

The Use of Plant Extracts as Sustainable Corrosion Inhibitors for Cultural Heritage Alloys: A Mini-Review

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Abstract: Corrosion inhibitors have traditionally been utilised to protect copper alloy sculptures from corrosion despite the recognised environmental and human health risks. Knowing the associated toxicity, ongoing extensive research seeks alternative substances for corrosion reduction, giving rise to the emergence of green inhibitors. In this pursuit, plant extract inhibitors have gained attention, particularly in the heritage field. This review discusses recent advancements in synthesising sustainable and eco-friendly products designed to preserve metallic heritage from corrosion. We discuss the key findings on plant extracts used for corrosion control in metal alloys, taking into account the extraction methods to ensure the comprehensive coverage of relevant details. The use of plant extracts as corrosion inhibitors for metallic materials in cultural heritage (CH) is a highly promising and valuable research area. This review highlights recent advancements in the field, providing utility for conservators, conservation scientists, and restorers in identifying the most effective, eco-friendly, and safe compounds for material application.

Keywords: corrosion; cultural heritage; inhibitors; green chemistry; plant extracts



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1. Introduction

Copper-based alloys play a crucial role in cultural heritage remains. Throughout history, copper-made artefacts have been continuously used and nowadays are used for the casting of artistic artworks. These types of objects hold immense cultural value and provide valuable technological insights into the cultures that develop them, enabling the identification of trade and technological routes. As a result, preserving these items for future generations is imperative. In contemporary times, there is a strong emphasis on environmental sustainability and health in various realms of research and technological applications. This sensitivity has a pervasive impact, affecting almost every field, including research and developments related to the preservation and restoration of cultural heritage (CH). Indeed, a multitude of substances and technologies find application in conservation science for diverse purposes, with coatings and inhibitors serving as just two examples of potentially harmful substances currently in use. Recently, the growing concern for environmental sustainability and operator well-being has emphasised the urgency to explore new frontiers in developing substances that are both environmentally and healthfriendly. Meeting sustainability requirements and the demands of conservation science is a challenge that can be overcome with confidence. Consequently, the next frontier in conservation science research lies in the synthesis and application of inhibitors that are not only sustainable in their production but also non-toxic for both human health and the environment. It is crucial to emphasise that sustainability involves the entire production cycle of the compound. The synthesis and application of a biocompatible and natural material cannot be considered sustainable without taking into account factors such as the waste generated during the production of the release of secondary substances [1].

Concerning CH materials, substances used as coatings or inhibitors must meet additional requirements, including aesthetic and material compatibility with the artistic surface. Reversibility and ease of application are a few of the mandatory features expected from these compounds in the context of artwork conservation. When a material is applied to an archaeological surface, it should be easily removable without altering the aesthetics of the surface, all while providing long-term protection [2]. To ensure the safety of both human health and the environment, it is necessary to seek out sustainable alternatives for corrosion inhibitors, rather than relying on synthetic compounds that may be harmful and

unsustainable [3].

Rani and Basu (2012) [4] offer a comprehensive definition of green corrosion inhibitors, characterizing them as "biodegradable and free from heavy metals or other toxic compounds". These inhibitors must meet specific criteria, encompassing non-bioaccumulability, low marine toxicity, and biodegradability. Within the wide array of classes and types of such compounds, our focus will be on inhibitors derived from plant extraction due to their richness in compounds containing N, O, P, and S, as well as polar groups that make them strong inhibitors [5]. Moreover, plant extract corrosion inhibitors possess biocompatibility, low toxicity, biodegradability, low cost, and abundant resources. This is a significant advantage as conventional organic corrosion inhibitors may have inadequate solubility and can contribute to environmental pollution. Our objective is to present an overview of the achievements in research within this domain, with the intent of providing conservators and restorers with an up-to-date resource to incorporate these materials into their daily practices. The adoption of innovative, green, environmentally friendly, and sustainable materials promotes their broader utilization. The interest in exploring these new sustainable avenues is evident in the increasing number of experimental studies and international projects dedicated to green compounds for conservation. For instance, PROMET (Innovative Conservation Approaches for Monitoring and Protecting Ancient and Historic Metals Collections from the Mediterranean Region) has been conducting research in this field for over a decade, achieving significant milestones [6,7].

This review aims to fill the gap in the literature regarding the specific application of plant extracts as green inhibitors on ancient copper and bronze. The potential integration of these inhibitors into everyday conservation procedures will also be explored. The focus will primarily be on green corrosion inhibitors for CH materials, given their essential role in the field of conservation. This area has seen significant advancements, justifying discussion and paving the way for a new paradigm where green substances become a routine part of conservation practices [8–10].

2. Inhibitors

2.1. What Is an Inhibitor?

Inhibitors are substances that reduce the rate of corrosion in metals by forming a layer that is adsorbed on the metal–solution interface, resulting in a change in the potential difference between the two phases. This adsorbed layer displaces the water molecules from the metal surface [11]. Inhibitors promote the formation of a passive corrosion product layer, which reduces the corrosion rate to negligible values or inactivates the aggressive species on the corrosion product layer [1]. The mechanism of action of inhibitors is depicted in Figure 1.

Inhibitors are used to counteract corrosion processes in metals, with a main focus on restricting the activity of oxygen and chloride ions. The oxygen reduction reaction is the most prominent in the corrosion of metals exposed to aqueous environments. By primarily targeting this reaction, the corrosion resistance of samples is significantly improved, resulting in a decrease in the corrosion rate. In addition, the use of inhibitors offers superior corrosion protection, thereby prolonging the lifespan of structures [12]. Corrosion inhibitors can be administered as coatings or integrated into the packaging materials used for storage conditions.



Figure 1. Mechanism of action of corrosion inhibitors. The inhibitor film is absorbed into the metallic surface, blocking the access of aggressive ions and water molecules and avoiding redox corrosion reactions.

Corrosion inhibitors have been used since the Roman era, where extracts of glue and gelatine were used to protect iron in acidic media. Given the economic and scientific importance of inhibitors, their use has therefore continued over time. Chromates were introduced as inhibitors in the 19th century [13], and in the 1930s, inhibitors were classified based on their mechanism of action, such as anodic and cathodic inhibition [11]. In the 1950s, the first adsorption-type inhibitors were developed. However, since 1970, there has been an increasing trend towards studying environmentally friendly inhibitors. It is important to note that despite their widespread use, organic inhibitors have several disadvantages, such as toxicity and environmental risk. In fact, lead and chrome present in their composition are not biodegradable, and they tend to accumulate in the environment, posing a contamination risk to human health and the environment [14,15].

2.2. Mechanisms of Protection

Corrosion inhibitors in aqueous media protect metals by forming an adsorbed layer on the metallic surface. This layer shields the metal and repels corrosive species. The adsorption mechanism can occur through physisorption, mixed adsorption, or chemisorption, with the corresponding standard free energy of adsorption (Δ Gads) having values of Δ Gads > -20 kJ/mol, -40 kJ/mol < Δ Gads < -20 kJ/mol, and Δ Gads < -40 kJ/mol, respectively. Physisorption is characterised by weak interactions between the inhibitor molecules and the metallic surface through electrostatic forces. In contrast, chemisorption is characterised by stronger interactions through the formation of covalent or coordinate types of chemical bonding [16].

The standard free energy of adsorption is a widely accepted parameter for distinguishing between the adsorption of different types of inhibitors. However, new criteria to properly distinguish between physisorption and chemisorption were postulated and rely on the use of computational modelling studies where molecule–surface distance, molecule– surface bonding, and electronic structure can be reliably determined. The chemisorption mechanism is indicated when the surface distance equals the sum of covalent radii and the electronic structure is significantly disturbed. Meanwhile, the physisorption mechanism occurs when the molecule is at a distance from the surface equivalent to the van der Waals radii and the electronic structure is weakly perturbed [17]. It is important to note that the majority of plant extract corrosion inhibitors act through a physisorption mechanism [18].

Corrosion inhibitors reduce or inhibit the rate of cathodic or anodic reactions. The cathodic reaction is commonly attributed to the oxygen reduction reaction described by the following equation:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \tag{1}$$

For cathodic inhibitors, the added molecules are adsorbed into the reduction active sites of the surface, which promotes a blocking effect and decreases the oxygen diffusion rate [16]. On the other hand, the anodic reaction consists of the active metal dissolution:

$$M \rightarrow Mn^+ + ne$$
 (2)

Anodic inhibitors decrease the active surface by forming a protective and stable corrosion product layer that passivates the metallic surface. This results in a reduction in the dissolution rate of metallic cations. The mixed corrosion inhibitors significantly reduce the rate of both the anodic and cathodic reactions.

2.3. Inhibitors for Cultural Heritage Metals

CH comprises invaluable items that embody the cultural and social heritage of a community. Preserving heritage materials requires adherence to essential criteria, such as the preservation of the original aesthetics of artefacts and ensuring the reversibility of any interventions. These principles align with the guidelines of restoration philosophy, which are universally applicable across all areas of conservation science. When it comes to the application of corrosion inhibitors for archaeological metals, a distinct approach is required [2].

In addition to inhibitors, coating systems such as microcrystalline waxes are frequently used because they strike a balance between efficiency and aesthetic considerations [19–21]. However, one drawback of microcrystalline waxes is their relatively limited durability and poor outdoor protection, and issues such as dusting have been reported [22–24]. Consequently, as the need arose to address severe cases of corrosion, inhibitors, which were already known in the industrial sector, also found application in the realm of CH.

Benzotriazole-based (BTA) organic inhibitors are widely used in the field, particularly for smaller metal objects [25]. The mechanism of action of BTA on a copper (Cu) surface involves the formation of a strong chemical bond between Cu and nitrogen (N) atoms. This bond effectively promotes the creation of a passive layer that inhibits the oxygen reduction reaction [25,26]. The success of this type of compound can be attributed to its ability to be used at low concentrations while still achieving efficient inhibition. Although it has been effective in inhibiting the corrosion process, particularly on bronze artefacts, its use has faced limitations in the European Union since 2010 due to concerns about its toxicity, as reported in several publications [27,28]. As discussed by Baglioni et al. in "Advanced Materials in Cultural Heritage Conservation" [29], research efforts have accelerated experimentation with novel corrosion inhibitors. Among these inhibitors are triazole thiones, which have demonstrated the ability to inhibit both the anodic and cathodic corrosion processes in bronzes [30]. The chemical structures of BTA (a), 1,2,4-triazole (b), and 1H-1,2,3-trizole (c) are depicted in Figure 2.



Figure 2. (a) Chemical structure of BTA, (b) 1,2,4-Triazole, and (c) 1H-1,2,3-triazole.

Recently, there has been a growing need to prioritise non-toxic compounds and inhibitors [31]. One of the early applications involved confining imidazolium salts within chitosan-based coatings or loading chitosan-based coatings with benzotriazole and mercaptobenzothiazole. Additionally, 2-mercaptobenzothiazole has been loaded using amorphous PVA and encapsulated in layered double hydroxide nanocarriers [32–34]. Particularly noteworthy are carboxylate solutions, which have gained appreciation due to their non-toxic and non-carcinogenic properties. These solutions are based on carboxylate compounds, $CH_3(CH_2)n-2COO(Na^+, H^+)$, derived from fatty acids extracted from vegetable oils, such as sunflowers [35,36]. These compounds facilitate the formation of a protective layer composed of a metal–carboxylate complex by reacting with metallic ions. In the case of this type of inhibitor, corrosion protection is achieved through the creation of a barrier layer consisting of fatty acids extracted from vegetable oils. This layer forms a metal–carboxylate complex that reacts with metallic ions. The mechanism of action on non-corroded surfaces occurs in two steps: the oxidation of Cu in solution and the subsequent reaction of Cu^{2+} ions with carboxylate anions (Equations (3) and (4)).

$$Cu + \frac{1}{2}O_2 + H_2O \rightleftharpoons Cu^{2+} + 2OH$$
(3)

$$Cu^{2+} + 2(CH_3) - (CH_2)_{n-2} COO \rightleftharpoons Cu[(CH_3) - (CH_2)_{n-2} COO]_2$$
(4)

The protection of treated copper is attributed to the formation of a thin layer of metallic soap, which makes the surface hydrophobic [36]. It is crucial to exercise caution when dealing with cultural surfaces, as the corrosion layer may be an integral part of an artefact's historical context and should not be removed without careful consideration. If the analysis identifies the presence of a corrosive layer, often referred to as a "*vile patina*", we can take measures to treat the surface and remove the hazardous compounds while preserving the artefact's historical integrity [37].

Given the diverse range of materials and sizes involved in CH, such as the Eiffel Tower or a Roman fibula, the application of corrosion inhibitors varies in efficiency and approach. The efficiency and approach of corrosion inhibitors may vary, but they are typically applied using solutions with near-neutral pH to avoid the risk of altering the surface or removing the corrosion film. The flexibility of corrosion inhibitor application allows them to be used at different points in the conservation process, depending on the conservation treatment and the stage of the procedure.

For instance, inhibitors can be used in the following manners:

- Vapour Phase Application: Volatile corrosion inhibitors, a type of corrosion inhibitor, can be applied in vapour form by incorporating reactive particles into packaging materials during short- or long-term storage. These chemical compounds vaporise and condense onto the metallic surface in the presence of moisture, providing reliable protection against environmental factors [38,39].
- Coating Systems: Corrosion inhibitors can be included in coating systems that are brushed over the surface, providing additional protection against corrosion. This approach is especially valuable for preserving metal cultural heritage [40,41].
- Immersion: Another method is immersing the item in a solution containing corrosion inhibitors. This can be applied before storage, as part of the stabilization procedures, or as the final step in the conservation treatment. A schematic diagram of this process is shown in Figure 3. As a first step, the corrosion inhibitor molecules are dissolved in a carrier medium, which can be either a polar or non-polar solvent (e.g., water or ethanol). The samples are then immersed in this solution, allowing for the corrosion inhibitor molecules to adsorb onto the metallic surface, thus delivering the desired protective effect. The process of adsorption occurs through various mechanisms, which will be explored further in subsequent sections. After immersion and rinsing, a protective coating is typically applied to enhance corrosion protection by acting as a barrier film. This prevents the access of water molecules to the metallic surface and extends the service life of the corrosion inhibitors [42–44].



Figure 3. Schematic diagram of the application procedure of inhibitors in cultural heritage artefacts. The corrosion inhibitor is dissolved in the proper media to cover the surface of the immersed item.

3. Plant Extracts

Historically, tannic acid has been the most commonly used corrosion inhibitor obtained from plant extraction [45,46]. Tannin is found in various types of plant materials and is extracted from sources such as oak galls, as well as other vegetable sources like sumac and willow. It is even present in green algae and mosses. Tannic acid is used to inhibit the corrosion of iron because it reacts with metallic iron or rust, resulting in the precipitation of ferric tannates. This process forms a protective layer with corrosion-inhibiting properties [47,48].

Tannic acid mixtures, often including orthophosphoric acid, are commonly applied as a final step in the conservation treatment process to coat archaeological iron. However, it is important to note that tannic acid has its limitations. In some cases, it can transform the surface colour from reddish to black, and its protective effect on iron has been found to be less effective [10,49]. Benzidia and collaborators conducted an experiment as detailed in their work titled "Investigation of Green Corrosion Inhibitor Based on *Aloe vera* (L.) Burm. F. for the Protection of Bronze B66 in 3% NaCl" [50]. They explored the application of tannins extracted from *Aloe vera* to inhibit the corrosion of bronze B66 in a chlorine-rich medium, simulating a marine environment.

Tannic acid, a polyphenol tannin, exists in the form of an amorphous powder that is highly soluble in water [51]. Its chemical formula ($C_{76}H_{52}O_{46}$) indicates that it consists of a mixture of polygallolyl glucoses or polygallolyl quinic acid esters ranging from 2 to 12 in number [52]. Specifically, tannic acid is a type of gallotannin containing glucose esters of phenolcarboxylic acids, and is widely used in various fields, ranging from medicine to dyeing [53,54].

In the field of metal conservation, tannic acid has shown inhibitory properties, initially on iron and subsequently on copper. Given the favourable outcomes observed with iron, researchers began investigating its application in other metals, including copper and its alloys. Leveraging the chemical characteristics of tannic acid, Benzidia et al. successfully applied tannic acid to bronze B66, which closely resembles the composition of archaeolog-ical bronze [50]. It is essential to note that during these experimental phases, it was not feasible to apply innovative products directly to original materials without first ensuring the product's safety and effectiveness on this type of metal. The results demonstrated that the *Aloe vera* extract effectively inhibits the corrosion of bronzes immersed in a 3% NaCl solution, with the level of protection correlating with the concentration of the plant extract. SEM-EDS analysis was instrumental in illustrating the formation of corrosion products after 24 h of immersion without protection and, conversely, the active inhibition provided by the *Aloe vera* extract when applied to bronze B66.

In their work [55], Kusmierek and E. Chrzescijanska evaluated the effectiveness of tannic acid, which is found in various plants, as a corrosion inhibitor for use in preserving Polish cultural heritage. In the procedure, as shown in Figure 4, the plants collected were dried at room temperature for 13 days and then crushed into a fine powder. The powdered pods were then placed in 250 mL of methanol for 5 days, and the extraction $(25 \times 30 \text{ mL})$ was repeated until the plant materials were exhausted. The extract obtained was concentrated using a rotary evaporator below 55 °C. The extract was evaporated, resulting in a solid form for the preparation of the stock inhibitor concentration. Their research confirmed the inhibitory properties of such compounds, particularly on copper and brass. The inhibitors were then added to water solutions at concentrations ranging from 0.25 to 25 mg/dm^3 . The corrosion behaviour was assessed using linear polarization resistance and weight loss methods. The results clearly demonstrated that tannic acid was an effective protective agent for Cu surfaces, with the highest inhibition efficiency observed in solutions with a concentration of 10 mg/dm^3 . Furthermore, the immersion method was tested, and the highest inhibition performance was achieved after 5 immersions in a solution containing 100 mg/dm^3 . The corrosion rate was strongly related to the inhibitor concentration. Surprisingly, the protection of brass was found to be more effective than that observed for other alloys such as Inconel and steel with a concentration above 20 mg/dm³.

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Drying of Plants: • Collect plants. • Allow them to dry at room temperature for 13 days.	Crush the dried plants into a fine powder.	Extraction: • Place the powdered pods in a container (e.g., 250 ml) with methanol. • Let it sit for 5 days to allow for extraction. • Perform repeated extractions (25 × 30 ml) until the plant materials are exhausted.	Concentration: • Take the extract obtained and concentrate it. • Use a rotary evaporator at a temperature below 55°C for the concentration process.	Evaporation: • Evaporate the concentrated extract to yield a solid form.	Preparation of Stock Inhibitor Concentration: • The solid form obtained from veaporation is used for the preparation of the stock inhibitor concentration.

Figure 4. The extraction procedure described by E. Kusmierek and E. Chrzescijanska in their work [55] that was used to obtain an inhibitor for brass, starting from *Aloe vera*.

Fouda and collaborators [56] conducted experiments using *Ceratonia siliqua* as a corrosion inhibitor for copper and α -brass in 1 M HNO₃ solutions. To prepare the inhibitor, they collected fresh plants, dried them at room temperature for 13 days, and subsequently crushed them to obtain a fine powder. The powdered pods were then immersed in 250 mL of methanol for 5 days, followed by repeated extractions (25 cycles of 30 mL each) until all the plant material was exhausted. The resulting extract was concentrated using a rotary evaporator at a temperature below 55 °C, eventually yielding a solid form suitable for preparing the stock inhibitor concentration. The procedure is schematised in Figure 5. Also, the extracted inhibitor was added to a 70% HNO₃ solution in concentrations of 50 to 300 ppm. The analytical procedure they used resembled previous work involving gravimetric and electrochemical analyses to assess the level of protection. The results obtained using a combination of weight loss analysis, electrochemical impedance spectroscopy (EIS), and polarization curves indicated that Ceratonia siliqua exhibited effective corrosion protection for both copper and brass, acting by increasing the energy barrier for the corrosion of copper and brass dissolution. Similar to tannic acid, the level of protection provided by C. siliqua increased with concentration but decreased with temperature because of the corrosion inhibition performed through the physical adsorption mechanism. and desorption was more prone to occur as the temperature increased. Of note, the metals

adsorbed the inhibitor in accordance with the Langmuir adsorption isotherm, involving a spontaneous and exothermic reaction, as evidenced by the negative values of free energy. *C. siliqua* primarily acted as a cathodic inhibitor in their research. These findings suggest that further investigations into the application of *C. siliqua* on archaeological metals would be worthwhile.

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1	2	3	4	5	6	7
Drying of Plants: • Collect plants. • Allow them to dry at room temperature for 13 days.	 Allow plants to dry at room temperature for 13 days. 	Crush the dried plants into a fine powder.	Extraction: • Immerse powdered pods in 250 ml of methanol for 5 days. • Perform repeated extractions (25 cycles of 30 ml each) until plant material is exhausted.	Concentration: • Use a rotary evaporator at a temperature below 55°C to concentrate the extract.	Solid Form: • Resulting extract evolves into a solid form.	Preparation of Stock Inhibitor Concentration: Use the solid form for preparing the stock inhibitor concentration.

Figure 5. The extraction procedure described by Fouda and collaborators [56] that was used to extract inhibitors from *Ceratonia siliqua*.

Fascinating investigations involving novel plant extracts have emerged from experiments with acacia fruit extracts (Robinia pseudoacacia L.) [57]. This work aimed to assess the viability of Robinia pseudoacacia L. extracts as Cu-10Sn corrosion inhibitors in saline media. To extract the inhibitors, fruit samples were collected, dried, and ground to obtain 30 g of powder. Later, the collected powder was soaked in 100 mL of double-distilled water and constantly shaken for 24 h at room temperature. The liquid was mechanically filtered to separate extracts and powder. Also, the extract was centrifuged at 2500 rpm and 4 °C and dewatered using a vacuum rotary device. The powder was diluted ranging from 200 to 1800 ppm. This dissolution was applied to as-cast Cu-10Sn bronze alloy with a composition similar to historical ones. These bronze samples underwent corrosion in a 0.5 M sodium chloride solution for four consecutive weeks. The researchers discovered that the green inhibitor derived from the acacia fruit aqueous extract could effectively inhibit bronze corrosion, increasing its inhibitory properties with concentration. Also, the highest corrosion protection was obtained after two weeks of constant immersion. For higher immersion times, the inhibitory efficiency decreased. However, at higher concentrations, it exhibited fungus growth, which could diminish the effectiveness of the acacia fruit aqueous extract. Based on the cathodic and anodic slopes, the authors indicated that the inhibitor corresponds to a mixed-type corrosion inhibitor. While this work provides preliminary results, it identifies Robinia pseudoacacia L. as a promising candidate warranting further study.

Another noteworthy study, reported by Rahal et al. [16], presented the results of using an olive leaf extract as a corrosion inhibitor for pure copper in 0.5 M NaCl solution. To extract the inhibitor compound, olive leaves were air-dried at room temperature for one month in the absence of light. The leaves were ground, and the dissolution of 100 g of olive leaf powder per litre of distilled water was prepared. The primary compound identified was oleuropein, and three solutions with varying concentrations of this compound (2.42 mmol L⁻¹, 1.21 mmol L⁻¹, 0.48 mmol L⁻¹) were tested. The samples were immersed for 24 h in a completely static 0.5 M NaCl solution at room conditions. The authors reported that the corrosion rate of the samples decreased as the inhibitor concentration increased. This olive leaf extract strongly modified the oxygen cathodic reduction reaction, indicating a cathodic inhibitor type. Furthermore, the inhibition efficiency exceeded 86% for the highest solution concentration and decreased with temperature in a similar manner to that previously indicated for *Ceratonia siliqua*.

Another eco-friendly alternative for copper protection was described by Gao et al., as detailed in their work [58]. In their study, a *Saccharum officiniarum* leaf extract was tested to identify its corrosion inhibition properties for copper in acidic media. The inhibitor extract was obtained by crushing dried leaves to obtain a fine powder. An alcoholic solution of leaf extract was obtained after 48 h of static immersion and subsequently dried in a rotary evaporating flask. Various amounts of the extract (ranging from 100 mg/L to 500 mg/L) were dissolved in a 0.5 M H₂SO₄ solution. The results indicated that the leaf extract formed a protective film on the copper surface, increasing the charge transfer resistance as the concentration increased. Also, *Saccharum officiniarum* acted as a mixed corrosion inhibitor. The inhibition efficiency reached 93% for the highest inhibitor concentration.

Elshahawi and collaborators [59] reported the efficiency of a Jatropha extract as a green corrosion inhibitor for bronze archaeological artefacts in a 3.5% NaCl solution. The Jatropha extract was obtained using cold pressing and was added by brushing the surface at concentrations of 10 ppm, 20 ppm, 30 ppm, 40 ppm, and 50 ppm. The authors conducted a series of electrochemical tests, correlating the results with the weight loss method and a salt spray exposure chamber. The electrochemical results indicated a mixed-type corrosion behaviour. All the results indicated that the addition of 30 ppm of the extract demonstrated the highest inhibition efficiency, reaching 86%. Also, as temperature increased the inhibitory efficiency decreased due to the desorption process that led to the detachment of the inhibitor molecules on the metallic surface, as evidenced by the studies [50,56]. It is relevant to note that this inhibitor was applied by brushing on an Egyptian archaeological bronze mirror with patina layers.

An interesting study reported by Tan et al. [60] aimed to identify the corrosion inhibitor properties of papaya leaf extract for copper in sulfuric acid media. The corrosion inhibitor was obtained by drying fresh papaya leaves in an oven for 24 h. Later, the leaves were powdered and added to 1 L of ultrapure water that was heated and evaporated to 200 mL and filtered with fine gauze. Again, the dissolution was heated to evaporate until 50 mL. The plant extract corrosion inhibitor was placed in a refrigerator for 10 h to completely freeze. The inhibitor was placed in a freeze-drying device for 24 h to finally obtain 5.23 g of dry powder. The plant extract was diluted in 0.5 mol/L of sulfuric acid with concentrations of 10, 20, 100, and 150 mg/L. The results showed that the addition of the plant extract corrosion inhibitor modified the kinetics of copper dissolution due to the adsorbed inhibitor layer. However, the icorr values of the cathodic and anodic branches of potentiodynamic polarization curves were reduced, indicating a mixed-type corrosion inhibitor behaviour. Also, a higher inhibition efficiency (93%) was obtained at 25 $^{\circ}$ C with 150 mg/L. The adsorption isotherm analysis indicated that this papaya-based inhibitor attached to the surface through a physico-chemical adsorption mechanism. These results indicated that the papaya leaf extracts could attach to the copper surface strongly, providing a dense barrier film inhibiting corrosion. More studies on this matter will be valuable. Another work by the same author [61] studied the corrosion inhibition properties of *Pasiflora edulia* Sims leaf extracts in protecting copper in a H₂SO₄ solution. To obtain the corrosion inhibitor, fresh Pasiflora edulia Sims leaves were dried in an oven at 343 K for 24 h and then ground into a fine powder. Later, 100 g of powder was added to the dissolution of 500 mL of ultrapure water. Also, the dissolution was heated and evaporated until it reached 200 mL and was then filtered. The dissolution was frozen for 24 h and then placed in a freeze-drying oven for 48 h. The Pasiflora edulia Sims leaf extract was dissolved in 0.5 M H₂SO₄ with concentrations of 100, 200, 400, 600, and 800 mg/L. The results showed that the inhibitor attached to the copper surface and increased the charge transfer resistance. Also, the corrosion inhibitory properties were strongly dependent on the inhibitor concentration. With a concentration of 600 mg/L, the diffusive processes became weaker, indicating the formation of a closed protective film on the Cu surface. The maximum inhibitory efficiency reached was 96.5% for a concentration of 800 mg/L. This type of inhibitor acted by modifying the cathodic behaviour and showed a physico-chemical adsorption model.

Myrthus communis was studied by Dahmani et al. [5] to inhibit the corrosion of copper in 0.5 M sulfuric acid. The plant extraction inhibitor was obtained by collecting fresh leaves and drying them in the shade at room conditions for 3 weeks, followed by the obtention of the essential oil using hydrodistillation for 2 h. The resulting volatile extract was dried and stored at 4 °C. The plant extract corrosion inhibitor was added in concentrations of 0.5 to 2 g/L. The inhibitor addition diminished the anodic and cathodic corrosion currents. However, this inhibitor relied on the mixed-type corrosion inhibitor and attached to the surface through a physisorption mechanism. Again, the inhibition properties depended on the inhibitor concentration, reaching a maximum efficiency of 93.2% for the concentration of 2 g/L. An interesting point in their study was that the inhibition properties remained almost constant after 16 h of constant immersion with the maximum concentration.

Cao et al. [62] studied the properties of *Dimocarpus longan* Lour leaf plant extract in inhibiting the corrosion of Cu in 0.5 M sulfuric acid media. The route of obtention of the corrosion inhibitor consisted of collecting the fresh leaves, which were dried and pulverised. The powder was placed into a baker containing the sulfuric acid 0.5 M solution for 36 h. The supernatant was decanted into a baker, freeze-dried, and kept in a dissector until it was used. The concentrations tested were 50 mg/L to 400 mg/L, which were added to a corrosive 0.5 M sulfuric acid solution. The addition of the plant extract corrosion inhibitor led to a decrease in the cathodic corrosion current, preferentially inhibiting the precipitating of oxygen at the cathodic active sites at the copper surface. The inhibition efficiency of this plant extract corrosion inhibitor was 98% for a concentration of 400 mg/L. In this case, a chemisorption mechanism was indicated.

In general, the route of obtention of the plant extract corrosion inhibitors is similar for almost all the studies reviewed. The route consists of a set of progressive stages, which are represented in Figure 6. As a first step, the plant is collected in fresh conditions, dried, and powdered and then added to a solvent (distilled water, methanol, and sulfuric acid). Later, the dissolution is concentrated using evaporation, centrifugation, or freeze-drying. Finally, the powder that can be added to the corrosive test solution is obtained. In special cases, Dahmani et al. [5] obtained a plant extract corrosion inhibitor using essential oils that were dried and stored in a powder form, which was added to the corrosive solution. Elshahawi et al. [59] drew upon the cold pressing method and applied an inhibitor directly by brushing the metallic surface.



Figure 6. Schematic representation of the route of obtention of plant extract corrosion inhibitors.

Once a corrosion inhibitor has been obtained, it can be applied to a metallic sample by directly immersing the object in a solution containing the plant extract corrosion inhibitor or by brushing the inhibitor solution onto the surface of the sample, as shown in Figure 7. The corrosion system is then sealed with a protective coating, as shown in Figure 3. It is worth noting that only a few works deal with the direct application of the inhibitor on metallic samples [55,59]; in the majority of the studies reviewed, the inhibitor was added to the corrosive test solution.



Figure 7. Examples of the application of plant extract corrosion inhibitors to cultural heritage copperbased alloys: (**a**) direct immersion and (**b**) brush application of the inhibitor-containing solution.

As expected by the diverse origin of plant extract corrosion inhibitors, different adsorbed molecules provide corrosion protection to the substrate. Table 1 shows the active compounds determined in the plant-extracted inhibitors that were reviewed. It is observed that different compounds can provide corrosion protection; however, the following premise is maintained: corrosion inhibitor molecules contain N, S, and O groups that can provide bonding sites for attaching the inhibitor layers to the metallic surface and exert corrosion protection through the barrier effect of the molecule into the metallic surface. To properly understand the protective effect of the active compounds, quantum chemical analysis tools such as DFT can shed light on the electronic behaviour, preferential attachment sites, and molecules responsible for corrosion inhibition. The work of Gao et al. [58] is a clear example of this powerful analysis tool since molecular simulation results allowed the authors to determine that N and O were preferential sites to form coordination bonds to the copper surface. Also, based on the molecular dipole, the authors determined that HMA and DHC molecules have higher corrosion performance. Similarly, Tan et al. [61] determined that the most favourable molecules for corrosion inhibition were PTH and DMT.

Plant Extract	Active Compounds	Reference	
Tannic acid	Tannic acid	Kusmierek et al. [55]	
Aloe vera mucilage	Acemannan	Benzidia et al. [50]	
Ceratonia siliqua	Sugar and condensed tannins	Fouda et al. [56]	
Robinia pseudoacacia L.	Arabinose, ramenoz, galactose, gluconic acid, rubinin, 4 methoxygluconic	Pourzarghan et al. [57]	
Olive oil	Oleuropein	Rahal et al. [16]	
Saccharum officiniarum	3-(-4-hydroxy-3-methoxyphenyl) (HMA), 1-methyl-3-nitrosoguanidine (MND), 3-(3,4-dihydroxyphenyl)acrylic acid (DDA); 5,7-dihydroxy-2-(4-hydroxyphenyl)-4H-chromen-4-one (DHC)	Gao et al. [58]	
Jatropha	Phytol, stigmasterol, campesterol, sitosterol	Elshahawi et al. [59]	
Papaya leaves	DL-Ascorbic Acid; 5,7-Dimethoxy-chromen-2-one (DCO); 2-Amino-4-methylsulfanyl-butyric acid (AMB); 3,4-Ditydroxy-benzoic acid (DBA); 2-Hydroxy-succinic acid (HSA); 3-[3-(3,4-Dihydroxy-phenyl)-acryloxyl]- 1,4,5-trihydroxy-cyclohexanecarboxylic acid (DTA)	Tan et al. [60]	
Pasiflora edulia Sims	(R)-2-Phenyl-2-((2R, 3R,4S, 5S, 6R)-3,4,5-trihydoxy-6-(hydroxymethyl)-tetrahydro-2 H- pyran-2-yloxy)acetonitrile (PTH); 2 R, 3 R,4 R,5 S,6 R)-2-(benzyloxy)- 6-(hydroxymethyl)-tetrahydro-2 H-pyran-3,4,5-triol (BHT); 8-(4,5-dihydroxy-6-methyl-tetrahydro-pyran-2-yl)- 2- (3,4-dihydroxy-phenyl)-5,7-dihydroxy-chromen-4-one (DMT)	Tan et al. [61]	
Myrtus communis	Myrtenyl acetate	Dahmani et al. [5]	
Dimocarpus longan Lour	TBE; TDF; PDH	Cao et al. [62]	

Table 1. Active compounds determined in the plant extract corrosion inhibitors.

Despite the powerful results provided by this computational molecular analysis, this analysis technique is not widespread in the plant extract inhibitor community, making the proper identification of the active compound a hard task and leading to the consideration that corrosion protection results from the synergic effect of several molecules.

It is interesting to note that most of these studies assess the inhibitory efficiency of plant extract corrosion inhibitors applied on clean and polished metallic surfaces. However, these conditions do not accurately represent the typical conditions of copper-based cultural heritage, which naturally develops a corrosion product layer grown over years of exposition to a corrosive environment or may be intentionally formed by the artist as part of the concept of their artwork. Only in the case of the Jatropha extract [59] was a patinated surface used, but the authors did not provide the electrochemical characterisation of these archaeological samples. The inhibitory efficiency of the Jatropha extract applied on a patinated bronze may differ from that obtained for a polished bronze surface where the molecule can properly attach to the active sites. Ben Chanouf et al. [63] indicated that the corrosion product layer modifies the corrosion inhibitor behaviour. The corrosion-inhibitory properties of the reviewed plant extracts depend strongly on their concentration. A higher concentration of corrosion inhibitor molecules promotes the formation of a dense layer that effectively protects the metallic surface, but the patina layer restricts the metallic surface exposed surface area. Thus, because corrosion inhibitors are greatly applied over patinated surfaces, further research should be conducted to identify the interaction of plant extract corrosion inhibitors on surfaces covered with stable corrosion product layers.

Since corrosion is an electrochemical process, it is necessary to mainly characterise the corrosion inhibitory response using electrochemical techniques, and the works reviewed mainly establish their conclusion based on electrochemical impedance spectroscopy and potentiodynamic polarisation curves. It is necessary to consider that the electrochemical response of a sample depends on the concentration of the electrolyte, pH, temperature, composition of the sample, and immersion time. Then, to properly compare the inhibitory efficiency of these studies, similar conditions must be applied. For our review, the exposure time of the works considered varies during a lapse time of 30 min to 24 h. However, for the main corpus of the papers reviewed, the electrochemical characterisation was performed after 30-60 min of constant immersion to reach the OCP and maintain the OCP potential during EIS tests. Only the works of Rahal [16] and Pourzaghan [57] evaluate the inhibition response of the plant-extracted corrosion inhibitors after 24 h and 672 h of constant immersion. The concentration of the electrolyte was kept from 0.5 to 1 M for H₂SO₄ and 0.5 M NaCl to 3.5 wt%. of NaCl. The testing temperature was at room conditions; however, the influence of temperature was studied by heating the inhibitor container from 15 to 80 °C. Table 2 summarises the inhibitory properties of the reviewed plant extract corrosion inhibitors. As shown, the use of plant extract corrosion inhibitors allows for obtaining high inhibition efficiency values, indicating that the contained molecules can successfully protect the metallic substrates. In addition, these inhibition values were obtained at higher test concentrations. It is also noted that the extraction method is relatively safe for the operators because of the use of water and methanol as extraction solvents. This is an advantageous feature that makes the process sustainable, with the exception of the works [58,62], where acidic solutions were used. Despite the different parameters used, it can be said that the highest corrosion inhibitory efficiency for copper in H₂SO₄ media was obtained for *Pasiflora edulia* Sims leaf extracts (96.5%) [61], and for chloride media, the Jatropha extract showed the highest inhibition efficiency (86%) [59]. As stated above, it is necessary to consider that the inhibitory properties can vary because there are no reports about the performance of these plant extract corrosion inhibitors on patinated surfaces.

Inhibitory Efficiency (%)	Metal or Alloy	Concentration	Solvent Used for Extraction	Corrosive Testing Solution	Reference
89.17	Cu	25 mg/dm^3	Methanol	Distilled water	[55]
85.94	Bronze	750 ppm	Not provided	3% NaCl	[50]
84.7	Brass	300 ppm	Methanol	1M HNO ₃	[56]
93.5	Bronze	1800 ppm	Distilled water	0.5 M NaCl	[57]
86	Cu	0.48 mmol/L	Distilled water	0.5 M NaCl	[16]
93	Cu	500 mg/L	H_2SO_4	0.5 M H ₂ SO ₄	[58]
86	Bronze	30 ppm	Not provided	3.5% NaCl	[59]
93	Cu	150 mg/L	Ultrapure water	$0.5 \text{ M H}_2\text{SO}_4$	[60]
96.5	Cu	800 ppm	Ultrapure water	$0.5 \text{ M H}_2\text{SO}_4$	[61]
93.2	Cu	2 g/L	Not provided	0.5 M H ₂ SO ₄	[5]
98	Cu	400 mg/L	H_2SO_4	0.5 M H ₂ SO ₄	[62]

Table 2. Inhibitory efficiency and relevant parameters of corrosion inhibitors extracted from plants.

The above suggests that plant extract corrosion inhibitors are suitable for protecting copper and copper-based alloys from corrosion in outdoor exposure conditions such as acid rain or chloride media. This is due to the presence of atoms (N, S, O) in the extracted molecules that promote attachment to the metallic surface, as well as high dipolar moments and unsaturated functional groups [61]. However, we consider that, at this point, it is difficult to relate inhibition efficiency to a single compound because the extraction methods are not oriented towards purifying and concentrating a specific molecule and the inhibitory response is associated with a synergistic response of the molecules extracted. Some works such as those reported by [16,60,61] indicate which molecule was mainly identified; however, the lack of information in the other studies reviewed prevents a complete

understanding of the relationship between the inhibitor compound and its inhibitory efficiency. On the other hand, Kokalji et al. [64] proposed a valuable method for identifying the inhibition properties of corrosion inhibitor molecules. They introduced the term "inhibition power" due to the lack of linearity in the classical inhibition efficiency and the negative correlation among the classical molecular electronic parameters. The future application of this methodology will be useful in this field because can allow us to elucidate new sets of plant extract corrosion inhibitors.

The study of green corrosion inhibitors derived from plant extracts represents a promising frontier in the field of materials conservation, particularly for metals like bronze and copper. Researchers have explored a variety of plant-based inhibitors, such as *tannic acid*, *Aloe vera*, *Ceratonia siliqua*, acacia fruit, olive leaf extract, *Saccharum officiniarum*, Jatropha extract, papaya leaves, *Pasiflora edulia* Sims, and *Dimocarpus longan* by assessing their effectiveness in inhibiting corrosion under different conditions. These studies have provided valuable insights into the potential of eco-friendly inhibitors to protect cultural heritage materials. While challenges such as concentration optimisation and temperature sensitivity persist, the continued research and development of green corrosion inhibitors offer a sustainable and environmentally friendly approach to preserving our cultural heritage for generations to come.

4. Features, Advantages, and Disadvantages of Plant Extracts as Corrosion Inhibitors

Corrosion inhibitors can be extracted from various parts of a plant, including the flower, leaf, root, seed, bark, gum, fruit, and stem, with each part providing distinct molecules such as polyphenols, flavonoids, or polysaccharides [1,65]. Leaf extracts generally exhibit better corrosion inhibition at lower concentrations [3]. The molecules in plant extracts consist of organic bioactive molecules that form heterocyclic constituents, such as alkaloids, flavonoids, carbohydrates, or proteins. These organic compounds typically contain polar functions with nitrogen, sulphur, oxygen, and phosphorus atoms and have triple or conjugated double bonds with aromatic rings in their molecular structures, serving as major adsorption centres on metallic surfaces [56,66]. Also, this type of inhibitor offers some advantages in comparison with traditional inhibitors. For example, plant extract corrosion inhibitors are related to the abundant nature of plant biomaterials, making them low-cost, economically viable, easily renewable, reliable, and biodegradable [18,67]. Plant extracts are easily soluble in water or other polar solvents, and they are less toxic to the environment and human health. However, some issues have sparked controversy regarding their use. For instance, the extraction and purification of plants are expensive and time-consuming processes [3]. Additionally, the active compound responsible for corrosion inhibition is not completely determined, and corrosion inhibition may result from the synergistic effect of several molecules [66,68]. Despite the promising alternative represented using plant extract corrosion inhibitors, some fundamental aspects are still unknown, such as the appropriate part of the plant for extraction and the proper determination of the active compound that exerts the corrosion inhibitory effect. This limitation can hinder their use and complicate the application of plant extract inhibitors on a large scale. The advantages and disadvantages of the plant extracts are summarised in Table 3.

An example of the inhibitory properties of plant extract corrosion inhibitors is shown in Figure 8. In an ongoing study, the authors immersed a quaternary bronze sample in a 0.5 M H₂SO₄ solution for 6 h. Sample (a) was not inhibited, while sample (b) was inhibited through previous immersion in a *Laurus Nobilis* distilled water solution. Additionally, surface topography plots of the (c) uninhibited (Ra = 0.494 μ m) and (d) inhibited (Ra = 0.196 μ m) bronze samples were presented. The samples showed their metallographic microstructure as a result of etching with the acidic solution. Within the first hour of immersion, leaching was more pronounced on the uninhibited bronze samples, resulting in a whitish appearance due to the copper dissolution and tin enrichment. In contrast, the inhibited sample retained its original surface appearance. After 6 h of constant immersion, the inhibited sample showed less corrosion and lower roughness. This behaviour indicated that the addition of the *Laurus nobilis* plant extract corrosion inhibitor increased the corrosion resistance of the bronze samples. It is important to note that the protective properties of the plant-based corrosion inhibitors depended strongly on the concentration and testing time.

Table 3. Summarised aspects of using plant extracts as corrosion inhibitors.

Aspect	Advantages	Disadvantages	
Source of inhibitors	Extracted from various plant parts: flower, leaf, root, seed, bark, gum, fruit, and stem [1,64].	Expensive and time-consuming extraction and purification processes [3].	
Corrosion inhibition mechanism	Molecules like polyphenols, flavonoids, or polysaccharides with polar functions and heterocyclic constituents.	Active compound responsible for corrosion inhibition not completely determined; may result from the synergistic effect of several molecules [65,67].	
Effectiveness at lower concentrations	Leaf extracts generally exhibit better corrosion inhibition at lower concentrations [3].	Fundamental aspects unknown, such as the appropriate plant part for extraction and the proper determination of the active compound.	
Economic and environmental factors	Abundant, low-cost, economically viable, easily renewable, reliable, and biodegradable [18,66].	-	
Solubility and toxicity	Easily soluble in water or other polar solvents; less toxic to the environment and human health.	-	



Figure 8. Surface appearance and topographic profiles of (a,c) uninhibited and (b,d) inhibited bronze samples exposed to a 0.5 M H₂SO₄ corrosive solution. Stereoscopic Microscope, 2×.

5. Future Work and Challenges

Based on the review performed, some challenges and future perspectives about the performance of plant extract corrosion inhibitors were observed by the authors. One of them is the evaluation of the corrosion performance of inhibitors applied on patina samples. Because the information regarding this subject is scarce and a patina layer is commonly found in archaeological and artistic copper alloys, it is worth understanding the behaviour

of the system formed with the patina layer and plant extract corrosion inhibitors. Another challenge that could be faced is the long-term corrosion characterisation of these inhibitors using laboratory tests, because, in a great part of the cases, the experiments were carried out with a short time perspective of constant immersion (24 h). Additionally, is worth evaluating the performance of corrosion inhibition for patinated samples under rain, dripping, or wet and dry cycles because these behaviours resemble, in a more similar way, atmospheric exposition, and the leaching effect of rain on patina layers has been evidenced. Then, the leach of the patina could affect the performance of the corrosion inhibitor. Another challenge that could be addressed is the possible modification of colour that could be promoted by solar exposition. The formation of fungus activity can also be considered. However, the main issue with the use of plant extract corrosion inhibitors is the lack of identification of the active compound and the interaction between the molecule and the metallic surface. This is a key point in the use of these types of inhibitors because proper identification can lead to the isolation of the active compound that increases an inhibitor's efficiency. Also, molecular simulation is relevant because it can provide information about the adsorption capacity of the plant extract inhibitors, which depends on the molecular structure and the electron cloud density. Despite the promising field of the use of plant extract corrosion inhibitors, there are many issues that constitute a challenge for corrosionists, conservators, and chemists that should be addressed to ensure the use of plant extract corrosion inhibitors and their application in cultural heritage copper alloys.

6. Conclusions

The exploration of green corrosion inhibitors derived from plant extracts stands as a promising frontier in materials conservation, particularly for metals like bronze and copper. Ongoing research has identified a range of plant-based inhibitors, including tannic acid, Aloe vera, Ceratonia siliqua, acacia fruit, olive leaf extract, and Jatropha extract, which have shown their effectiveness in inhibiting corrosion under diverse conditions. This review has delved into recent advancements in synthesising sustainable and eco-friendly products, emphasizing their potential to preserve metallic heritage from corrosion. While challenges such as concentration optimisation and temperature sensitivity persist, continuous research and the development of green corrosion inhibitors offer a sustainable and environmentally friendly approach to safeguarding our cultural heritage. Despite the advantages of using plant extract corrosion inhibitors, such as their low cost, renewability, and biodegradability, controversies arise due to the expensive and time-consuming extraction process, uncertainties regarding the active compound, and potential synergistic effects of multiple molecules. This review serves as a valuable resource for conservators, conservation scientists, and restorers, providing insights into the most effective, eco-friendly, and safe compounds for material application in the field of cultural heritage.

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