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Green Corrosion Inhibitors, Past, Present, and Future

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Abstract

Green corrosion inhibitors are of interest because there has been an increase in environmental awareness and a change in regulations that restrict regular corrosion inhibitors due to their toxicity. Natural products are a good source of green corrosion inhibitors, where most of their extracts containing the necessary elements such as O, C, N, and S, which are active in organic compounds, assist in adsorption of these compounds on metals or alloys to form a film that protects the surface and hinders corrosion. Numerous natural products and their application in different processes, especially in steel reinforcement embedded in concrete, are discussed. Development of green chemistry and green chemical technologies offers novel synthetic methods for ionic liquids, which are considered as new corrosion green inhibitors, and their mechanism of adsorption, how these green inhibitors act in different media, and their protective role for different metals and alloys are discussed. Finally, industrial applications of vapor-phase inhibitors and their mechanisms are presented.

Keywords: green inhibitors, corrosion protection, green chemistry, ionic liquid, vapor-phase inhibitors

1. Introduction

Corrosion is a natural phenomenon where metals and alloys try to revert to their more stable thermodynamics form due to reaction with the environment that surrounds them. Corrosion is expensive due to loss of materials or their properties, which leads to loss of time during maintenance, the shutting down of systems, and severe failure of some structures, which in some cases may be hazardous and cause injury.

To protect metals or alloys from corrosion, approaches such as isolating the structure from aggressive media (using coatings or film-forming chemicals) or compensating for the loss of electrons (corrosion is an oxidation process) from the corroded structure (e.g. cathodic protection by impressed current or by using active sacrificial anodes) are employed.

Corrosion inhibition may include organic or inorganic compounds that adsorb on the metallic structure to isolate it from its surrounding media to stop the oxidation-reduction process. Organic inhibitors create their inhibition by adsorbing their molecules on the metal or alloy surface to form a protective layer [1]. Alternatively, inorganic inhibitors act as anodic inhibitors and their metallic atoms are enclosed in the film to improve their corrosion resistance. Most investigated corrosion inhibitors are toxic and cause severe environmental hazards upon disposal. Therefore, their use has been limited by environmental regulations. Nevertheless, inhibitors still play a critical role in corrosion prevention. Inhibitors are classified according to:

- Three types of electrode process, namely, anodic, cathodic, and mixed;
- The chemical nature of the environment to acid inhibitors (organic or inorganic), neutral inhibitors, alkaline inhibitors, and vapor-phase inhibitors.

Hazards caused by toxicity of regular inhibitors have led to the use of new green corrosion inhibitors. Most of these inhibitors derived from natural products act as anticorrosion agents, which are eco-friendly and harmless upon disposal. Other green inhibitors such as rare earths and organic polymers are not focused on in this chapter and further information may be found elsewhere [2–4]. This chapter will focus on green inhibitors from natural products, ionic liquids, and safety vapor-phase inhibitors, with a brief description of their mechanisms of action.

Green inhibitors act when they are added in very low concentrations to treat the surface of metals or alloys in a corrosive environment. Plant extracts are deemed to be rich, naturally synthesized chemical compounds [5] that affect the corrosion rate by adsorption of effective species on metal surfaces when added to many industrial systems through:

- Changing the rate of anodic and/or cathodic reactions;
- Effecting the diffusion rate of aggressive ions interacting with metallic structures;
- Increasing electrical resistance of the metal surface by forming a film (coat) on it.

During corrosion, metal ions move into the solution at active areas (the anode) and pass electrons from the metal to an acceptor at less active areas (the cathode); the cathodic process requires the presence of an electron acceptor such as oxygen, oxidizing agents, or hydrogen ions. Corrosion can be minimized by retarding or completely stopping the anodic or cathodic reactions, or both. Inhibitors are adsorbed on the metal surface, forming a protective barrier, and interact with anodic and/or cathodic reaction sites to decrease the oxidation and/or reduction of corrosive reactions [6].

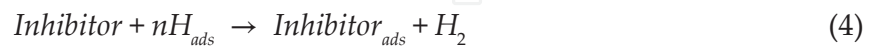
There are several different, common cathodic reactions in corrosive media:



Reduction reaction is hydrogen gas evolution as follows:



In Eq. (3) hydrogen ions adsorbed on the metal surface are catalyzed in combination with other hydrogen ions hold hidden giving evolved hydrogen gas on cathode surface, in presence inhibitor amount of hydrogen bubble refer to ability of inhibitor to prevent this reaction and protected metal from corrosion [7]. The action of inhibitors molecules occurs due to their adsorption on an exposed metal surface in the form of neutral molecules instead of hydrogen ions adsorbed from the metal surface.



or by displacement of water molecules on the surface, as described in Eq. (2). Green inhibitors have adsorptive properties, known as site-blocking elements [8, 9].

Figure 1 shows the interest shown in green inhibitors in the last few decades, as explained by the number of publications in that period. We summarize the research focused on using natural products that have been used as green inhibitors in various aggressive media for corrosion protection of different alloys and metals as depicted in **Table 1**. The table shows the numerous studies arranged in chronological order and discussed in the reference next to each type of inhibitor. Each inhibitor's percentage of inhibition efficiency is reported at the maximum

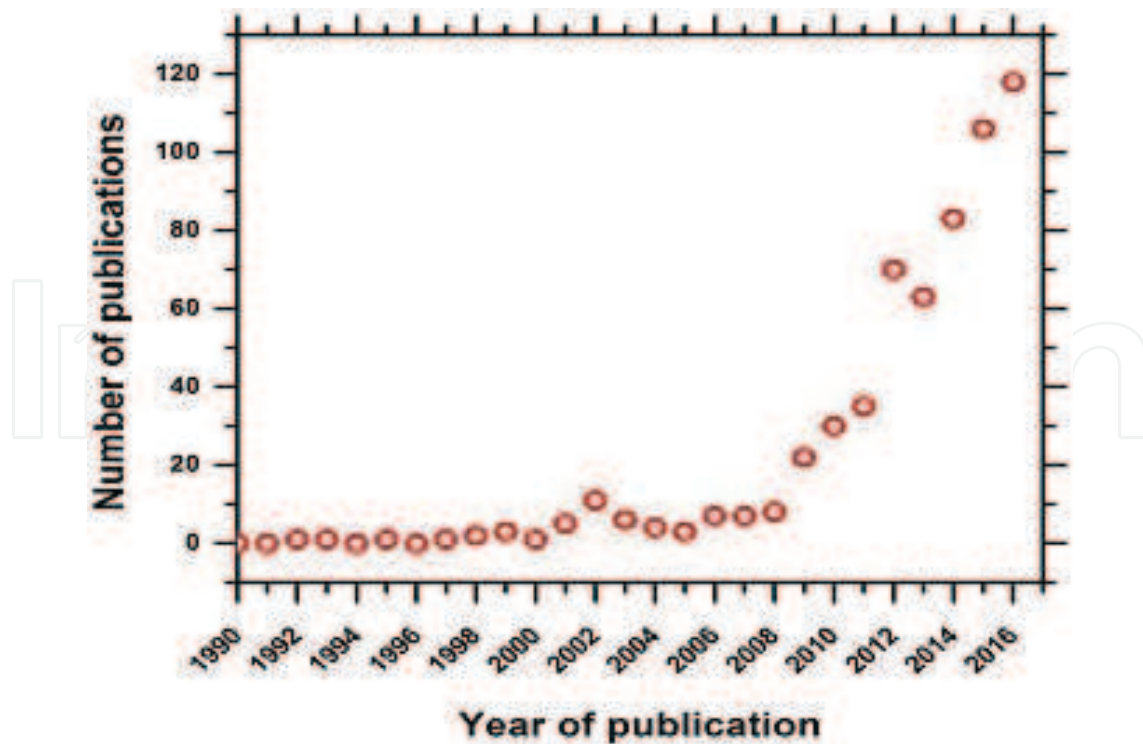


Figure 1. The interest in green inhibitors versus corrosion as indicated by number of publications. Keywords of corrosion and green inhibitors were used to retrieve the data from Web of Knowledge®.

| Source of natural products | Metal/alloy studied | Agg. media studied | Efficiency (%) | References |
|--|----------------------------------|---------------------------|---------------------------------------|------------|
| Flour and yeast | Iron | Acid media | 65–82 | [10] |
| Furit—peels of pomegranate | Aluminum | Acid media | 83 | [11] |
| <i>Hibiscus sabdariffa</i> extract | Al and Zn | HCl | 85 | [12] |
| Tobacco leaves | Mild steel and Aluminum | Neutral then acidic media | 87.5 (steel), 77.5 (Al) | [13] |
| Castor seeds | | | 71.0 (steel), 45.9 (Al) | |
| Black pepper | | | 87.5 (steel), 65.8 (Al) | |
| Soya bean | | | 65.5 (steel), 27.1 (Al) | |
| Gum (acacia) | | | NA (steel), 21.8 (Al) | |
| Catechu | | | 50.0 (steel), 6.3 (Al) | |
| Opium (0.1%) | | | NA (steel), 42.7 (Al) | |
| Opuntia extract | Steel, Aluminum, Zinc and Copper | Acid media | 75 (steel), 70 (Al), 55 (Zn), 56 (Cu) | [14] |
| <i>Aloe eru</i> leaves | | | 80 (steel), 64 (Al), 43 (Zn), 43 (Cu) | |
| Orange peels | | | 80 (steel), 59 (Al), 59 (Zn), NA (Cu) | |
| Mango peels | | | 82 (steel), 82 (Al), 80 (Zn), 30 (Cu) | |
| Pomegranate fruit shell | | | 65 (steel), 81 (Al), 71 (Zn), 73 (Cu) | |
| <i>Papaia</i> | Mild steel | Acid media | 94 | [15] |
| <i>Poinciana pulcherrima</i> | | | 96 | |
| <i>Cassia occidentalis</i> | | | 94 | |
| <i>Datura stramonium</i> seeds | | | 93 | |
| <i>Calotropis procera</i> | | | 98 | |
| <i>Azadirachta indica</i> | | | 84 | |
| <i>Auforpio turkiale</i> sap | | | 69 | |
| <i>Swertia angustifolia</i> | Mild steel | Acid media | 75–96 | [16] |
| <i>A. indica</i> | Mild steel | Acid media | 88–96 | [17] |
| <i>A. indica</i> | Mild steel | NaCl | 86.1 | [18] |
| <i>Punica granatum</i> | | | 79.2 | |
| <i>Momordica charantia</i> | | | 82.4 | |
| <i>Pongamia glabra</i> , <i>Annona squamosa</i> | Mild steel | Acid media | 89–95 | [19] |
| <i>Acacia arabica</i> | Mild steel | Acid media | 93–97 | [20] |
| Natural honey | Carbon steel | NaCl | 82–91 | [21] |
| <i>Rosmarinus officinalis</i> | Al–Mg alloy | NaCl | 75 | [22] |
| Mimosa tannin | Carbon steel | Acid media | 66–87 | [23] |
| Vanillin | Carbon steel | Acid media | 93–98 | [24] |
| Dodecanohydrazide, cis-9-octadecanohydrazide and 10-undecanohydrazide derived from fatty acids | Mild steel | Acid media | 85 | [25] |

| Source of natural products | Metal/alloy studied | Agg. media studied | Efficiency (%) | References |
|---|---------------------|-----------------------------------|--------------------------|------------|
| Herbs (thyme, coriander, hibiscus, anis, black cumin, and garden cress) | Steel | Acid media | 37–92 | [26] |
| Reducing saccharides fructose and mannose | Aluminum and Zinc | Alkaline media | 92 | [27] |
| Opuntia extract | Aluminum | Acid media | 76–96 | [28] |
| <i>Vernonia amygdalina</i> | Al alloys | Acid media | 49.5–72.5 | [29] |
| <i>Allium cepa</i> , <i>Allium sativum</i> , <i>M. charantia</i> | Mild steel | Acid media | 86–94 | [30] |
| Guar gum | Carbon steel | Acid media | 75–93.88 | [31] |
| <i>Zanthoxylum alatum</i> | Mild steel | Acid media | 76–95 | [32] |
| <i>Nypa fruticans</i> | Mild steel | Acid media | 75.11 | [33] |
| Caffeine–Mn ²⁺ | Carbon steel | Chloride ions | 50 | [34] |
| Caffeine and nicotine | | | 80–90 | [107] |
| Eugenol from cloves | Steel | Acid media | 80 | [35] |
| <i>acetyleugeno</i> | | | 91 | |
| <i>Ricinus communis</i> leaves | Mild steel | NaCl | 43–84 | [36] |
| Berberine extracted from <i>Coptis chinensis</i> | Mild steel | Acid media | 79.7 | [37] |
| Halfabar | Steel | Acid media | 90.50 | [38] |
| Chamomile | | | 92.97 | |
| Black cumin | | | 88.43 | |
| <i>Kidney bean</i> | | | 88.43 | |
| <i>Sansevieria trifasciata</i> | Aluminum | Acid and alkaline media + halides | 94.3 (HCl) 95.3 (KOH) | [39] |
| Exudate gum from <i>Dacryodes edulis</i> | Aluminum | Acid media | 42 | [40] |
| Gum arabic | | | 80 | |
| Exudate gum from <i>Raphia hookeri</i> | Aluminum | Acid media + halide | 56.3 | [41] |
| Exudate gum from <i>Pachylobus edulis</i> | Mild steel | Acid media | 56 | [42] |
| <i>Bambusa arundinacea</i> | Steel rebar | Chloride and nitrite | 85 | [43] |
| Parts of the kola tree (leaves, nuts, and bark) and tobacco | Steel rebar | NaCl | 70–91 | [44] |
| <i>Artemisia pallens</i> | Mild steel | Acid media | 93–98 | [45] |
| <i>V. amygdalina</i> | Steel rebar | NaCl | 90.8 | [46] |
| <i>Chamaerops humilis</i> L. | Steel rebar | Alkaline media | 42.2 | [47] |
| Mangrove tannin | Copper | Acid media | 82.4 | [48] |
| Chitosan | Copper | Acid media | 93 | [49] |
| <i>Myrtus communis</i> | Copper | Acid media | >85 | [50] |
| <i>Tagetes erecta</i> | Copper | Acid media | 98.07 | [51] |

| Source of natural products | Metal/alloy studied | Agg. media studied | Efficiency (%) | References |
|---|---------------------|----------------------|----------------|------------|
| <i>Morinda lucida</i> | Steel rebar | NaCl | 92.8 | [52] |
| <i>Opuntia ficus indica</i> | Carbon steel | Acid media | 70–91 | [53] |
| <i>Alhagi maurorum</i> plant extract | Copper | Acid media | 33–83 | [54] |
| Egyptian licorice extract | Copper | Acid media | 89.55 | [55] |
| <i>Tridax procumbens</i> <i>Chromolaena odorata</i> | Stainless steel | Oilfield environment | 82.03 95.6 | [56] |
| <i>Corchorus olitorius</i> | Mild steel | Acid media | 93 | [57] |

Table 1. Natural products and their anticorrosive properties on metals or alloys in different aggressive.

value when different conditions are applied, according to conditions of study in each reference (temperature, concentration of inhibitors, concentration of aggressive media, conditions of study, and adsorption isotherm).

Figure 2 shows examples for the most used natural green corrosion inhibitors from past to present times as a real image.



Figure 2. Various sources for natural green corrosion inhibitors.

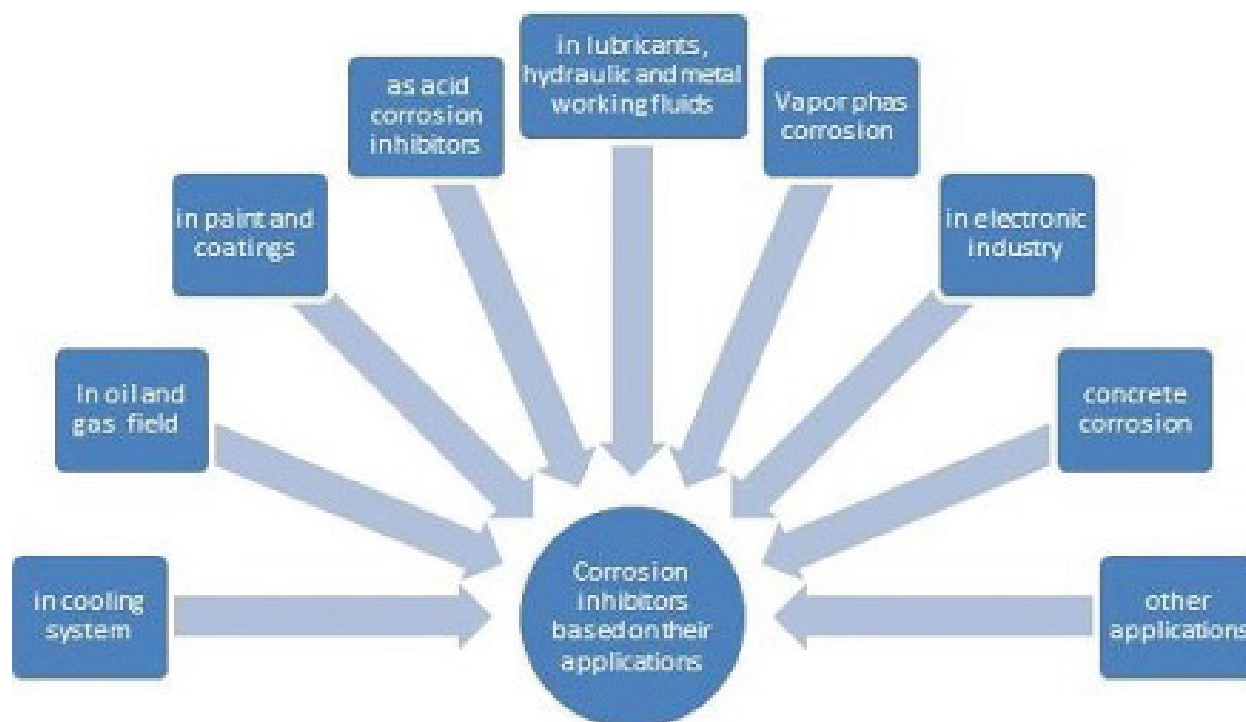


Figure 3. Usage of green corrosion inhibitors in various industries.

Figure 3 presents the importance of green corrosion inhibitors in large industrial applications. Most of these inhibitors contain functional groups and/or π -electrons in conjugation with triple or double bonds, which affect organic compounds by specific interaction between necessary elements such as nitrogen, sulfur, and oxygen through free lone pairs of electrons, which are adsorbed on the metal surface or by supplying electrons through π -orbitals [58].

2. Mechanism of green inhibitors as corrosion inhibitors

Corrosion is a spontaneous process; the relative rate of corrosion is related to the change in standard Gibbs free energy (ΔG°). A more negative value of ΔG° is related to higher spontaneous reaction, i.e. higher corrosion rate [59]. Metals and alloys when exposed to the environment corrode to form stable corrosion products [60]. Utilization of additive corrosion inhibitors is necessary to mitigate corrosion rate. Corrosion products such as rust and scale can also act as corrosion inhibitors because they can accumulate on the surface and act as physical protective barriers; however, the relative rate of corrosion of any particular metal depends on the Pilling–Bedworth ratio [61, 62], which is used at high-temperature oxidation (corrosion); the ratio is defined as:

$$\frac{M \cdot d}{n \cdot m \cdot D} \quad (5)$$

where m and d are the atomic weight and density of the metal, respectively, M and D are the molecular weight and density of scale (corrosion product) accumulated on the metallic surface, and n denotes the number of metallic atoms in the molecular formula of the corrosion product. The magnitude of the Pilling–Bedworth ratio can be used to explain the status of

surface film, i.e. whether it will be protective or not. When the volume of corrosion product is smaller than the volume of metal from which it is formed, then $Md/nmD < 1$ and in this situation it is expected that the surface film of the corrosion product contains pores and cracks that would be relatively nonprotective. When the volume of the corrosion product is larger than the volume of metal for $Md/nmD > 1$, it is expected that the surface film of the corrosion product is relatively more compressed and compact than would result in a more protective film.

Adsorption is the first step in forming a corrosion protective film or coat in the presence of aggressive media that occurs on metallic surfaces on the active sites. Several factors affect the adsorption of inhibitor on the metallic surface and isolate it including adsorption mode, chemical and electronic characteristics of the inhibitor, temperature, type of electrolyte employed, steric effects, and the nature and surface charge of metals [63]. The Langmuir adsorption isotherm is the most favorable to clarify interaction between the inhibitor and metal surface [53]. Adsorption on the corroded surfaces approximates to a steady-state adsorption that may be physical adsorption (physisorption) or chemical adsorption (chemisorption), or a mixed adsorption mechanism that is considered ideal for effective corrosion inhibition.

Physical adsorption is related to the standard free energy of adsorption $\Delta G_{\text{ads}}^{\circ}$ in aqueous solution. If its value is $-20 \text{ kJ}\cdot\text{mol}^{-1}$ or less negative it is associated with an electrostatic interaction between charged centers of molecules and the charged metal surface, which results in a dipole interaction of the molecules and metal surface [64]. However, chemical adsorption is a process that involves the transfer or sharing of electrons from the inhibitor to the metallic surface and results in the formation of a coordinate covalent bond. The bonding strength is much larger than physical adsorption where the value of $\Delta G_{\text{ads}}^{\circ}$ is around $-40 \text{ kJ}\cdot\text{mol}^{-1}$ or more negative [65, 66]. Adsorption of green corrosion inhibitor retards corrosion by deduction of the active metallic surface area, leaving inactive sites on the surface exposed to corrosive media. Green inhibitors are more efficient at room temperature or low temperatures, while inhibition efficiency is decreased with an increase in temperature in most cases.

The action of green inhibitors depends on the structure of the active ingredient; many researchers have postulated numerous theories to explain the mechanism of their effect. The active ingredient derived from natural inhibitors changes from one plant species to another but their structures are closely related to their organic coordinate. As an example, garlic contains allyl propyl disulfide, mustard seeds contain an alkaloid berberine that has a long chain of aromatic rings and an N atom in the ring, carrot contains pyrrolidine, and castor seed contains the alkaloid ricinine. Eucalyptus oil contains monomtrene-1,8-cineole. Lawsonia extract contains 2-hydroxy-1,4-naphthoquinone resin and tannin, coumarin, gallic acid, and sterols. Gum exudate contains hexuronic acid, neutral sugar residues, volatile monoterpenes, canaric and related triterpene acids, and reducing and nonreducing sugars. Garcinia kola seed contains primary and secondary amines, unsaturated fatty acids, and bioflavonoids. Calyx extract contains ascorbic acid, amino acids, flavonoids, pigments, and carotene [67]. The corrosion inhibition activity of these plant extracts could be due to the presence of heterocyclic constituents like alkaloids, flavonoids, etc.

3. Green inhibitors for rebar embedded in concrete

Kundu et al. [68] reviewed green inhibitors' effect in rebar embedded into concrete under an alkaline environment of nearly pH 12–13 to protect rebar from premature deterioration. Its

mechanism depends on the strong hydrophobic effect of *Bambusa arundinacea* that supports the formation of a product layer of two faced oxides (Fe_2O_3 and Fe_3O_4) adherent to the steel surface [69] or as spinel $\alpha\text{-Fe}_3\text{O}_4\text{-}\gamma\text{-Fe}_2\text{O}_3$ solid solution, which is proposed to form a passive film on steel [43]. Moreover, efficiency of *B. arundinacea* was due to its strong adsorption parallel to the metal surface, which restricted the number of surface active sites available for chloride ion ingress. In another investigation, Eyu et al. [70] studied the effect of *Vernonia amygdalina* extract within 70 days of immersion on carbon steel reinforcement in concrete exposed to a chloride-laden environment to compare efficiencies of other inhibitors, while Loto et al. [44] studied plant extract by a potentiometric method to compare the percentage of efficiency between tobacco and extract of kola nut, leaves, and bark in 5% NaCl. Okeniyi et al. [71, 72] studied the bark extract of the *Rhizophora mangle* L. plant for rebar in concrete in an acidic environment.

4. Green corrosion inhibitor based on ionic liquids

Nowadays, worldwide growing ecological awareness and strict environmental protocols prevent synthesis and utilization of hazardous traditional volatile corrosion inhibitors. So, there is a vital need for improvement in synthetic and engineering chemistry by environmentally friendly materials. Use of alternative synthetic strategies toward green synthesis [73, 74] has become necessary as multicomponent reactions (MCRs) in combination with ultrasonic (sonochemical) and microwave irradiation. So, scientists have been directed to develop drugs from plant extracts that are characterized by their natural and biological origins and nontoxic nature [75] to act as green corrosion inhibitors. Pathak et al. [76] studied different classes of drugs in different media; their effectiveness depends on their chemical composition, molecular structure, and affinities for metallic surfaces. The most effective of them depend on heteroatoms like nitrogen, oxygen, and phosphorus.

However, extraction and purification of plant extracts is tedious, exhausting, and extremely expensive as well as time consuming, and requires relatively large amounts of organic solvents that may adversely affect the environment and living beings; high temperature can also decompose the active constituents and thereby decrease relative inhibition efficiency. For these reasons the use of drugs as corrosion inhibitors for ferrous and nonferrous metals is also limited [75]. Therefore, there is a need to develop green inhibitors by proper design of the synthesis, which can be achieved by using cheap and environmentally friendly products. This is onset of green chemistry as ionic liquids that are eco-friendly and sustainable solvents composed of ions that can displace a wide range of inorganic and organic compounds. Ionic liquids follow the principles of green chemistry proposed by Anastas and Warner [77]. Ionic liquids have a promising future in the field of green chemistry, and have attracted great attention because they are widely used in various applications [78, 79]. **Figure 4** shows important properties of ionic liquids and their applications as green corrosion inhibitors [80–82]. They show high performance to adhere to the surface of steel with the formation of thin films to protect steel [78], copper [83], zinc [84], titanium, and aluminum substrates [85].

Chitosan is a linear copolymer of (1-4)-2-amido-2-deoxy-d-glucan (glucosamine) and (1-4)-2-acetamido-deoxy-d-glucan (*N*-acetylglucosamine), which are considered sources for ionic liquids [86]. Chitosan is extracted from crab shell [87] based on aminopolysaccharides and is used to produce several new materials [88]. Their high ability for functionalization makes them applicable to apply in several industrial applications because of their better solubility

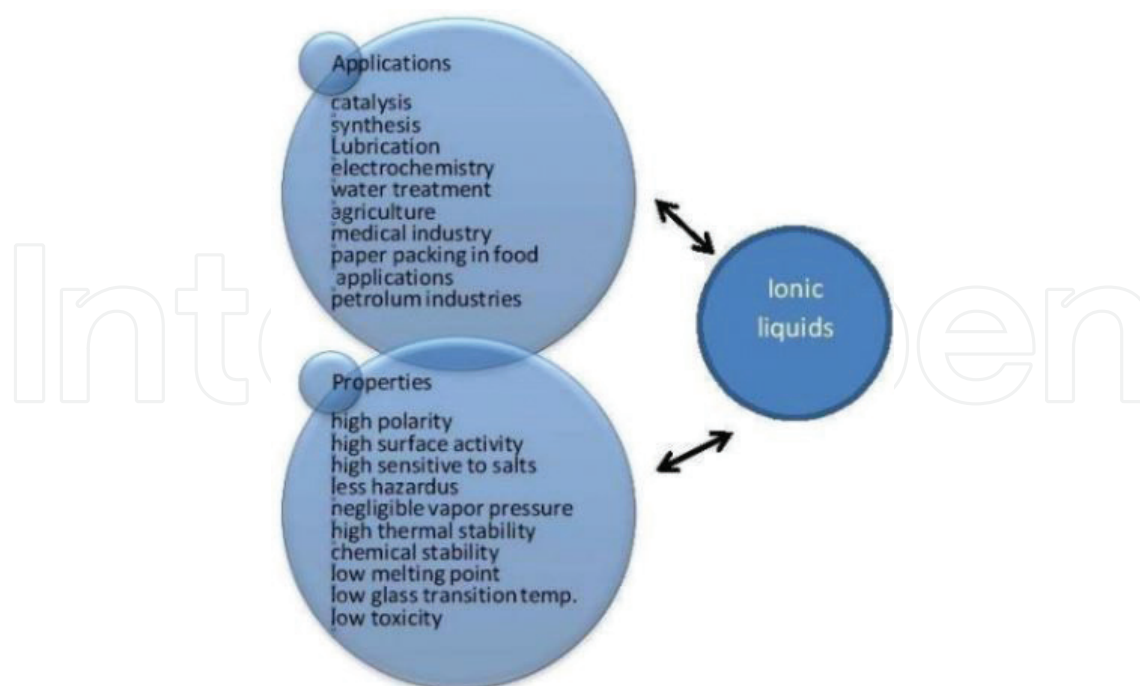


Figure 4. Important properties of ionic liquids and their impact as green corrosion inhibitors for many applications.

in organic solvents and water than chitosan itself. This chemical functionality is extremely relevant when chitosan is used as a corrosion inhibitor [89]. Chitosan can inhibit the corrosion of copper in acidic media because HCl is used as a mixed-type inhibitor, which follows a Langmuir isotherm [49]. Chitosan possesses unique physicochemical properties, namely, biocompatibility, antimicrobial activity, biodegradability, and excellent film-forming ability. Indeed, it can be used to form thin coatings to protect metallic surfaces.

Ionic liquids have been classified into 11 categories according to Hajipour and Refiee [90], namely, neutral ionic liquids, acid ionic liquids, basic ionic liquids, ionic liquids with amphoteric anions, functionalized ionic liquids, protic ionic liquids, chiral ionic liquids, supported ionic liquids, bio-ionic liquids, poly-ionic liquids, and energetic ionic liquids, and have described common features and properties of these ionic liquids. However, Angell et al. [91] classified ionic liquids in four classes, including aprotic, protic, inorganic, and solvate (chelate) ionic liquids. Their adsorption on metallic surfaces takes place via chemisorption, which obeys the Langmuir adsorption isotherm as reported by Verma et al. [92] in their recent review, which showed several ionic liquids and their properties as green corrosion inhibitors for different metals and alloys such as mild steel, aluminum, copper, zinc, and magnesium in several electrolytic media. A similar observation has been reported by other authors for different metals including copper, nickel, and stainless steel [93], while Shetty et al. [94] have reviewed adsorption of ionic liquids on an aluminum surface that obeyed the Temkin adsorption isotherm.

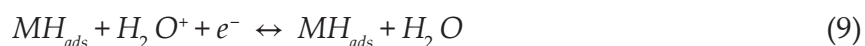
Inhibition of metallic corrosion in the presence of ionic liquids involves blocking of anodic oxidative metallic dissolution as well as cathodic hydrogen evolution reactions [95] described as follows:





where M is the anodic dissolution of metals in aqueous corrosive solution, and $ILsC^+$ and X^- represent the cationic counterpart of the ionic liquid and anionic counterpart of the ionic liquid, respectively. Both anionic charged species attract positively charged cationic counterparts of the ionic liquids ($ILsC^+$) by electrostatic force of attraction (physisorption) and form a monomolecular layer as an insoluble complex on the metallic surface [95]. The adsorption of the $ILsC^+$ on the metallic surface causes a change in the surface polarity, which induces the adsorption of $ILsC^+$ and X^- ions again, which results in a multimolecular layer [95]. The multimolecular layers are stabilized by van der Waal's cohesion force acting between organic moieties of the ionic liquids, which causes a more closely adsorbed film at metal/electrolyte interfaces. Generally, the cationic part ($ILsC^+$) interacts with the metallic surface and forms the multimolecular layers, while the rest of the ionic liquids form hydrophobic hemimicelles, admicelles, and/or surface aggregation [95, 96]. The adsorbed multimolecular layers of the ionic liquids isolate the metal (M) from the corrosive environment and protect it from corrosive dissolution.

During cathodic hydrogen evolution reactions, hydronium ions are adsorbed on the metallic surface by the Volmer mechanism followed by discharge of hydrogen gas by the Heyrovsky and Tafel mechanism [97, 98], represented as follows:



The cationic part of ionic liquids ($ILsC^+$) starts competing with hydrogen ions for electrons; however, $ILsC^+$ has a larger molecular size so replaces a greater number of water molecules from the metallic surface. After their adsorption the cationic part of the ionic liquids accepts electrons from the metal (M), which results in the formation of electrically neutral ionic liquids (inhibitors). The neutral species transfer (donation) their nonbonding (of heteroatoms) and π -electrons into the d-orbitals of the surface metallic atoms resulting in the formation of coordinate bonds between metal and ionic liquids (chemisorption) as reported for several organic conventional inhibitors [95]. However, metals are already electron-rich species; this type of donation causes interelectronic repulsion, which results in the transfer of electrons from d-orbitals of the surface metallic atoms to antibonding molecular orbitals of the ionic liquids (retrodonation). Both donation and retrodonation strengthen each other through synergism [99].

Development of corrosion inhibitors requires correlating the inhibition efficiency of the inhibitors with their molecular properties through study interactions between inhibitors and the metallic surface and describing the adsorption behavior of ionic liquids on the metallic surface. This is achieved by density functional theory (DFT). DFT is one of the most important methods

used in theoretical chemistry for corrosion inhibition to accurately predict the inhibition efficiencies based on the calculations provided by mechanistic information about metal–inhibitor interactions and can be performed for inhibitor molecules even before their synthesis [100–105].

5. Vapor-phase inhibitors

Vapor-phase inhibitors (VPI) are volatile corrosion inhibitors. They are considered a revolution in green inhibitors and are required in many fields covering electronics, packaging, industrial processing, reinforced concrete, coatings, and metalworking fluids due to their nontoxic properties. They are free of nitrites, halogens, and phosphates, and are completely safe to handle. In addition, they also inhibit the corrosion of ferrous and nonferrous metals. In a review of the literature, Bastidas et al. [106] studied various factors influencing VPI performance and mechanisms. Nanovapor-phase inhibitors made from renewable agricultural by-products do not destabilize the natural balance of the environment. Their impact depends on their diffusion, filling all void spaces and active areas with protective vapor molecules that

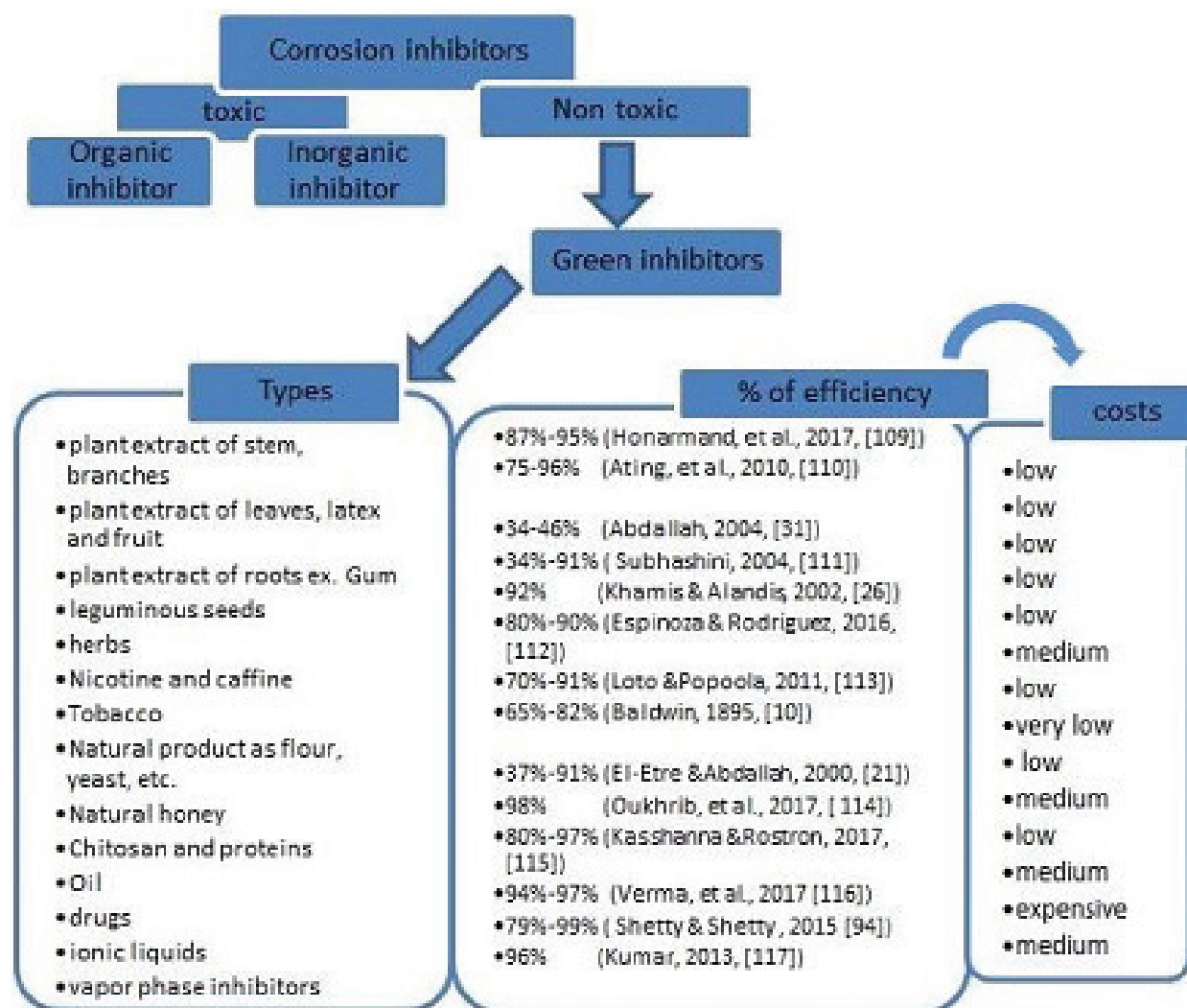


Figure 5. Accessibility of green corrosion inhibitors from nature with approximated cost of extraction and percentage of efficiency according to the cited literature [109–117].

are attracted to metallic surfaces and adsorbed physically and/or chemically onto the resulting formation of a nanoprotective barrier layer [107, 108].

Several factors must be considered to control the cost of extractions, which sometimes may be very high when the quantities needed are high. Also, the estimated percentage of an inhibitor's efficiency must be controlled, including temperature, concentration of inhibitors, type of metallic surface exposed to aggressive environments, etc. **Figure 5** summarizes the accessibility of green corrosion inhibitors from nature with approximate estimations of cost of extraction between low, medium, and expensive, and the percentage of efficiency according to the cited literature.

The objective of this chapter was to review natural compounds as effective green corrosion inhibitors because of their biodegradability, easy availability, and nontoxic nature. The literature revealed that natural plant extracts are effective green corrosion inhibitors against various metals and alloys. In addition, the chapter focused on why the efficiency of green and sustainable inhibitors of ionic liquids for the corrosion of metals and alloys is preferred compared to traditional corrosion inhibitors because of their advantageous physiochemical properties. Finally, attention was given to the adsorption behavior of ionic liquids generally, following the Langmuir isotherm, the Temkin adsorption isotherm, and in particular the adsorption behavior of ionic liquids on metallic surfaces using DFT-based quantum chemical calculations. Quantum chemical calculations (DFT) provide a good insight into the inhibition mechanism and experimental order of inhibition efficiency. The tendency to explore vapor-phase corrosion inhibitors and green nano-inhibitors is a new area for future research.

A lot of potential is still untapped, especially computational modeling of the major extract components of various metals and alloys. Further research should also be focused on plant extraction methods and their active constituents as well as scale-up experiments for industrial applications that are needed to commercialize these natural extracts to effectively replace conventional chemicals.

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