pollution. This category includes also new polymer nanocomposite products, composed by an organic matrix (again epoxy, polyurethane, or acrylic resins) in which inorganic nanoparticles (typically SiO_2, TiO_2, nanoclay) are finely and uniformly added. The nanoparticles are often added to control and tune the coating features, adapting them to any specific application. The incorporation of suitable nanoparticles, for instance, can, reduce the flammability and/or the gas permeability, improve the durability of the polymeric matrix [20–22], and enhance the corrosion protection of reinforced concrete [23]. Although the nano-filled coatings would offer improved performance, production costs increase up to values that are too high, limiting the application of nanomaterials in this field [24].

Inorganic coatings are more stable and more durable. Sodium silicate solutions are among the most widely used inorganic treatments, followed by products based on lithium silicate, fluosilicate, and potassium silicate [25,26]. Among the inorganic coatings, layers of cement mortar must also be considered, which form a low permeability film with a thickness of about 2–10 mm. The addition of a polymeric phase in a cementitious coating can improve its protective properties, mechanical strength and chemical resistance, and its adhesion to concrete substrate. The cementitious coatings can be, in fact, modified with the addition of the polymers used as organic coatings, such as acrylate, polyurethane or epoxy resins. The addition of an organic compound, however, can produce some disadvantages, such as a greater vulnerability to fire, or a reduced permeability to water vapor; moreover, they can release toxic volatile organic compounds (VOCs) during their application. Furthermore, the carbon footprint of organic coatings is much higher than that of inorganic ones [27].

Although different surface treatments for concrete are commercially available, experimental research is constantly developing new products to improve their features or increase their functional characteristics. Due to a growing attention to environmentally friendly materials, the use of products containing solvents or materials that can be harmful to human beings and to the environment is no longer tolerated. Both academic and industrial research has, therefore, been focused on the development of solvent-free coatings or of coatings with a very limited content of solvents [28,29], and on coatings able to cure through UV radiations without solvent emission [30,31]. Recently, attention is turning to the development of coatings based on green materials, namely "bio-based coatings", obtained through sustainable processes that do not generate toxic emissions. This trend is also confirmed by the increase in scientific publications on this topic, as illustrated in Figure 1 where it is possible to observe how the papers published from 1998 to today dealing with "bio-based coating", regardless of the specific application, have progressively increased.

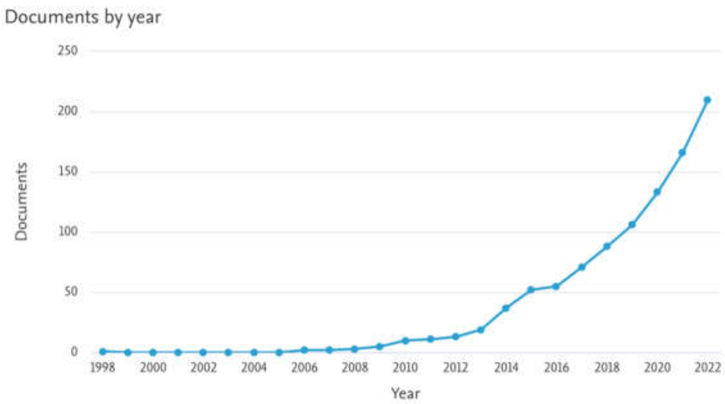

Figure 1. Papers containing "bio-based coating" in their keywords, published from 1998 to November 2022 (source: Scopus database).

The countries that have contributed most to this thematic area are shown in Figure 2. As can be seen from the graph, the countries are well distributed all over the world.

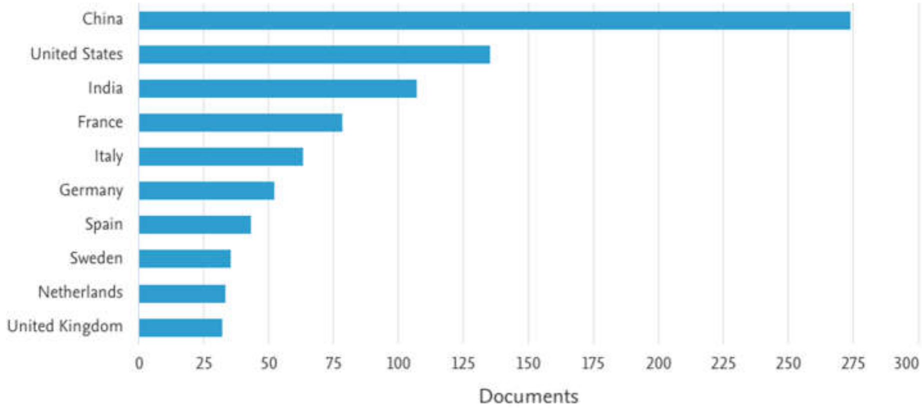

Figure 2. Top 10 countries by number of publications relating to "bio-based coating" (source: Scopus database).

Thanks to this brief bibliometric analysis, it is possible to state that the research in this sector is constantly growing. Until a few years ago, the solution adopted was the reconstruction of degraded reinforced concrete structures [32]; in recent years this trend is changing because protecting a structure is much cheaper than rebuilding it [9]. In addition, the growing attention to the environment has favored the use of surface treatments for concrete since the disposal of demolition materials poses considerable issues.

This review aims to describe bio-based/sustainable materials that have recently been proposed to develop coatings for the protection of concrete and of its reinforcing bars. This paper collection also introduces new bio-based coatings, not yet tested in these applications but have the potential to extend the service life of concrete constructions if applied on concrete or on rebar surfaces.

2. Sustainable Technologies for Producing Coatings

Over the past decade, the coatings industry has been revolutionized with the introduction of eco-friendly technologies, such as processes involving UV-cure, treatments with less or no solvents, waterborne (WB) products, hyperbranched (HYP) and high solid (HS) coatings. In some cases, these methods have been combined to achieve high-performance sustainable coatings. The mentioned technologies were originally introduced to produce organic and/or inorganic treatments employed for different applications, possibly for those that are not entirely sustainable. Only recently have these technologies been adopted to produce coatings centered on bio-based materials in order to obtain a treatment that is sustainable from both the point of view of the production process and the raw materials used.

UV-cure is a process in which UV radiations are employed to initiate a photochemical reaction producing a cross-linked polymeric network. This technology has several advantages: the curing process occurs at low temperatures (even an ambient one), it is a high-speed process without the use of any solvent (the film is formed by polymerization instead of by coalescence of the macromolecules upon evaporation of the solvent), resulting in reduction of risks for health and the environment. The same advantages can be recognized in WB coatings: in them the water is employed as a solvent to dissolve the polymer, which is often a bio-based resin [33,34]. These products offer a low VOC content (even if the drying procedure takes longer) and outstanding surface finishes with excellent protection characteristics as advantages. A few examples of these have been described in the literature. A solvent-free hydrophobic photo-polymerizable organic–inorganic (O-I) nanostructured coating was experimented on different concretes [35]. Preliminary experiments demonstrated the effectiveness of this UV-cured hybrid system in reducing the ingress of liquid water into concrete substrates, enhancing its durability. In another study

[36], different coatings were produced that combined the advantages of being bio-based (i.e., based on acrylate epoxidized soybean oil), waterborne and UV-curable. The results of this investigation demonstrated that the introduction of glycerol in a polyester, with the addition of epoxidized acrylate soybean oil, resulted in excellent protective properties, good adhesion to the substrate and flexibility, high pencil hardness, and excellent solvent resistance. HS coatings are gaining interest as they have a higher solid content (i.e., 70%–80%), including binders, pigments, and additives, and consequently a lower VOC content than traditional solvent-based coatings [37]. HYP coatings, although having a slightly higher solvent content, display other advantages over HS coatings as they are synthesized at low costs in a single step process. In addition, the low viscosity of the final product allows an easier film formation [38].

All the technologies just mentioned involve different materials, but they are not fully sustainable. If the focus must be on bio-based materials only, most of the published works converge on vegetable oils. The latter can be chemically modified to obtain the polyols and isocyanates necessary to develop a bio-based polyurethane (PU) able of replacing synthetic PU in traditional coatings. As an example, Kong et al. [39] proposed several bio-based polyols synthesized from 5 different vegetable oils. The obtained polyols were then used as raw materials to produce high solid PU coatings, with a bio-based content of around 60%: all of these coatings showed good thermal and mechanical properties, high water contact angle, good abrasion resistance and shore hardness.

3. Sustainable/Bio-Based Coatings for Concrete

A coating can be deemed sustainable if, when it is applied in solution/suspension, water or low toxic substances must be used as solvents/suspended media (i.e., avoiding the use of harmful solvents), or if it is able to dry without using excessive energy (in terms of heat or radiation) [40]. Green solvents are those that are not toxic for human health or the environment, they are not flammable and do not produce explosions, they are dispersed in the environment, and they dissolve in water, soil, and air without producing harmful substances. Bearing in mind the mentioned requirements, water is certainly the best candidate as a solvent/suspended medium [41]. Besides water, a green solvent is generally not derived from petroleum, i.e., it is not synthetic, it is rather a plant-based/biomass substance with solvent capacity.

The use of bio-based or even waste materials for the production of coatings for different purposes is becoming increasingly popular; so far, not all of these coatings have been applied also to concrete. The food packaging, pharmaceutical, biomedical and automotive sectors are the fields where bio-based coatings are frequently applied [40,42]. However, the experimental bio-based coatings reported in the literature are mostly of general use, making them suitable for diverse applications in different fields, not excluding the building sector.

In the field of construction, the sustainable products proposed as potential protective coatings for concrete substrates can, for simplicity, be divided into: (i) geopolymers and (ii) natural bio-based substances, such as agricultural waste, oil, wax, cellulose and others. These products can offer different protective characteristics and different properties as surface treatments, as illustrated in the next sections. However, this is a fairly new topic that is only recently attracting great interest, also due to the growing concern for the environment.

3.1. Geopolymers

Geopolymers are considered sustainable materials due to their low curing temperatures and the possibility to use a wide variety of raw materials to produce them, including industrial waste (i.e., secondary raw materials, SRM). Geopolymers, in fact, can be synthesized via alkaline activation of aluminosilicate precursors reusing (i.e., recycling) solid waste, such as fly ash (FA), slag, and other active byproducts [43]. They are constituted by a network developed during geopolymerization reactions, leading to the formation of a strong structure supplying them with good final properties [44,45] in terms of water impermeability, high mechanical properties, and good chemical and thermal resistance and durability [46]. Geopolymers, when applied on concrete surfaces, are able to seal and protect them from the attack of aggressive external agents. Balaguru et al. [45] reported the example of a geopolymer coating still able to exert protective properties after nearly 10 years of exposure to a marine environment. Similar results were reported by Zhang et al. [47–49]: the authors of the study concluded, therefore, that geopolymers are more resistant to sea water than organic polymers.

Several studies highlighting the properties of geopolymers used as coatings for concrete have been published: Wang et al. [50] and Ma et al. [51,52], for instance, reported their suitable workability and high mechanical strength, their good resistance to corrosive agents, frost and fire, and the ease of their application. Furthermore, geopolymers possess a glassy structure, and this feature can make them resistant even to graffiti [53]. Taking into consideration the reinforced concrete, the corrosion of steel rebars is the first cause of its deterioration. Several studies reported that the use of geopolymers as coatings for rebars is able to prevent their corrosion when exposed to chloride-rich environments. Aguirre-Guerrero and Mejía de Gutiérrez [54] studied the effectiveness as coatings of geopolymers, taking as reference an uncoated concrete (UCC) and a commercial epoxy coating (CEC). They used a natural volcanic pozzolan with 5% of acrylic emulsion to produce an alkali-activated mortar (AMCP5) and an alkali-activated paste (APCP5). In the same study, fly ash with 1% of acrylic emulsion was employed to obtain an alkali-activated mortar (AMCF1). The authors analyzed the corrosion taking place in reinforced protected or uncoated concrete specimens when exposed to a NaCl solution (3.5%) for prolonged times, up to 112 h. The results demonstrated that the reinforced concrete protected with alkali-activated materials was able to efficiently resist this mild exposure when compared to UCC and even to the reference commercial coating; the corrosion rate was reduced by 86% when the concrete was protected with AMCP5 and by 96% when APCP5 was applied. Under more severe exposure conditions, as expected, the commercial epoxy-based coating proved to be the most effective in protecting the concrete. The cracking registered during this test for the CEC, AMCP5, AMCF1, and AMCP5 specimens, respectively, are illustrated in Figure 3.

Figure 3. Coated and uncoated reinforced concrete samples submitted to impressed voltage test: (**a**) UCC sample; (**b**) CEC sample; (**c**) AMCF1 sample; (**d**) AMCP5; (**e**) APCP5; and (**f**) steel bars after the test. Reprinted from [54], with permission from Elsevier (November, 2022).

A fly ash-based geopolymer was proposed by Rostami et al. [55] as a coating for steel bars. These authors found that the corrosion rate was significantly minimized when the steel bars were protected by the geopolymer. Duan and et al. [56] proposed a new geopolymer containing metakaolin with a hydrophobic surface by adding a low-cost fatty acid as a modifier: fatty acid molecules were linked to the surface of the geopolymer via esterification between carboxyl of fatty acid and alcoholic hydroxyl present on the surface of metakaolin matrix. The contact angle of the geopolymer paste, which measures its hydrophobicity, was, in fact, increased from 36° in the starting geopolymer to 132° in the modified one.

3.2. Coatings Based on Agricultural Waste

Agricultural organic waste, i.e., products that are constantly generated, can be profitably exploited for different purposes, giving an economic value to a waste and reducing the costs for their disposal. The main use of agricultural and animal waste is represented by their transformation into natural gas and biomass; in addition, bio-based materials and fillers, such as silica, carbon and silicates, can be also obtained from agricultural waste and used to develop superhydrophobic sustainable coatings. Wu et al. [57] produced a bio-based epoxy resin (i.e., based on wood pulp) as a coating for cementitious substrate able to prevent water ingress. The developed coating exhibited strong water-repellent characteristics and, at the same time, offered a good breathability, both being very important properties for effective protection of concrete. In addition, a good adhesion between the experimented coating and the concrete substrate was developed. Shen et al. [58] described that, through a process of gasification/pyrolysis of rice husk (RHA), it is possible to obtain a material that contains over 60% silica, from 10 to 40% carbon, and small quantities of other minerals: all these constituents can be, then, used to produce protective coatings. As another example, Husni and et al. [59] employed silica particles obtained from rice husk ash to produce a superhydrophobic coating for concrete. The coating was based on a solution of ethanol and 1H,1H,2H,2H- perfluorodecyltriethoxysilane (2% vol.) in which the rice husk ash is dispersed. The obtained mixture was sprayed on a layer of a commercial adhesive primer applied on the concrete surface. The authors reported that the penetration of water into the coated concrete, under a water pressure of 500 kPa, was significantly reduced, although the protection was not complete. The water contact angle measured on the coated and uncoated concrete specimens is shown in Figure 4.

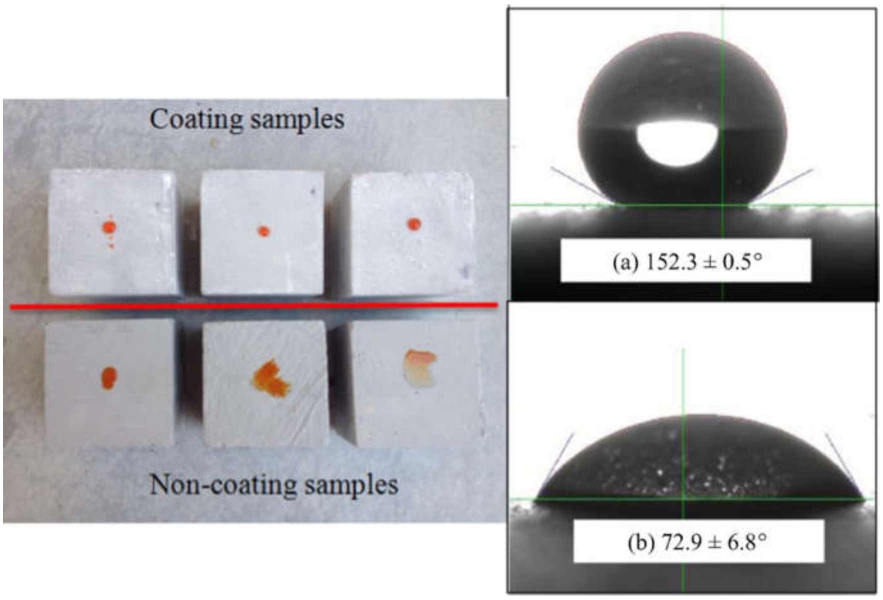

Figure 4. Image of the contact angle measured on concrete with superhydrophobic rice husk ash coating (**a**) and on concrete without any coating (**b**). Reprinted from [59],with permission from Elsevier (November, 2022).

The use of RHA to prepare a superhydrophobic coating for concrete was also proposed by Junaidi et al. [60]: the authors measured a very high contact angle value, up to 158°, on the concrete where this coating was applied.

Bio-based coatings have also been proposed for the protection of steel bars in reinforced concrete. In the study described in [61], for instance, RHA was chosen as a filler for an epoxy coating used to protect the steel bars from corrosion. It was found that the coating filled with RHA, in addition to protect the substrate, improves its surface mechanical properties (scratch and wear resistance) if compared to the unfilled epoxy treatment.

3.3. Vegetable Oil and Fatty Acids

Vegetable oils are already widely used to produce solvent-free coatings or coatings containing a low amount of synthetic solvents in WB, HYP, and HS technologies [37,38,62]. Vegetable oils are abundant, non-toxic, and bio degradable natural resources, and they have been used for centuries, but mainly in food applications. The recent use of vegetable oils in technologies intended for the preservation of a substrate (for example: concrete) can represent a sustainable solution and a promising alternative to synthetic products. Oil and its derivatives can be used in this area, in fact, due to their chemical structure and ability to form films.

Vegetable oils are mainly composed of triglycerides (three fatty acids linked to glycerol via ester bond), with monoglycerides and phosphoglycerides as minor components. They offer numerous advantages, such as the already mentioned non-toxicity and biodegradability, low costs, and they do not require solvents/plasticizers during application as they have a high fluidity. Depending on the application, they can provide antimicrobial characteristics and biocompatibility to coatings, and are able to protect the substrate from corrosion. Thanks to the presence of long chains of aliphatic fatty acids, the chains of vegetable oils are flexible; in addition, due to the presence of reactive sites (epoxy unsaturation and ester groups), they can be chemically modified. As an example, vegetable oil can participate in the curing reaction of a thermosetting resin, becoming part of the final material; it can be also modified to produce polyols to develop polyurethane films [63]. Bio-based polyurethane (PU) films have been used extensively in the last years to replace synthetic coatings: in addition to their low environmental impact, they are widely available at low cost [64].

As a first example, a new material was developed by Akram et al. [65] introducing boron into the backbone of castor oil (CasO) to produce boron-modified polyester and polyurethane: these products were then proposed as coatings for protection against corrosion, using the least possible quantity of solvents in the production process. The results of this study showed that boron can affect the physicochemical characteristics of the coating, increasing its thermal stability and performance especially in alkaline media, even when compared to traditional synthetic coatings. Starting from a polyester polyol HYP, produced from castor oil and 2,2-bis (hydroxymethyl) propionic acid, Wei et al. [66] developed a UV-curable WB-HYP polyurethane coating, adopting an emulsifier-free process. The final coating, intended for different applications (i.e., not specific for concrete), showed good adhesion to substrate and durability. Deka and Karak [67] produced hyperbranched polyurethanes synthesized from the monoglyceride of *Mesua ferrea L.* seed oil, poly (ε-caprolactone) diol, 2,4-toluene diisocyanate and glycerol, without the use of catalysts. The analyses carried out on the final product confirmed the formation of a polymeric film, i.e., a hyperbranched polyurethane coating, produced from a vegetable oil, possessing high thermal stability and good mechanical properties. A new bio-based water-repellent coating was developed combining 2-mercaptoethanol-modified castor oil, as the precursor, and polydimethylsiloxane (PDMS), as the repellent agent [68]. The resulting surface treatment, in addition to outstanding water repellency, anti-graffiti, and self-cleaning capabilities, also offered high resistance to corrosion and chemicals. The new coating was able to maintain its outstanding water-repellent properties, even greater than commercial silicone-based or fluorinated superhydrophobic coatings, after 5000 abrasion cycles. Although not intended for this specific application, based on its excellent performance, the product may be a good candidate as a concrete coating.

Fatty acids are also being investigated as potential base materials for coating development. Fatty acids are macromolecules of biological origin consisting of hydrocarbon chains and ending with carboxylic acid groups. Fatty acids and their derivatives are the main components of lipids (up to 70% by weight). The length and degree of saturation of the hydrocarbon chain varies considerably from one fatty acid to another and, consequently, their physical properties (e.g., melting point and/or fluidity) may be different. Almost all fatty acids are hydrophobic in nature and insoluble in water. Stearic acid, a saturated fatty acid with a chain of 18 carbon atoms (IUPAC name: octadecanoic acid), is one of the most widely used to develop superhydrophobic coatings [69–71]. It has the appearance of a waxy solid, and it is one of the most common saturated fatty acids found in nature in addition to palmitic acid [72]. As reported in current literature, stearic acid is particularly suitable for the development of coatings for the protection of metal surfaces: therefore, it can be recommended for the protection of steel bars in reinforced concrete. Feng et al. [73], for example, manufactured a nano-zinc coating for steel based on modified stearic acid: the presence of the stearic acid layer assisted in obtaining a coating with a superior hydrophobicity (water contact angle around 159°). On the other hand, a contact angle of 74.8° was measured on the steel bars without any coating. The authors highlight that 20 min was the best depositing time to obtain optimal hydrophobic performance for all the electrodepositing current densities analyzed (i.e., from 50 to 200 mA/cm^2), as can be seen in Figure 5.

Hu et al. [74] produced a multifunctional stearic acid/zinc composite coating with a hierarchical micro/nanostructure by co-deposition of TiO_2 nanoparticles and zinc ions on carbon steel substrates. The water contact angle measured on the experimental coating reached 160°. The produced coating offered good mechanical properties, chemical stability, and an excellent corrosion resistance.

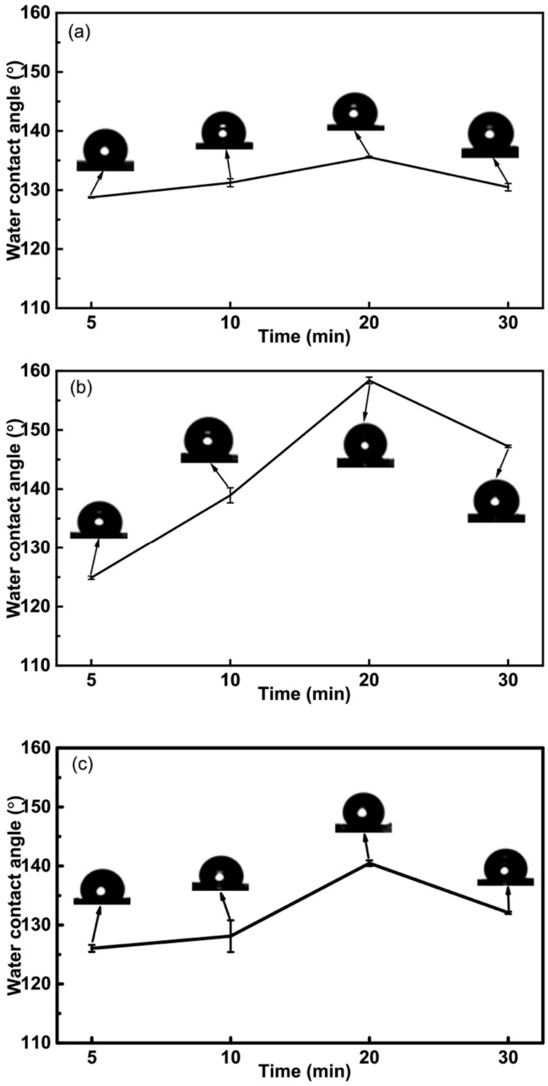

Figure 5. Contact angle measurements as a function of different electrodepositing times, using the following current densities: (**a**) 50 mA/cm², (**b**) 100 mA/cm², and (**c**) 200 mA/cm². Reprinted from [73], with permission from Elsevier (November, 2022).

3.4. Proteins

Very recently, proteins have been proposed to develop coatings with good hydrophobic characteristics. Lysozyme, for instance, is composed of a microfiber network containing amyloid which, when applied to the surface of a metal, adheres to it and increases its resistance to corrosion [40]. Despite the potential of protein-based hydrophobic coatings, their application is so far limited, mainly due to their low mechanical strength [75–78].

A new soy-based coating to protect the reinforcing bars of concrete slabs from corrosion was developed by Sajid et al. [79]. Soy-based coatings were synthesized using denatured soy protein and a corn-derived sorbitol plasticizer. The investigation demonstrated that soy-based coatings offer good abrasion resistance and provide a high corrosion protection to the reinforcing bars, appreciably reducing the density of the current of corrosion (up to 96% compared to bare rebars) when the latter are exposed to a solution containing 3.5% wt. of sodium chloride. Figure 6 shows the corrosion levels achieved by soy protein-coated reinforcement bars in a Portland cement mortar compared to uncoated reinforcements. Corrosion resistance, in addition, proved to be stable even over a long period of time. These encouraging results confirm that the proteins could be used for the development of coatings to protect reinforced concrete from corrosion.

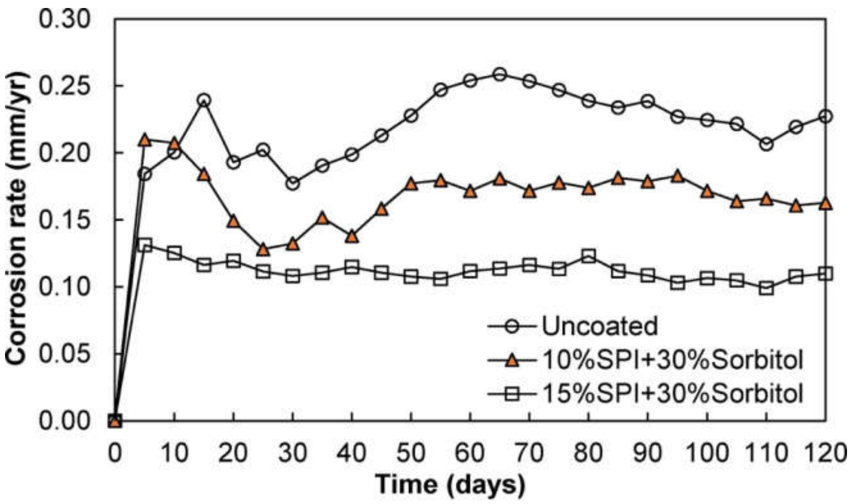

Figure 6. Corrosion rate for uncoated and coated rebars, employing coatings based on 10% and 15% soy protein isolate (SPI) and 30% of sorbitol. Reprinted from [79], with permission from Elsevier (November, 2022).

3.5. Cellulose

Cellulose, the most abundant natural polymer on earth, is a low-cost renewable resource: it is generally recognized as a potential candidate for the production of green superhydrophobic coatings. The interest in this material is growing as the cellulose fibrils show a very high mechanical strength: they can be, therefore, effectively exploited as bio-based micro/nano fillers. Wang et al. [80] produced a sustainable superhydrophobic coating based on oxidized cellulose, polydimethylsiloxane (PDMS) and silica nanoparticles: the obtained coating displayed a contact angle of 158.5°, good tensile strength and good chemical stability when exposed to various unfavorable environments. In a similar work, Chen et al. [81] developed a surface treatment composed by hydrophobic SiO_2 nanoparticles dispersed in water with the addition of cellulose nanofibers (CNF), able to improve the dispersion of SiO_2 in water, and methyl-tri-methoxy-silane (MTMS). The high hydrophobicity of the coating (confirmed by a contact angle equal to 162°) was preserved even after 10 abrasion cycles, also thanks to the presence of the MTMS capable of promoting the adhesion of the coating to the substrate. In order to improve the mechanical strength of the coating, Huang et al. [82] used cellulose nanocrystals (CNCs) dispersed in ethanol to prepare a CNC/SiO_2 nanostructure as the main component of the superhydrophobic surface treatment. The resulting coating exhibited very high mechanical strength even when exposed to severe external conditions, such as UV radiations, and acid or alkaline environments. In conclusion, the authors proposed the use of this coating in several demanding applications. Barnat-Hunek et al. [83] studied the mechanical properties (compressive, flexural, and tensile strength) and durability (freeze-thaw resistance) of concrete slabs treated with an admixture of cellulose nanofibrils (ACNF) and cellulose nanocrystals (CCNC) with different small nanocellulose amounts (i.e., 0.5% and 1% wt.). They also analyzed absorption behavior, density, open porosity, contact angle, and surface free energy on treated and un-coated concrete. The authors found that the use of ACNF or CCNC coatings leads to improvements in the waterproof characteristics of concrete, as can be seen in Figure 7. Finally, the study also proved that the application of a cellulose-based coating can improve the freeze-thaw resistance of the concrete.

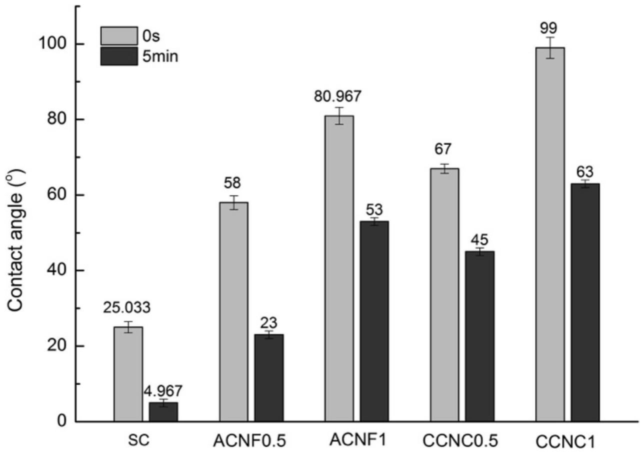

Figure 7. Contact angle of concrete specimens treated with different coatings, measured at time 0 and after 5 min from the application of the coating, in comparison to un-treated concrete (SC). Reprinted from [83], with permission from Elsevier (November, 2022).

3.6. Plant-Based Wax Coatings

A wax, a mixture of fatty acid esters and fatty alcohols, is a lipid substance with relatively high molecular mass synthesized by many animals and plants [84]. The main properties of waxes are their moderate melting point of about 45 °C (which makes the waxes deformable at room temperature) a low viscosity in the molten state, they are insoluble in water, and they show good water repellency, a feature that makes them particularly suitable for use as coatings.

Plants produce waxes in and on the surface of their cuticles to control water evaporation and, consequently, their hydration. One of the most famous examples of the role of waxes is represented by the surface of the lotus leaf, known for its exceptional hydrophobicity. Starting from materials of vegetable origin dispersed in water, Morrissette et al. [85] developed superhydrophobic self-cleaning coatings for different applications. The authors of the study showed, in particular, that those based on a natural wax binder (e.g., carnauba wax or beeswax) filled with lycopodium and subjected to moderate heating (70–100 °C), were able to offer excellent hydrophobicity, with contact angles greater than 160°.

The durability of these coatings was the subject of several investigations. Torun et al. [86] used a combination of natural (carnauba) wax and polydimethylsiloxane (PDMS), both dispersed in ethanol, to prepare a superhydrophobic coating. Its composition, i.e., the wax/PDMS ratio, was optimized to achieve excellent hydrophobicity and high durability. Gupta et al. [87] prepared two non-fluorinated superhydrophobic coatings using natural carnauba wax from the *Copernicia prunifera* palm, one with the addition of alumina particles and the other containing no particles. Both coatings showed very high waterproof characteristics, with contact angles greater than 150°. The wax-based coatings, in addition, displayed a high durability, in terms of resistance to simulated rain and weathering, and good mechanical properties and abrasion resistance. The study demonstrated, therefore, that the coatings based on carnauba wax can be proposed as sustainable superhydrophobic surface treatments for concrete and reinforced bars. El Shami et al. [88] studied the ability of aubepine and molokia extracts to protect the reinforcement bars of reinforced concrete from the attack of chloride ions in marine environments. The plant extracts can act, in fact, as effective corrosion inhibitors due to their high concentrations of flavonoid compounds: the inhibition effect was found to be directly proportional to the concentration of the molokia and aubepine extracts. In the work of Wang et al. [89], the inhibitory effect of ginger extract against the corrosion of steel bars of concrete was analyzed. For comparison purposes, three commonly used corrosion inhibitors for steel rebars (namely kelp, $Ca(NO_2)_2$, and a commercial product) were selected as reference. In Figure 8, the evolution of the corrosion potential (E_{corr}) offered by the different products is reported as a function of the inhibitor content (from 0.5 to 4% by weight).

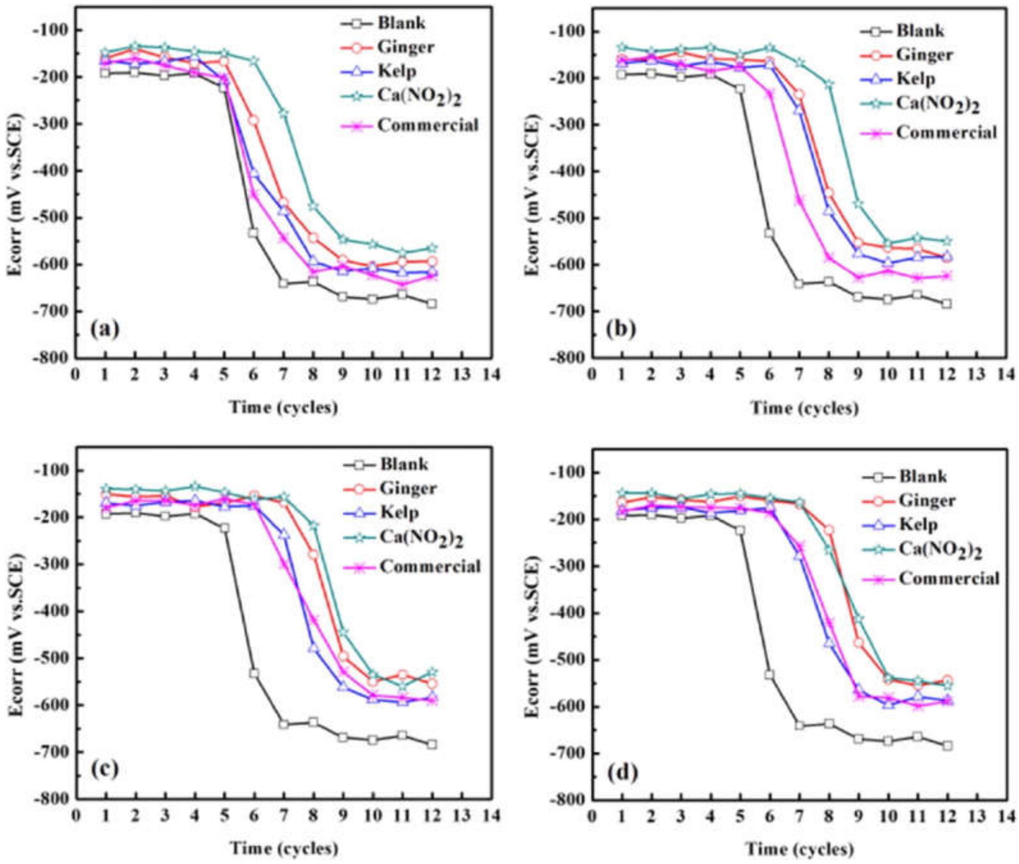

Figure 8. E_{corr} of steel bars embedded into cement mortars containing different corrosion inhibitors at different amounts: (**a**) 0.5% wt.; (**b**) 1% wt.; (**c**) 2% wt.; and (**d**) 4% wt. Reprinted from [89], with permission from Elsevier (November, 2022).

The results of this study confirmed that ginger extract is able to reduce the corrosion of steel bars in reinforced concrete; this ability was mainly attributed to the formation of a carbonaceous organic film on the surface of the steel. Furthermore, the addition of the ginger corrosion inhibitor had a positive effect on the workability of the concrete paste and negligible effects on its strength in the hardened state.

4. Concluding Remarks

Protecting a concrete structure with a coating is a much cheaper solution than repairing or rebuilding a new structure: effective products and technologies have been, and still are, therefore, sought for this purpose. Since traditional coatings involve the use of synthetic materials that are potentially toxic or dangerous for human beings and the environment, scientific and industrial research pushes towards the development of new sustainable coatings, made with bio-based or non-toxic materials, using green technologies. The purpose of this review is, therefore, to provide an overview of the bio-based/sustainable materials proposed for the development of original coatings to protect concrete works. Coatings based on natural materials with excellent water-repellent characteristics were also introduced as potential protective treatments for concrete and for its reinforcing bars. The use of these new materials as coatings could bring several advantages: the most obvious is the sustainability of the new solutions that are harmless to humans and the environment, that they can be applied using the same techniques and methods as for traditional coatings, without additional costs, and finally, as in some of the presented examples, waste materials can be exploited. Additionally, the studies carried out so far have especially highlighted the excellent protective properties offered by these materials, not considering any difficulties in the production processes and possible increased costs. Bio-based coatings could, in fact, replace traditional polymer-based treatments but probably not in the short term: higher production costs, scale-up problems, demand for high quantities of bio-based raw materials, competition with food and feed for the supply of raw materials, technological barriers, and including industrial conversion for new productions are some of the barriers that slow down the introduction of these materials to the market.

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