



## Review

# Bibliographical Synthesis on the Corrosion and Protection of Archaeological Iron by Green Inhibitors

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**Abstract:** Iron is a widely used metal due to its low cost and availability, but it is susceptible to corrosion in many circumstances. This corrosion can result in economic and environmental losses, and negatively affect the physical and chemical properties of the metal. This chapter provides a background on iron corrosion in archaeology and introduces various inhibitors used for its protection. It starts with a general overview of corrosion and metallurgy of iron, followed by an in-depth explanation of the mechanisms of iron corrosion in water and air. The chapter concludes with a review of different corrosion inhibitors, focusing on those made from natural plant extracts.

**Keywords:** archeological iron; corrosion; mechanism; green inhibitors; protection



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## 1. Introduction

Corrosion is a major issue in industry, causing the loss of 100 million tons of steel per year, which is nearly 15% of the world's production. It is a complex phenomenon that depends on several factors such as the environment, composition of the metal, and its properties. Corrosion results in direct costs such as replacement of corroded structures and labor, and indirect costs such as production losses, efficiency loss, product contamination, and more, which add up to billions of dollars in losses annually. Due to the long-term nature of corrosion, it is often underestimated in the design of equipment and structures, leading to further losses [1,2].

Corrosion is an important issue to consider as it can cause significant damage to historical and cultural artifacts. The process of corrosion can cause a loss of important information and details about the artifact, and can also change its appearance. This can make it difficult for archaeologists and historians to understand and preserve the history of a particular site or artifact, making it an important issue to address [3].

Corrosion is a slow process that affects the structural safety of various industries, including transportation, chemical, petrochemical, and construction. The rate of corrosion depends on the environment, the metal's composition, and its properties. It is often underestimated in design and results in direct costs such as replacement and labor, as well as indirect costs including production loss and efficiency loss. In heritage conservation, corrosion leads to the disappearance of historical artifacts and alters archaeological history [4,5].

## 2. History of Iron and Metallurgy

Iron is a very abundant metal on the earth's crust, mostly in the form of oxides. The metallurgy of iron dates back to 1700–1500 BC in regions south of the Caucasus and spread to Europe via Greece and the Danube valley [6]. Iron working was developed in Europe around 800 BC with the Hallstatt civilization and spread to Switzerland and Gaul [7].

The production of iron was traditionally carried out using the direct method or “blast furnace” process, where iron ore was reduced in the presence of wood, coal, and oxygen.

This method was widely used until the beginning of the Middle Age and allowed for the production of iron in a single stage using low furnaces. The resulting iron was used to make various tools, weapons, household items, and construction materials [6].

The use of hydraulic power in the 15th century led to the creation of larger blast furnaces and the ability to produce cast iron. Cast iron was used for a variety of purposes, such as chimney caps, cooking pots, cannonballs, and pipes. The process of producing cast iron dates back to 4th century B.C. in China and was first seen in Europe in the late 14th century.

The use of coke in the blast furnace during the 18th century revolutionized iron production by making it more efficient and cost-effective. The decarburization process further purified the iron, allowing for the production of high-quality cast iron products such as domestic objects, steam engine cylinders, and rails.

The indirect process of steelmaking has had a significant impact on the society by leading to increased production capabilities, especially in the fields of artillery and transportation. This has led to a growth in the number of machine tools and the ability to produce parts in larger series.

The use of iron and steel in architecture and engineering became more prominent in the 19th century, leading to the construction of iconic structures such as the Eiffel Tower, Grand Palais, railway stations, and many others. Iron and steel were used in the form of chain-linkages, tie rods, etc., and played an important role in the construction of these buildings, even though their use was often concealed.

Iron and its alloys (such as steel and cast iron) are widely used in various fields, including metal construction, building, public equipment, and transportation. Iron has been an important metal in heritage collections and historical monuments. Many iron-based objects from archaeological excavations have a layer of corrosion products, such as oxides, which can cause an inhomogeneous surface appearance with gray and oxidized areas. These areas are often fragile and susceptible to environmental conditions [4].

To protect iron against degradation, it is important to use methods such as coatings, cathodic protection, and inhibitors. The optimal method of protection depends on the specific conditions and environment in which the iron will be used [8]. The study of corrosion protection and conservation of iron will be discussed in the following sections.

### 3. Iron Corrosion

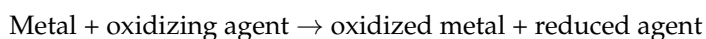
Aqueous corrosion and atmospheric corrosion are two types of corrosion that often affect archaeological iron. Aqueous corrosion is caused by the reaction of iron with water and atmospheric corrosion is caused by the reaction of iron with air. These types of corrosion are important to study in the field of archaeology as they often affect the iron artifacts being studied [9].

#### 3.1. Corrosion of Iron in Aqueous Media

##### 3.1.1. Behavior of Iron in Aqueous Medium

The corrosion of iron in an aqueous environment is due to an irreversible oxidation–reduction reaction between the metal and an oxidizing agent contained in the environment.

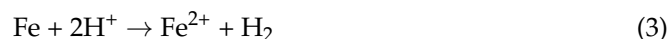
The oxidation of the metal involves the reduction of the oxidizing agent.



In wet corrosion, the two main oxidizers are:

- Solvated protons ( $\text{H}^+(\text{aq})$ ).
- Dissolved oxygen ( $\text{O}_2$ ).

In the case of iron corrosion, for example, if we consider the overall oxidation-reduction Reaction (3), it can be broken down into a partial oxidation reaction or anodic Reaction (1) and a partial reduction reaction or cathodic Reaction (2):



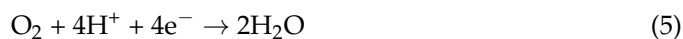
The anodic and cathodic partial reactions to be considered for iron corrosion in the presence of water are generally:

Anodic partial reaction (oxidation):

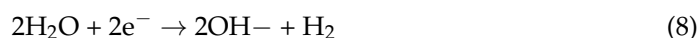


Cathodic partial reactions (reduction):

- In an aerated environment (aerobic):



- In a deaerated (anaerobic) environment:



In the case of corrosion in aqueous media, aeration or de-aeration generally corresponds to the presence or absence of dissolved oxygen [10].

### 3.1.2. Thermodynamic Approach

The Nernst potential, acidity constants, and solubility products are used to predict the thermodynamics of iron corrosion reactions in aqueous media using Pourbaix diagrams [11]. These diagrams show the stability ranges of the chemical species involved, but do not provide information on the reaction kinetics.

Figure 1 gives an example of an equilibrium diagram established by Descostes [12] based on data from Chivot [13,14]. Considering the following species:



Thus, we can determine:

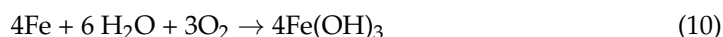
- A domain of immunity where the metal (Fe) is thermodynamically stable.
- Corrosion areas where the ions resulting from the dissolution of iron either in acidic media ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) or in very basic media ( $\text{HFeO}_2^-$ ) are responsible for the corrosion.
- Areas of passivation (possible) where the formation of a solid compound in a neutral and basic medium ( $\text{Fe}(\text{OH})_2$  or  $\text{Fe}(\text{OH})_3$ ) can be protective (or not).

The stability range of species can vary based on solid phases considered. Goethite has the broadest thermodynamic stability range, but similar diagrams can be created for different compositions of total iron and complexing ions in solution (carbonates, sulfates, etc.,) [15].



In the case of corrosion in an aqueous environment with oxygen present, followed by corrosion in a deaerated (anaerobic) environment due to oxygen depletion (for example in storage), we can consider the following hypothetical equilibria between iron and its oxides or hydroxides. Iron/oxide equilibria are stable, while iron/hydroxide equilibria are unstable [10].

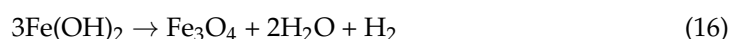
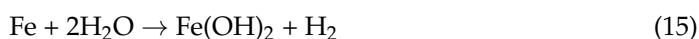
Oxidation of iron in the presence of oxygen, aerobic corrosion:



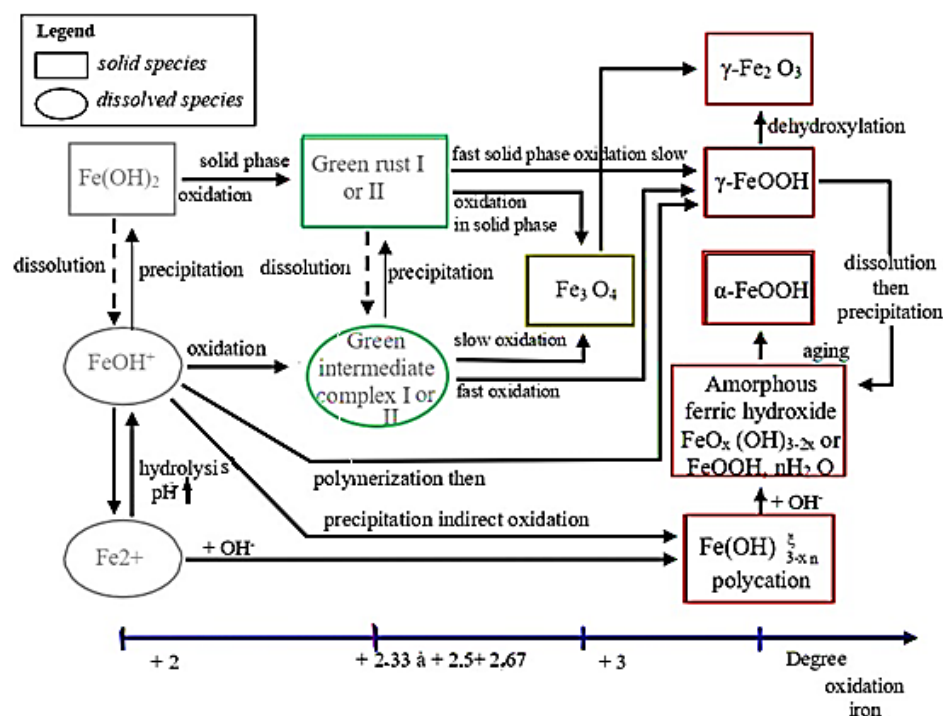
Reduction of the oxide or hydroxide surface:



After consumption of oxygen, anaerobic corrosion:



Based on these reactions, Misawa et al. and Cornell and Schwertmann [21,22] conducted studies on the formation of compounds resulting from oxidation. These studies established a relatively complex reaction scheme that governs the appearance and evolution of species in aqueous solution, starting from the formation of ferrous ions ( $\text{Fe}^{2+}$ ) (Figure 2):



**Figure 2.** Reaction scheme governing the appearance and evolution of species in aqueous solution during the iron oxidation process.

For this study, Misawa et al. and Cornell and Schwertmann found that the presence of ferrous ions in solution is dependent on the oxygen level and pH. When the oxygen level is high and the pH is below 6, ferrous ions remain in solution. However, if the pH is above 6, ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ) precipitates and quickly transforms into  $\text{Fe}(\text{OH})_3$  due to oxidation and hydrolysis.

The oxidation rate of green rusts ( $\text{Fe}(\text{OH})_2$ ) determines the formation of lepidocrocite ( $\gamma\text{-FeOOH}$ ) or magnetite ( $\text{Fe}_3\text{O}_4$ ). Magnetite is a thermodynamically stable phase, but in the presence of iron in an oxidation state between +II and +III, it can evolve into a similar structured phase, maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), at a higher iron oxidation degree.

$\gamma\text{-FeOOH}$  can transform into various forms including  $\gamma\text{-Fe}_2\text{O}_3$ , amorphous ferric oxyhydroxide ( $\text{FeO}_x(\text{OH})_{3-2x}$ ), or ferrihydrite ( $\text{FeOOH}$ ,  $n\text{H}_2\text{O}$ ) through different processes such as dehydroxylation or dissolution–precipitation. These phases have poor crystallization and eventually evolve over time to become the more thermodynamically stable phase, goethite  $\alpha\text{-FeOOH}$ .

In the long term,  $\text{Fe}(\text{OH})_3$  can transform into goethite  $\alpha\text{-FeOOH}$  through loss of water. If the oxygen level is low, ferrous ions can react directly with OH anions to form unstable compounds such as  $\text{Fe}(\text{OH})_2$  or  $\text{Fe}_2(\text{OH})_3\text{Cl}$  in the presence of chlorine [15].

### 3.2. Atmospheric Corrosion of Iron

Metals are not only unstable when in contact with or immersed in corrosive solutions, there is another type of corrosion in contact with air, called atmospheric corrosion. This type of corrosion is due to the degradation of metal objects when exposed to air and its elements such as oxygen, humidity, and pollutants. The formation and disappearance of liquid films on metal surfaces contribute to this corrosion. The rate of atmospheric corrosion varies depending on the environment the metal is exposed to, with industrial environments being the most corrosive, followed by urban and rural environments. The difference in the rate of corrosion is due to the presence of pollutants in the atmosphere [10].

Most studies on atmospheric corrosion do not distinguish between outdoor and indoor atmospheric environments. Both environments can cause variations in relative humidity leading to moisture cycling on metal surfaces and result in corrosion. Outdoor atmospheric environments can also result in electrolyte run-off and the presence of a surface water film, while indoor atmospheric corrosion occurs under shelter. Nevertheless, the influence of relative humidity and moisture cycling remains significant in both environments [15].

#### 3.2.1. Mechanisms of Atmospheric Corrosion of Iron

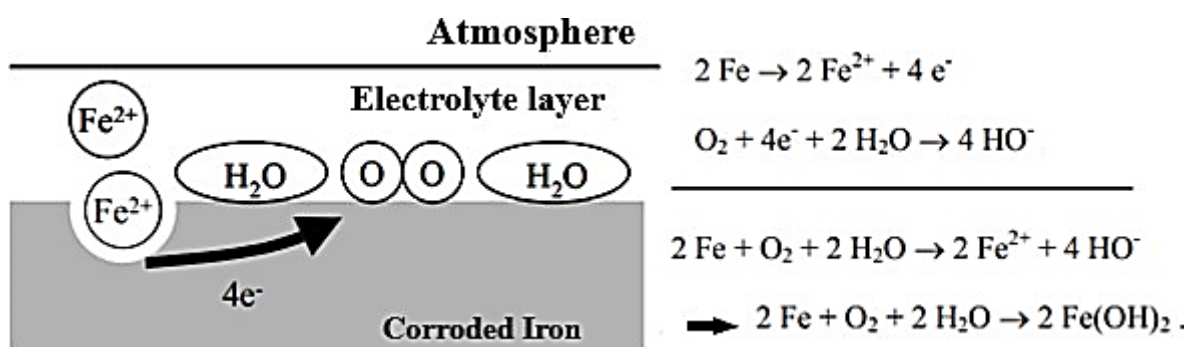
When iron is exposed to moist air, it reacts with the oxygen in the air and forms iron oxide (rust) through a process called atmospheric corrosion. This process is an electrochemical reaction, where electrons are transferred between the iron and oxygen atoms in the air. This reaction forms a protective layer of iron oxide on the surface, which helps prevent further corrosion. The accompanying Figure 3 provides a diagram of the atmospheric corrosion process, including the various steps involved in the process and the specific chemical reactions that take place.

The early studies in the 1930s showed that atmospheric corrosion of metals cannot be described by a simple oxidation reaction and that more complex mechanisms are involved. Researchers subsequently highlighted the role of moisture cycling in the corrosion process and demonstrated that the kinetics of electrochemical reactions play a crucial role in atmospheric corrosion [23]. This work expanded the understanding of atmospheric corrosion and showed that it is a multi-faceted process that involves a range of chemical, physical, and electrochemical phenomena. These findings have had a lasting impact on the field of corrosion science and continue to inform current research and understanding of atmospheric corrosion.

Schikorr [24] proposed the “acid regeneration” model, which suggests that iron oxides form in areas of acidic pH and that the presence of sulfur dioxide catalyzes the corrosion reactions through the formation of sulfuric acid, which is regenerated during moisture

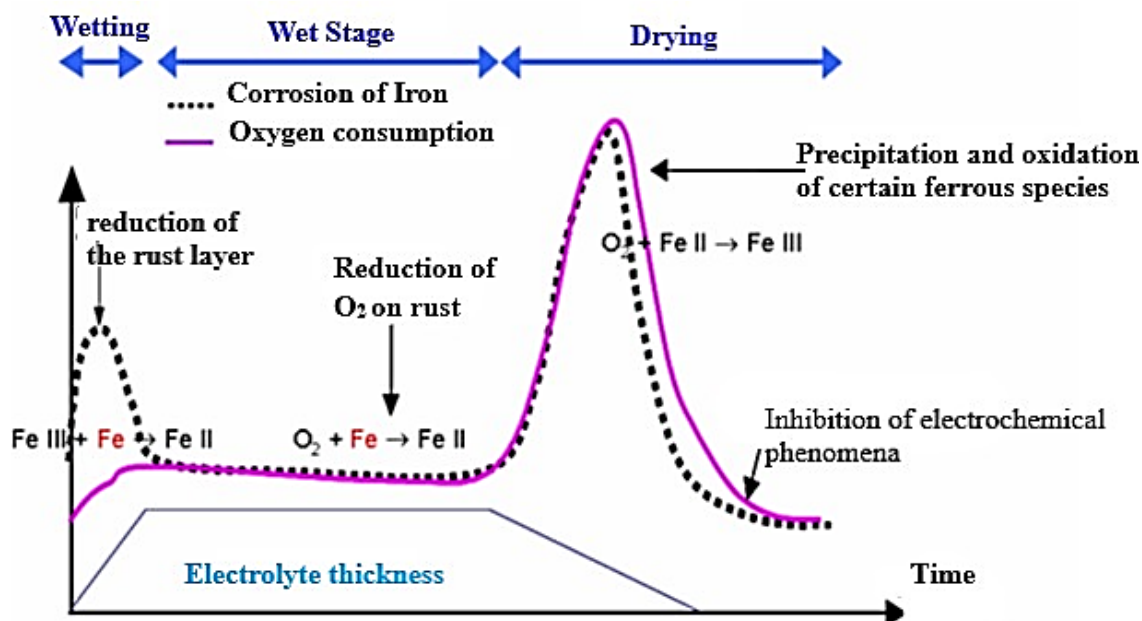


cycling. This model was later expanded upon by Evans and Taylor [25], who proposed the “electrochemical cycling” model based on electrochemical reactions. This model states that the corrosion process is controlled by a humidification–drying cycle and was experimentally verified by Stratmann et al. This work further advanced our understanding of atmospheric corrosion and showed the important role of electrochemical reactions in the process. The “electrochemical cycling” model is widely accepted today as a key mechanism that governs atmospheric corrosion [26,27].



**Figure 3.** Diagram of the atmospheric corrosion process at the surface with the reaction balance involved.

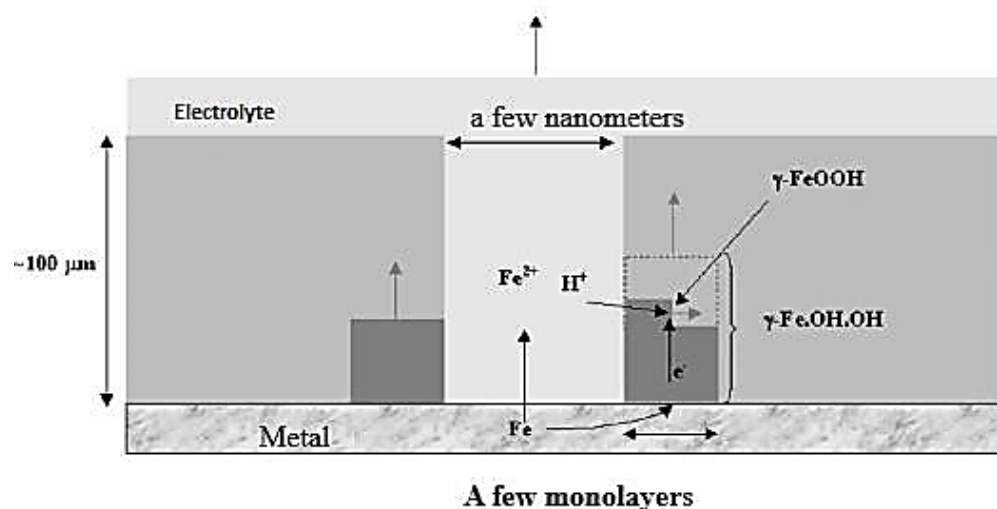
The humidification–drying cycle in atmospheric corrosion (Figure 4) is divided into three stages, each defined by the evolution of the thickness of the electrolyte film on the surface of the metal object. During the first stage, there is a wetting stage where the metal surface is initially wetted by moisture. The second stage is the wet period, during which the electrolyte film has a significant and constant thickness. The third stage is the drying stage, during which the moisture evaporates and the electrolyte film becomes thinner. These stages play an important role in the electrochemical reactions that take place during atmospheric corrosion, and the progression of the cycles is driven by the relative humidity and temperature conditions in the environment.



**Figure 4.** Stratmann humidification–drying cycle. NB: iron consumption (bold dotted line) oxygen consumption (bold solid line).

### Anchor Stage

During the humidification–drying cycle, the formation of an electrolyte film on the metal surface triggers the anodic dissolution of iron, and the electrons produced by the oxidation reaction must be consumed by a reduction reaction. During the wetting phase (Figure 5), a strong dissolution kinetics of iron is observed due to the fact that the rust layer formed is not conductive and therefore oxygen cannot reduce on its surface. This leads to a reduction of the metal surface accessible through a network of tortuous and nanometric pores, which contributes to the overall corrosion process. This highlights the importance of the wetting stage in atmospheric corrosion and the complex interplay between electrochemical reactions, the thickness of the electrolyte film, and the physical and chemical conditions of the environment [3].



**Figure 5.** Representation of the phenomena involved in the wetting phase.

The corrosion product layer itself is responsible for the corrosion, and the anodic dissolution of the metal is balanced by the reduction of a constituent of this layer [28]. Research by Matsushima [15] showed that the reaction of ferric species is dominant in the cathodic reaction on corroded iron in wet corrosion. This finding was later confirmed by Evans and Taylor [25], and Stratmann, [29], further solidifying the importance of the wetting phase in atmospheric corrosion and the role of the corrosion product layer in the electrochemical reactions taking place. This work highlights the complex and multi-faceted nature of atmospheric corrosion and the need for a comprehensive understanding of the various processes involved to effectively prevent and mitigate the effects of corrosion in metal materials.

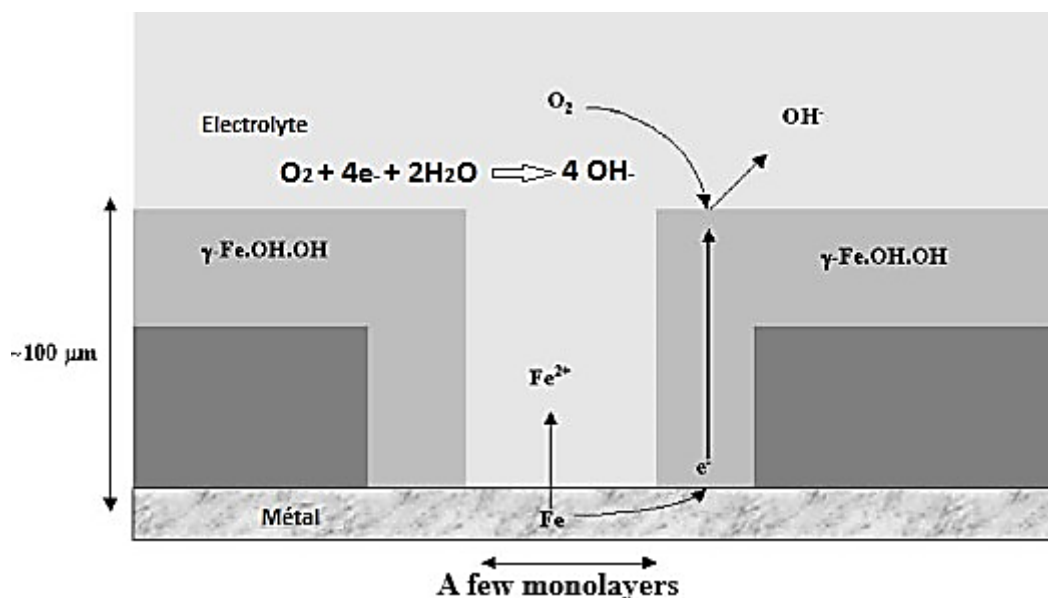
According to Anthony [30], the phases most likely to reduce during the wetting phase are lepidocrocite, ferrihydrite, and ferroxhyte. However, Monnier stated that lepidocrocite is the most likely phase to reduce and that amorphous phases tend to reduce at lower potentials [31]. As a result, electron consumption during the wetting step may correspond to the reduction of several phases, highlighting the complex nature of the electrochemical reactions taking place during atmospheric corrosion. This work underscores the need for a comprehensive understanding of the various processes involved in atmospheric corrosion, including the role of different phases of corrosion products in the electrochemical reactions and the factors that influence their reduction potential [15].

### Wet Stage

In the second stage of the wetting–drying cycle, the electrolyte thickness is assumed to be constant and uniform on the surface of the sample, i.e., on the existing and partially reduced corrosion product layer. Figure 6 shows that the iron and dissolved oxygen consumptions are equal, which indicates that the cathodic reaction is the reduction of dissolved



oxygen in the electrolyte and the anodic reaction is the oxidation of the metal substrate. This stage of the humidification–drying cycle highlights the key role that dissolved oxygen plays in atmospheric corrosion, as well as the importance of the corrosion product layer in the overall corrosion process. Understanding the complex interplay between the metal substrate, electrolyte film, and dissolved oxygen is essential to effectively prevent and mitigate the effects of atmospheric corrosion on metal materials [15].



**Figure 6.** Representation of the phenomena occurring during the wet phase.

In this stage of the wetting–drying cycle (Figure 6), the oxygen reduction reaction is believed to take place largely on the outer surface of the corrosion product layer, which consists of a conductive reduced phase produced during the wetting step and in contact with the iron metal [31]. This conductive layer allows the electrons produced by the oxidation reaction to be consumed by the reduction reaction, leading to a stable and uniform corrosion rate. On the other hand, the anodic reaction would take place at the bottom of the pores where the metal and the electrolyte are in direct contact, which leads to a decoupling of the anodic and cathodic zones. This separation of the anodic and cathodic zones creates conditions for the formation of local cells, leading to a non-uniform corrosion rate and a more complex overall corrosion process.

#### Drying Stage

The drying stage of the electrolyte process has two parts: first, as the thickness decreases, reaction speed increases due to improved oxygen diffusion and iron consumption. At a critical electrolyte thickness, there is a sudden drop in iron oxidation and oxygen reduction currents because of water film dislocation [15,25,32]. In the second part of the drying stage, an increase in dissolved species leads to precipitation and surface coverage, resulting in a weak oxygen reduction current and anodic control of the system [28].

During the drying stage (Figure 7), the high concentration of oxygen in the residual electrolyte film causes polarization of the corrosion layer at high potentials, leading to re-oxidation of iron species and the formation of lepidocrocite and goethite [16].

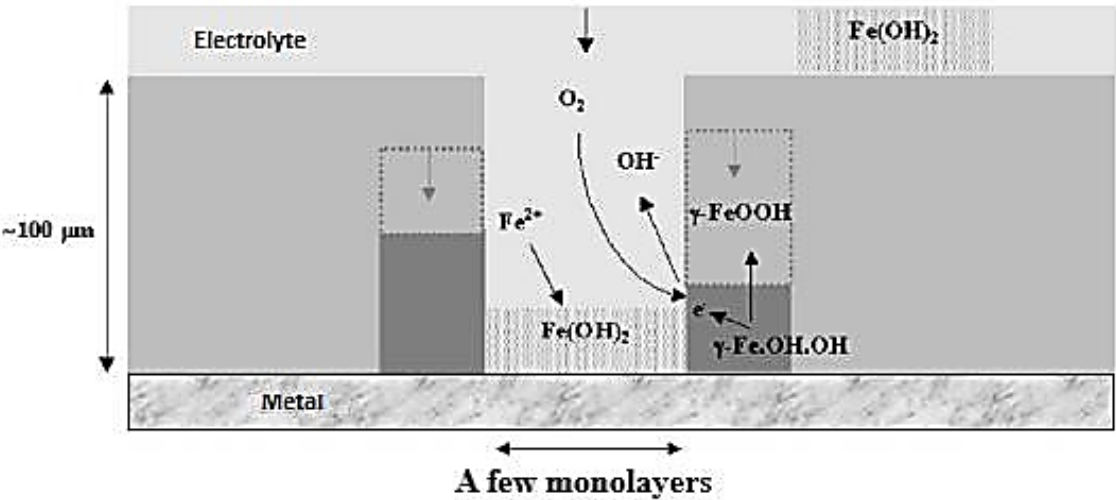


Figure 7. Representation of the phenomena involved in the drying process.

3.2.2. Products of Atmospheric Corrosion of Iron

Atmospheric corrosion refers to the corrosion of materials caused by the exposure to the atmosphere and its environmental conditions, such as humidity, temperature, presence of pollutants, and pH. The corrosion rate is influenced by the alternation of wet and dry periods, leading to the formation and disappearance of an electrolyte film on the surface. The corrosive power of the atmosphere can be determined by these factors, and the end result is usually a mixture of iron oxides and oxyhydroxides.

Magnetite and maghemite are the two most commonly encountered iron oxides that result from atmospheric corrosion. The corrosion products may also include polymorphic oxyhydroxides of iron, such as goethite ( $\alpha$ -FeOOH), lepidocrocite ( $\gamma$ -FeOOH), feroxyhyte ( $\delta$ -FeOOH), and sometimes akaganeite ( $\beta$ -FeOOH) which contains chlorine. In addition, the corrosion layer may also contain ferrihydrite, which is a poorly crystallized and hydrated compound [3]. Table 1 displays the iron oxides and oxyhydroxides present in rust layers that are formed due to atmospheric corrosion.

Table 1. Iron oxides and oxyhydroxides encountered in rust layers resulting from atmospheric corrosion [15,33,34].

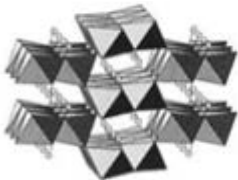

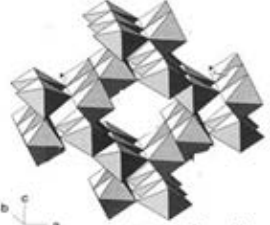

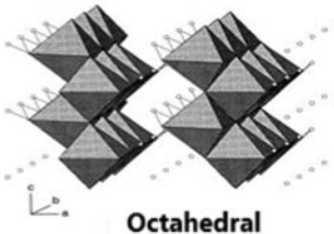
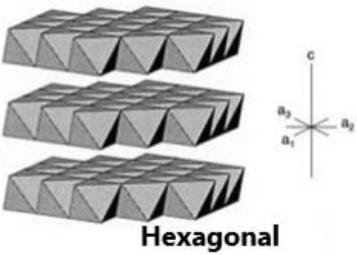
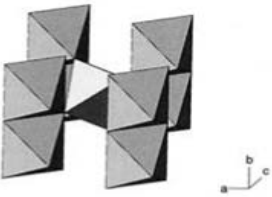
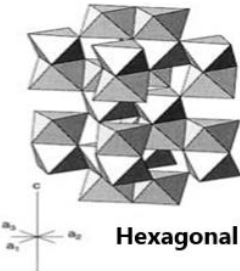
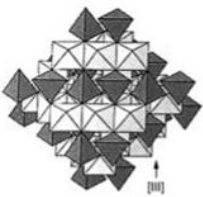
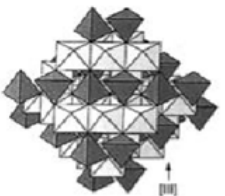
	Names	Formula	Space Group	Color
Oxyhydroxides	Goethite	$\alpha$ -FeOOH		Crystals: black brown Powder: yellow brown
			 <b>Octahedral</b>	
	Akaganeite	$\beta$ -FeOOH		Light brown
			 <b>Octahedral</b>	

Table 1. Cont.

Names	Formula	Space Group	Color
Lepidocrocite	$\gamma\text{-FeOOH}$	 Octahedral	Crystals: brown-red Powder: orange-yellow
Feroxyhyte	$\delta\text{-FeOOH}$	 Hexagonal	Brown
Ferrihydrite	$\text{Fe}_2\text{O}_3, n\text{H}_2\text{O}$	 Octahedral	Yellow-brown to black-brown
Hematite	$\alpha\text{-Fe}_2\text{O}_3$	 Hexagonal	Crystals: Dark grey Powder: Dark red
Oxides	Maghemite	 Tetrahedral and Octahedral	Brown
	Magnetite	 Tetrahedral and Octahedral	Crystals: dark grey Powder: black

In general, the composition of the rust layer is primarily influenced by atmospheric conditions and the composition of the metal [35]. The rust layer may be relatively homo-

geneous in some cases [36], but in many cases, it is composed of two parts: an adhesive “sub-layer” containing magnetite and various amorphous oxyhydroxides such as goethite, akageneite, lepidocrocite, and feroxyhyte ( $\delta$ -FeOOH), and an outer, more porous and crystallized layer containing mainly goethite and lepidocrocite oxyhydroxides [37,38].

Iron (II) and (III) hydroxides can be identified using X-ray diffraction and are unstable in aerated media, undergoing transformation into a green rust-like intermediate before the formation of lepidocrocite or magnetite, which are considered thermodynamically stable phases [39–41]. Under atmospheric conditions, the rust layer can reach significant thicknesses (a few millimeters) over a very long period of time (more than 50 years) [16].

The work of J. Monnier [15] has confirmed that lepidocrocite is rarely connected to the metal and that highly reactive phases, such as feroxyhyte and ferrihydrite, are abundant in the corrosion product layers of objects that have undergone long-term corrosion. The reduction and re-oxidation of these phases can result in a mixture of maghemite and magnetite or lead to the reprecipitation of reducible phases such as lepidocrocite, ferrihydrite, and/or feroxyhyte.

#### 4. Protection of Iron by Corrosion Inhibitors

The high cost of annual material degradation has prompted the use of protection methods to save materials and energy, and to meet new requirements, such as the use of non-toxic products.

The protection of materials from corrosive environments can be achieved through various actions at the metallurgical, structural, electrochemical, and environmental levels. Three degrees of action are identified [42]:

1. Actions on the material, such as modifying its composition or microstructure or isolating it from its environment through a metallic or organic coating or anodization.
2. Actions on the environment, such as incorporating corrosion inhibitors or avoiding moisture accumulation in the structure.
3. Actions on the electrochemical corrosion process, such as cathodic protection.

The protection of metal heritage requires consideration of both preservation of surface information and protection against corrosion. Organic coatings, such as varnishes and waxes, can provide protection. Anodic, cathodic, and galvanic protection, as well as the use of inhibitors, are common and effective methods of protection.

##### 4.1. Background

The Romans were aware of corrosion and its effects on metal objects. Pliny the Elder, a Roman naturalist and historian, mentioned in the first century A.D. the use of oil or bitumen for protecting bronze and pitch, gypsum or ceruse for iron from corrosion.

This shows that even in ancient times, people were aware of the need for protection against corrosion and sought methods to preserve their metal objects.

The study of corrosion has a long history, dating back to the 17th century. However, it was not until the 19th century that the means of protecting against corrosion were studied scientifically. The number of references dealing with corrosion inhibitors increased rapidly after 1945, with numerous articles written on the subject in various fields such as aviation, oil refining, and diesel engines. In recent years, there has been a significant increase in works on corrosion inhibition, reflecting technological advancements in the field [43].

##### 4.2. Definition

A corrosion inhibitor is a substance added to a corrosion system to slow down the corrosion rate of a metal without significantly altering the concentration of corrosive agents in the environment. The definition used by the National Association of Corrosion Engineers (NACE) states that an inhibitor is a substance that retards corrosion in low concentration. The international standard ISO 8044 defines an inhibitor as a chemical substance added to the corrosion system in a chosen concentration to decrease the corrosion rate of the metal. The properties of an effective inhibitor include lowering the corrosion rate, stability in

the presence of other constituents, stability at temperatures of use, effectiveness at low concentrations, compatibility with non-toxicity standards, and cost-effectiveness [44,45].

#### 4.3. Classification

Inhibitors can be classified based on different criteria such as mechanism of inhibition, application, or chemical nature. This classification helps in better understanding the working of inhibitors and selecting the right inhibitor for a particular corrosion problem. The different classifications of inhibitors provide a comprehensive understanding of the different types of inhibitors and their uses in various corrosion scenarios [46].

The classification of inhibitors (Figure 8) based on their field of application is a useful way to differentiate between inhibitors used in different environments. For example, inhibitors used in acidic media are mainly used to prevent electrochemical attack during pickling processes and in drilling fluids in the oil industry. Inhibitors for neutral media are mainly used to protect cooling circuits. In organic media, a large number of inhibitors are used in engine lubricants and gasoline to protect against corrosion caused by the presence of water and ionic species. This classification helps in selecting the appropriate inhibitor for a specific corrosion problem and ensures maximum protection against corrosion [47].

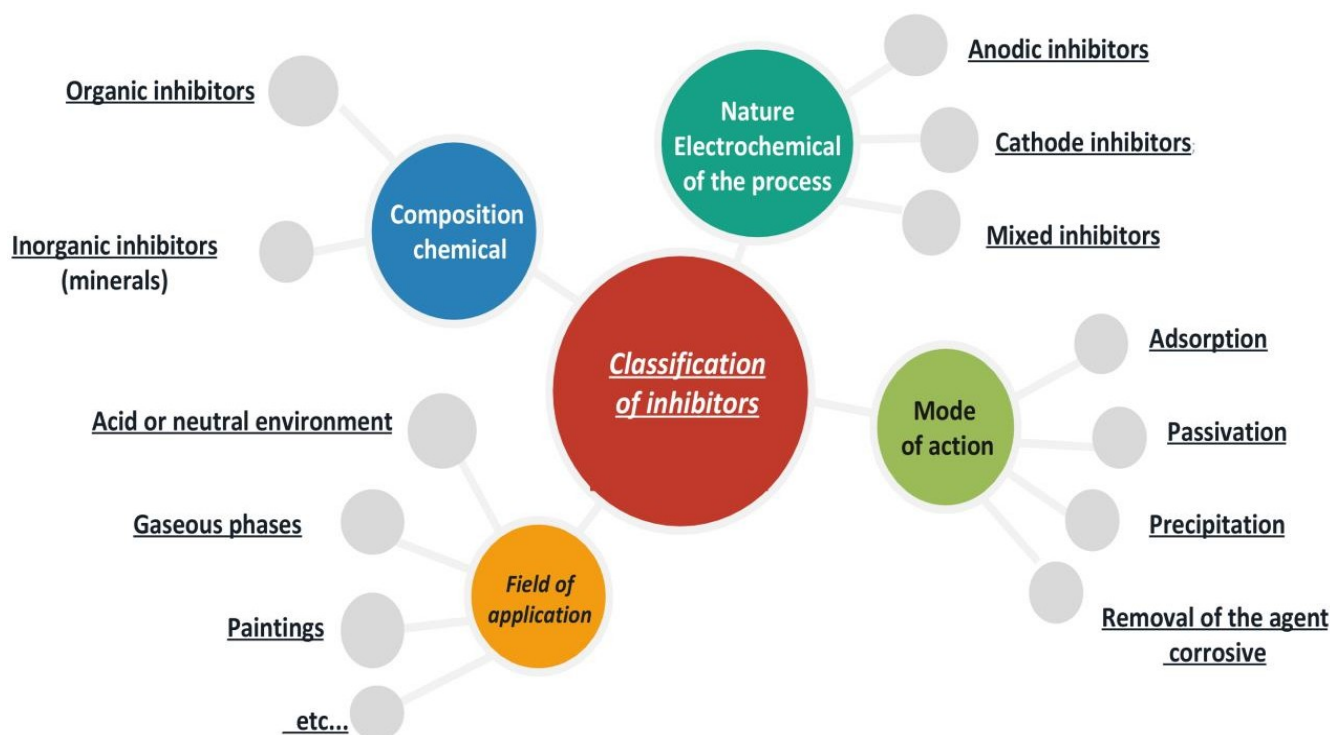


Figure 8. Classification of corrosion inhibitors.

Inhibitors for paints and gas phases are used to temporarily protect various packaged objects from corrosion during transport and storage. Electrochemically, inhibitors are classified as anodic, cathodic, or mixed inhibitors, depending on their effect on the rate of oxidation and reduction reactions. Anodic inhibitors slow down the oxidation of the metal, cathodic inhibitors slow down the reduction of the oxidant, while mixed inhibitors affect both anodic and cathodic domains. The electrochemical effect of inhibitors on the surface can be explained by various physico-chemical mechanisms. In some cases, the inhibitor forms a physical barrier between the metal and the corrosive medium, as in the case of thick coatings such as waxes and varnishes. In other cases, the inhibitor operates through a pH or redox buffer effect, which can passivate the metal and reduce the corrosion rate. The mode of action of an inhibitor can also involve the formation of surface films due to the

precipitation of inorganic salts or poorly soluble organic complexes. These films reduce the accessibility of oxygen to the metal surface and partially block the anodic dissolution [48].

The technique of removing the corrosive agent from the medium is only applicable in closed systems, such as in the closed hot water circuits of thermal power stations. Additionally, it is important to note that many inhibitors act through multiple mechanisms simultaneously, which can increase their effectiveness in preventing corrosion [49].

#### 4.4. Inhibitors Specific to Ferrous Metals in an Acid Medium

Different corrosion inhibitors can effectively protect ferrous metals from corrosion in acidic environments, either individually or in combination. The selection of the appropriate inhibitor depends on various factors such as the type of metal, environment, and specific conditions [50].

##### 4.4.1. Synthetic Inhibitors

Organic inhibitors contain elements such as nitrogen, sulfur, and oxygen that can exchange electrons with the metal and protect it from corrosion. These inhibitors work through a chemical process called spontaneous adsorption and provide good results in inhibiting steel corrosion in acidic medium [51]. Organic inhibitors have several advantages over inorganic inhibitors, as they provide uniform passivation on the metal surface for maximum protection, while inorganic inhibitors form brittle and porous films that can lead to localized corrosion [52]. There is a large body of literature available discussing the use of organic compounds as corrosion inhibitors for ferrous metals in acidic media, as listed in Table 2.

**Table 2.** Examples of inhibitors used for the protection of iron and its alloys in acidic media.

	Compounds	References
Nitrogenous	Hexamethylenetetramine or methenamine	[52]
	Diazoles: imidazole and its derivatives	
	Triazoles and its derivatives such as benzotriazole	
	Bipyrazole derivatives	
	Oxadiazoles	
	Quinoline derivatives	
	Quinone derivatives such as Quinoxaline-2,3-dione	
	Pyridine derivatives	
	Mixed compounds such as Schiff's Bases which result from the condensation of an amine with an aldehyde	
Sulphur	Aliphatic amines (ethylamine, dimethylamine, butylamine, diethylamine, butyldiethylamine) Octylamine derivatives	[53,54]
	Thiourea and its derivatives	[52]
	Thiadiazole and its derivatives	
Oxygenated	Lactones	
	Carboxylic compounds in combination with heterocycles (furans, imidazoles, thiophenes, isoxazole derivatives and several other moieties)	[55–57]
	Linear sodium carboxylates	

The addition of organic compounds to the acid solution generally reduces its aggressiveness, however, these compounds are toxic and harmful to the environment, leading to



the need for alternative, eco-friendly, and efficient inhibitors. One such alternative is the use of natural substances, including vegetable oils [58].

#### 4.4.2. Corrosion Inhibitors Based on Natural Substances

The use of natural substances such as vegetable oils is attractive due to their low cost and abundant availability as environmentally friendly and biodegradable compounds. The use of plant extracts as corrosion inhibitors dates back to 1930, with the use of Chelidonium majus and other plants in a pickling bath of  $H_2SO_4$ . The first patent on corrosion inhibition was granted to Baldwin, who used molasses and vegetable oils for pickling steel sheets in acidic media [59].

Currently, many research groups around the world are exploring the use of plant products as corrosion inhibitors for metals and alloys in various corrosive environments [60]. There is an increasing number of publications addressing this topic, as shown in Table 3, which details some of the main green inhibitors for the corrosion of ferrous metals in acidic medium.

**Table 3.** Literature review on the use of natural substances as corrosion inhibitors.

Non-Toxic Inhibitors	Type of Inhibitor	IE (%)	Environment	Substrate	Adsorption Mechanisms	References
Henna, <i>L. inermis</i>	Cathodic	92.1	HCl (1 M)	Mild steel	Chemisorption	[61]
<i>N. fruticans</i> Wurmb	Mixed	75.1	HCl	Mild steel	Physisorption	[62]
Eugenol derivatives	Mixed	91	HCl (1 M)	Steel	Chemisorption	[63]
Khillah extract (seeds ( <i>A. visnaga</i> ))	Mixed	99.3	HCl (2 M)	Steel SX 316	Chemical adsorption	[64]
Natural oil extracted from pennyroyal mint ( <i>Mentha pulegium</i> , PM)	Cathodic	80	HCl (1 M)	Steel	Simple blocking of the available surface, intermolecular synergistic Active molecules of this oil	[65]
Plant extract of <i>Z. alatum</i>	Cathodic	95	HCl (5%)	Mild steel	Chemisorption	[63]
Flavonoids (Monomers)	Cathodic	>70	HCl (0.5 M) aerated	Steel	Chemisorption	[66]
Succinic acid (SA)	Anodic	97.5	HCl (1.0 M) aerated unstirred	Low carbon steel	Film of inhibitor adsorbed on electrode surface	[67]
Aqueous extract of olive leaves ( <i>O. europaea</i> L.)	Mixed	91	HCl (2 M)	Carbon steel	Physical adsorption	[68]
<i>T. occidentalis</i> , (TO)	Cathodic	91–97	HCl (1 M)	Mild steel	Physisorption	[69]
<i>A. indica</i> , (AI)						
<i>H. sabdariffa</i> , (HS)						
<i>G. kola</i> (GK) seed extract						
Extract from <i>J. gendarussa</i> (JGPE)	Mixed	93	HCl (1 M)	Mild steel	Physisorption	[70]
Extracts of leaves and seeds of <i>P. amarus</i>	Mixed	80.1–94.1	HCl (2 M)	Mild steel	Chemisorption	[71]
<i>L. albus</i> L.	Mixed	77.6	HCl (2 M)	Steel	Chemisorption	[72]
		85	$H_2SO_4$ (1 M)		Physisorption	
Pennyroyal oil from <i>M. pulegium</i>	Cathodic	80	HCl (1 M)	Steel	Chemisorption	[65]

Table 3. Cont.

Non-Toxic Inhibitors	Type of Inhibitor	IE (%)	Environment	Substrate	Adsorption Mechanisms	References
Zest of (Mango, Orange, Passion, Cashew)	Mixed	80–95	HCl (1 M)	Carbon steel	Adsorption of organic compounds present in the extracts on the active sites of the electrode surface	[73]
Juniperus phoenicea (Cupressaceae) essential oil	Mixed	83	HCl (1 M)	Mild steel	adsorption of aromatic compounds on the metal surface	[74]
Methanolic extract of <i>A. Pallens</i>	Mixed	96.5	HCl (4 N)	Mild steel	Formation of a very tightly adhering adsorbent film on the metal surface	[75]
Guar gum	Mixed	93.6	H <sub>2</sub> SO <sub>4</sub> (1 M)	Carbon steel	Formation of passive, active and continuously propagating centers.	[76]
Chamomile ( <i>C. mixtum</i> L.)	Mixed	90.2	H <sub>2</sub> SO <sub>4</sub> (1 M)	Steel	Adsorption of the stable complex to the steel surface	[77]
Halfbar ( <i>C. proximus</i> )						
Black cumin ( <i>N. sativa</i> L.)						
Kidney bean ( <i>P. vulgaris</i> L.)						
Berberine	Mixed	98	H <sub>2</sub> SO <sub>4</sub> (1 M)	Mild steel	Chemical adsorption	[78]
Fenugreek leaves (AEFL)	Mixed	88.3	H <sub>2</sub> SO <sub>4</sub>	Mild steel	Chemical adsorption of inhibitor molecules on mild steel	[79]
Black pepper extract		90				[80]
Saffron-o (SO)		65				[81]
Alizarin Yellow (GG)		85	H <sub>2</sub> SO <sub>4</sub> (2 M)	Mild steel	Physisorption	[82]
Caffeic acid	Mixed	83.9	H <sub>2</sub> SO <sub>4</sub> (0.1 M)			[83]
Lignin extracted from black liquor of the pulp and paper industry	Cathodic	95	H <sub>2</sub> SO <sub>4</sub> (0.5 M)	Mild steel	Adsorption of more lignin molecules on the metal surface, preventing the electrochemical corrosion process	[84]
Galactomannan extracted from Carob seeds ( <i>Ceratonia Siliqua</i> )	Mixed	86.6	HCl (1 M)	Archaeological iron	Establishment of inhibitor film on iron substrate surface	[85]
Formulations based on oils	Opuntia ficus indica (OTH)	99.6	Acid rain-simulated environment pH = 3.6	Archaeological iron	Establishment of inhibitor film on iron substrate surface	[86]
	<i>Nigella sativa</i> (FBN)	99.3				[87]
	<i>Jatropha Curcas</i> (JAC)	97				[88]
	<i>Ceratonia Siliqua</i> L., (FCSL)	98.6				[89]
	<i>Aleurites moluccana</i> (ALM)	97				[90]
	<i>Opuntia Dillenii</i> (FOD)	99				[91]

## 5. Conclusions

Corrosion inhibitors are a cost-effective and practical solution for protecting metals and alloys against corrosion. The unique aspect of this method is that the anti-corrosion treatment is applied to the corrosive environment instead of directly to the metal, making it a convenient and inexpensive method in comparison to other corrosion control methods.

There are different types of inhibitors that work based on different mechanisms, leading to varying levels of effectiveness in different environments. Among the inhibitors, plant-based inhibitors have proven to be particularly effective and have gained widespread popularity, especially due to their low toxicity and eco-friendly nature. However, there are still some challenges and problems associated with the use of these inhibitors. Here are some perspectives on the problems of green corrosion inhibitors and future research directions in the field of iron protection [46–51]:

1. Inhibitor effectiveness: the effectiveness of green corrosion inhibitors can be influenced by several factors, such as the type of metal, the corrosive environment, and the inhibitor concentration. Therefore, further research is needed to optimize the performance of these inhibitors under various conditions.
2. Compatibility with other materials: green corrosion inhibitors may not be compatible with other materials used in the metal protection process, such as coatings or paints. Therefore, research efforts should focus on developing inhibitors that are compatible with other materials used in metal protection.
3. Environmental impact: although green corrosion inhibitors are considered to be environmentally friendly, their impact on the environment should be carefully evaluated. For example, some natural inhibitors may cause eutrophication in water bodies or have other unintended consequences. Therefore, further research is needed to ensure that these inhibitors do not harm the environment.
4. Cost: the cost of green corrosion inhibitors can be high, particularly for large-scale applications. Therefore, research efforts should focus on developing cost-effective inhibitors that can provide effective protection at a lower cost.

Overall, green corrosion inhibitors offer a promising solution for metal protection with reduced environmental impact. However, there are still some challenges that need to be addressed. Future research efforts should focus on developing eco-friendly and cost-effective inhibitors, optimizing their performance under various conditions, exploring new approaches to corrosion protection, and developing smart corrosion inhibitors that can respond to changes in the environment and adjust their effectiveness accordingly.

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