

Green Inhibitors for Corrosion of Metals: A Review

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Abstract

Corrosion is an unavoidable but a controllable process. Due to the issues of toxicity of substances like chromate inhibitors, there is an increasing interest in exploration and utilization of eco-friendly inhibitors, which are also known as green inhibitors. This review briefly discusses some of the interesting features of the green inhibitors reported during the last decade.

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Introduction

Metals are the pre-eminent important materials used in structural and decorative applications. The corrosion, deterioration or destruction of metals is an unavoidable but controllable process. The corrosion of metals has a significant impact on the development of a country, which can be compared to any natural disasters like earthquake, flood, etc. For example; the direct metallic corrosion cost in the US was estimated as approximately \$276 billion on an annual basis, which is several times greater than the normalized loss incurred due to the natural disasters (\$17 billion per annum). It was also suggested that about 25-30% of the annual corrosion costs could be saved by means of optimum corrosion management practices [1].

Several different methods can be employed to slow or prevent corrosion of metallic structures. The most commonly used methods are protective coatings on metals using organic molecules, plastics, polymers; and cathodic and/or anodic protection using organic or inorganic inhibitors. The initial report of corrosion inhibition by organic inhibitors is attributed to Speller [2], who examined the corrosion inhibition of scaled water pipes in HCl. Since then, many organic and inorganic compounds that are added to the corrosive fluids have been investigated for this purpose.

There are growing concerns about certain compounds like chromates as inhibitors for corrosion processes, mainly due to the issue of toxicity. Green inhibitors like natural products from plant extracts and substances from other renewable sources are of the interest of the researchers who are interested in “green chemistry” or “eco-friendly” technologies. The literature contains a number of references on green corrosion inhibitors. Rather than concentrate on the more historical work on green inhibitors added to the

corrosive fluids, this review concentrates on the advances made in the last ten years. However, in order to highlight the growing interest on “corrosion inhibition of mild steel in corrosive fluids”, the authors have performed a survey on the literature published during 1950-2010.

Table 1 Recent trends in publications related to corrosion inhibitors

Decades	Number of publications
1951-1960	29
1961-1970	1235
1971-1980	1711
1981-1990	2685
1991-2000	4819
2001-2010	9873

The number of articles published has been doubled during the last decade (2001-2010) compared to 1991-2000 (**Table 1**). The increasing number of publications clearly indicates the interest in exploring the new inhibitors for a variety of corrosive environments in order to control the corrosion of various metals. Although the number of investigations on corrosion inhibitors has dramatically increased, only 5% of the literature published during the last decade concerns green inhibitors.

While other reviews [3-7] deal with the mechanisms of corrosion inhibition, this review focuses primarily on the effectiveness of green inhibitors in corrosive fluids, which are mainly plant extracts. The significance of natural polymers like starch and cellulose derivatives against corrosion of metals is also discussed. The selectivity of green

inhibitors towards metals and the effect of aging are as well discussed.

Green inhibitors

An inhibitor is a substance (or a combination of substances) added in a very low concentration to treat the surface of a metal that is exposed to a corrosive environment that terminates or diminishes the corrosion of a metal. These are also known as site blocking elements, blocking species or adsorption site blockers, due to their adsorptive properties [8, 9]. The term “green inhibitor” or “eco-friendly inhibitor” refers to the substances that have biocompatibility in nature. The inhibitors like plant extracts presumably possess biocompatibility due to their biological origin. Similar to the general classification of “inhibitors”, “green inhibitors” can also be grouped into two categories, namely organic green inhibitors and inorganic green inhibitors.

Organic green inhibitors

The organic green inhibitors are the flavonoids, alkaloids and other natural products obtained from natural sources like plants [4]. It also includes synthetic compounds with negligible toxicity. Some of the notable developments on organic green inhibitors especially plant extracts are discussed here.

Plant extracts

The authors have so far investigated the application of plant extracts [10, 11], as well as other organic inhibitors [12-17] against corrosion of steel in acidic fluids. Loto had reported the application of the extract of *Mangifera indica* (Common name: mango, indigenous area: India and other tropical regions) leaves and bark for corrosion of mild steel in diluted sulphuric acid (H_2SO_4) medium [18, 19]. The weight loss measurements and electrochemical impedance spectroscopic studies were used to determine the inhibition efficiency of the inhibitors. Though the extract of leaves and bark showed a significant effect on the corrosion rate separately, the combination of these two extracts exhibited rather higher efficiency.

The inhibitive effect of *Zanthoxylum alatum* (Winged Prickly Ash, East and South Asian Countries) fruit extract was reported for corrosion of mild steel in phosphoric acid medium at temperatures ranging from 50–80 °C [20]. The surface analysis using X-ray photoelectron spectroscopy (XPS) revealed the layer formation of the plant extract on the surface of mild steel. And the results were indicated the possible formation of iron phosphate that was catalyzed by the formation of the iron-plant extract organo-metallic complex.

Satapathy et al studied the methanol extract of *Justicia gendarussa* (Willow-leaved justicia, India, Indonesia) leaves for corrosion inhibition of mild steel in hydrochloric acid medium (HCl) [21]. The authors have made an attempt to characterize the organic compounds present in the methanol extract by means of gas chromatography- mass spectrometric technique. The results showed that the compounds present in the methanol extract were difficult to separate, since the

retention times of majority of the compounds were close to each other. The electron spectroscopy for chemical analysis and atomic force microscopy were employed to obtain the information about the film formation on the surface of the mild steel specimen.

The inhibitive action of leaves, seeds and a combination of leaves and seeds of *phyllanthus amarus* (Stonebreaker, India and other tropical regions) was reported by Okafor et al, for corrosion of mild steel in HCl and H_2SO_4 [22]. The half-life time of mild steel in the electrolyte solution containing the acid and the combined extract of leaves and seeds showed increased resistance for the mild steel towards both the corrosive environments. The positive values of heat of adsorption revealed the chemical adsorption of the inhibitors on the mild steel surface, which was well supported by adsorption measurements.

In an interesting study, El-Etre investigated the stem extract of *Opuntia* (Paddle cactus, India, Mexico, North Africa and some parts in Europe) for corrosion inhibition of aluminium in HCl acid solution, in which the extract was obtained by squeezing the stem instead of extracting with some solvent, and the juice was directly applied as the inhibitor [23]. The aging effect of the inhibitor was also studied, which is discussed in the later section.

Natural oils are one of the green inhibitors from plant sources. Pennyroyal oil was extracted from *Mentha pulegium* (Pennyroyal Mint) and studied for corrosion inhibition of steel in HCl corrosive medium [24]. The major constituent of Pennyroyal oil was *R-(+)-pulegone* [25]. The inhibition efficiency of the inhibitor increased with temperature, which clearly indicated the chemisorption of the inhibitor on the surface of the steel. And the inhibitor was classified as cathodic type inhibitor.

According to Riggs [26], if the displacement of corrosion potential during electrochemical polarization of the metal is more than ± 85 mV with respect to the corrosion potential of the blank, the inhibitor can be considered as a distinctive cathodic or anodic type. Similarly, inhibition effect of Jojoba oil (*Simmondsia chinensis*, Arizona, California, Mexico) and *Artemisia oil* (Mugwort, India, Nepal, China, Korea and Japan) were studied for steel corrosion in HCl medium under different temperatures [27, 28]. Abdullah et al studied the inhibitory effect of natural clove oil for corrosion inhibition of nickel and its alloys namely, Inconel 600, and Inconel 690 in different concentrations of HCl solutions [29].

Sethuraman et al has performed a series of investigations on corrosion inhibition of mild steel in acidic medium using various plant extracts. For example, black pepper [30], *Datura metel* (Angel's trumpet, India and other tropical regions) [31], and *Strychnos nux-vomica* (Poison nut, India and South-East Asia) [32] have been studied against the corrosion of mild steel in HCl as well in H_2SO_4 .

The extract of khillah seeds (*Ammi visnaga*) was studied against the corrosion of SX 316 stainless steel in HCl solution [33]. The mechanism of inhibitive effect of the khillah seed extract was studied by comparing the complexing ability of the compounds khellin and visnagin that are major constituents of khillah seed extract. The conductometric titrations showed the possible

formation of Fe-khellin or Fe-visnagin complex, which is usually attributed to chemisorption or chemical bonding between the iron and inhibitor molecules. But in contrary to that the inhibition efficiency of the extract significantly decreased with increasing the temperature, which indicated the mechanism of adsorption of the inhibitor molecules were predominantly physisorption. Though the decrease in the inhibition efficiency was observed at elevated temperatures, the seed extract exhibited mostly 71% of inhibition efficiency for 120 ppm at 80 °C.

The anti-corrosion behavior of lupine (*Lupinus albus* L., White lupine, Egypt, Sudan, Ethiopia, Central and Western Europe) extract on the corrosion of steel in aqueous solution of H₂SO₄ and HCl was investigated by Abdel-Gaber et al [34]. The corrosion data were tested with kinetic-thermodynamic model to reveal the adsorption mechanism of inhibition. The inhibitor showed comparatively higher efficiency in HCl than in H₂SO₄.

Abiola et al described the inhibition of corrosion of aluminium in sodium hydroxide (NaOH) solution using leaves and seed extract of *Gossipium hirsutum* L. (Upland Cotton) [35]. The leaf extract showed significantly higher inhibition efficiency (97%) than the seed extract (94%). In a similar manner, the extracts of *Carica papaya* leaves, seeds, heartwood, and bark were evaluated for corrosion inhibition of mild steel in H₂SO₄ acid solution [36]. The leaf extract showed an higher inhibition efficiency compared to the extracts from seed, heartwood and bark.

The *Gongronema latifolium* extract was studied for corrosion inhibition of aluminium in both acidic and basic conditions [37]. The inhibitor showed higher inhibition efficiency in HCl than in NaOH. The suggested mechanism for the predominant corrosion inhibition in HCl solution was chemisorption, whereas physisorption was attributed for the inhibitor's effectiveness against NaOH solution.

Corrosion inhibition of zinc in HCl solution was studied using *Aloe vera* (Arabian Peninsula, North Africa and other tropical regions) gel extract [38]. In this case, the gel was squeezed out from fresh leaves. The juice was appropriately diluted and then the solution was directly studied acid corrosion of zinc. The corrosion data from weight loss measurements were found to have first-order kinetics relationship.

El-Etre evaluated the inhibition potential of the aqueous extract of zallouh root for corrosion of carbon steel in HCl solution [39]. The relatively low value of activation energy in the presence of zallouh extract indicated that the mechanism of inhibition was provided by the physical adsorption of inhibitor molecules on the steel surface.

Inorganic green inhibitors

Inorganic elements or metals have a crucial role in living organisms, when they are at trace amounts. The higher concentrations of many metals cause toxicity to all forms of lives. It is also applicable for the derivatives of metals. For example, chromium compounds, mainly chromates were widely used as potential corrosion inhibitors in aqueous

systems due to their high efficiency [40-42]. Besides the high inhibition efficiency, chromates exhibit high toxicity and consequently prohibited to use for industrial applications [43]. In search of alternatives for chromate inhibitors, lanthanide salts are found to show excellent inhibition properties [44, 45]. Lanthanide salts like lanthanide chlorides were reported to possess toxicity that is comparable with sodium chloride [46]. Hence lathanide salts can also be considered as green inhibitor or eco-friendly inhibitor (Table 2).

Table 2 Inorganic-green inhibitors

Inhibitor	Metal	Medium	Ref.
CeCl ₃	AA5083, galvanized steel	NaCl	47
CeCl ₃ .7H ₂ O	Tinned iron	NaCl	48
La(NO ₃) ₃ , Sm(NO ₃) ₃ , LaCl ₃ , and SmCl ₃	AISI 434 SS	NaCl	49

A few research studies were reported on the corrosion inhibition properties of lanthanides during the last decade. For example, Arenas et al reported the application of CeCl₃ as an inhibitor for an aluminium alloy (AA5083) and galvanized steel in aerated NaCl solutions [47]. The study has provided evidence for the formation of an inhibitor layer on the surface of alloy as well on galvanized steel. The presence of Ce⁴⁺ was observed which was due to the oxidation of Ce³⁺. The phenomenon of "over precipitation" of cerium particles was observed on some areas of galvanized steel surface. This was attributed to the loss in the film coherence that occurs when it reaches critical thickness. The yellow coloration of the layer formed on the galvanized steel was not observed for the aluminium alloy, which may be due to the microscopic sizes of the precipitates.

In another attempt by Arenas et al, CeCl₃.7H₂O was employed as corrosion inhibitor for tinned iron or tin plate in NaCl solutions [48]. The coulometric studies revealed the cathodic nature of the inhibitor, which was similar to their previous report [47]. Similarly, Bernal et al reported the inhibitive effects of lanthanum nitrate (La(NO₃)₃), samarium nitrate (Sm(NO₃)₃), lanthanum chloride (LaCl₃), and samarium chloride (SmCl₃) for corrosion of AISI 434 SS in sodium chloride solutions [49]. Even though the nitrate ion is considered as an anodic inhibitor, the studied rare earth nitrates (La(NO₃)₃, Sm(NO₃)₃) were demonstrated as mixed-type inhibitors, which was attributed to the presence of lanthanide ions in the solutions. Interestingly, for rare earth chlorides decrease in inhibition efficiency was observed on increasing the inhibitor concentration. This negative effect was interpreted as due to the increase in the concentration of the chloride ions.

Natural Polymers

Polymers are the materials that have

excellent adhesive properties on metal surfaces. A wide range of polymers has been studied for their anti-corrosive properties in the form of both pre-coating [50-55] on the metal as well as inhibitor in a variety of corrosive fluids [56-63] (**Table 3**). The inhibitory mechanism of mimosa tannin against corrosion of low-carbon steel in acid solution was reported by Martinez et al [56]. The adsorption mechanism of the mimosa tannin was studied at pH 1-3. It is interesting to note that at pH 1-2 the inhibitor adopts chemisorption mechanism, where as the mechanism of inhibition switched to physisorption at pH 3.

Table 3 List of natural polymers and derivatives studied as corrosion inhibitor

Inhibitor	Metal	Medium	Ref.
Mimosa tannin	Low carbon steel	H ₂ SO ₄	56
Guar Gum	Carbon steel	H ₂ SO ₄	57
Gum Arabic	Mild steel	H ₂ SO ₄	58
Exudate Gums	Aluminium	HCl	59
Carboxymethyl cellulose	Mild steel	HCl	60
Carboxymethyl cellulose	Mild steel	H ₂ SO ₄	61, 62
Starch	Mild steel	H ₂ SO ₄	63

Guar gum, a naturally-occurring polysaccharide was examined for corrosion inhibition of carbon steel in sulfuric acid solutions [57]. An adsorption mechanism was proposed for the inhibitive nature of Guar gum. The increase in the concentration of the inhibitor had increased the resistance to pitting corrosion, which was supported by the shifts in the pitting potentials. The interaction between the oxygen atoms present on the side chains, and ferrous ions were probably impossible. Therefore, the possible mode of coordination type bonding was assumed to occur between the ferrous ions and the oxygen atoms present in the backbone of the polymer.

In an attempt to compare the inhibition efficiencies of a natural polymers and synthetic polymers, Umoren et al [58] studied gum Arabic and polyethylene glycol for corrosion inhibition of mild steel in sulphuric acid solutions. The synergistic effects of halide derivatives were also studied. The authors have also reported the inhibitive properties of exudate gum for aluminium corrosion inhibition in acidic medium [59]. Though the time dependence of the inhibition efficiencies of exudates gum followed almost similar trend to gum Arabic, the effect of temperature was different. The inhibition efficiency was increasing on temperature scale for the former, where as it was decreasing for the later. Therefore, the exudate gums was proposed to have physically adsorbed on the surface of aluminium.

Cellulose is a most abundant water-insoluble natural polysaccharide. Carboxymethyl cellulose is a water-soluble (semi-) synthetic analog of cellulose. The anti-corrosion properties of carboxymethyl cellulose (CMC) were studied for mild

steel in different acid solutions [60-62]. Bayol et al have studied the adsorptive behavior of CMC on mild steel in HCl solutions [60]. Umoren et al reported the inhibition potential of CMC for sulphuric acid corrosion of mild steel [61, 62] and also the effects of synergism and antagonism of halide ions with CMC on corrosion inhibition.

Another natural polymer, starch was investigated by Mobin et al [63], for inhibition of mild steel corrosion in sulphuric acid. The synergistic effects of surfactants such as sodium dodecyl sulfate and cetyl trimethyl ammonium bromide on the corrosion inhibition behavior of starch was also studied. Similar to the previous reports on the anti-corrosion properties of natural polymers as described above, the inhibition mechanism of starch was proposed as physical adsorption.

Bio-mimicking of Green Inhibitors

It is well known that green inhibitors like plant extracts contain numerous organic compounds. It is rather difficult to understand the mechanism of inhibition for a cluster of different compounds present in a plant extract. Investigation of the synthetic analogs of naturally occurring flavones, amino acids are very much dexterous to figure out the mechanisms involved in the inhibition process. For example, 3-hydroxy flavone, 2,3-dihydroxy flavanone were investigated by the authors for acid corrosion of mild steel [12, 13] (**Table 4**).

Table 4 Model green inhibitors

Inhibitor	Metal	Medium	Ref.
3-Hydroxyflavone	Mild steel	HCl	12
2,3-Dihydroxy flavanone	Mild steel	HCl	13
Methionine	Mild steel	H ₂ SO ₄	64
Tryptophan	low-carbon steel	HCl	65
Cysteine, glycine, leucine, & alanine	Mild steel	HCl	66
Cysteine	Copper	NaCl, HCl	67
Serine, threonine, & glutamic acid	Copper	HCl	68

The flavone derivatives were found to adsorb on the mild steel surface via both physical and chemical adsorptions. Similarly, amino acids alanine, cysteine, glutamic acid, glycine, leucine, serine, threonine, tryptophan were studied mainly for corrosion inhibition of steel [64-66] and also for copper corrosion [67, 68].

Oguzie et al [64] investigated the inhibition mechanisms of methionine for acid corrosion of mild steel along with synergistic effect of iodide ion. The results showed that the synergistic effect of iodide ion increased on increasing the population of specific adsorbed I⁻ ions for ion-pair formation with methionine cations. The adsorption of L-tryptophan on low-carbon steel was evaluated by Fu et al [65].

The quantum chemical calculations determined the possible adsorption centers of L-tryptophan and also its flat orientation with respect to the Fe surface. Similarly, quantitative structural activity relationship for four amino acids namely, cysteine, glycine, leucine and alanine were studied [66]. And cysteine was found to possess higher inhibition efficiency than the other studied amino acids.

Khaled et al [67] has examined cysteine for corrosion inhibition of copper. The synergistic effect of Cu^{2+} ions was investigated. At higher concentrations of Cu^{2+} ions, decrease in inhibition efficiency was reported in this study. And at very low concentrations (0.01 mM) of Cu^{2+} ions, the inhibition efficiency did not change, which may be due to the adsorbed layer formation by amino acid itself. Similarly, Zhang et al [68] examined the corrosion inhibition property of Serine, threonine and glutamic acid against copper corrosion. Glutamic acid showed higher inhibition potential due to the presence of carboxylate ions.

General Characteristics of Green Inhibitors

Green inhibitors have properties that are similar to the 'non-green' inhibitors. Most of the green inhibitors adsorb on the metal surface by means of both physical and chemical adsorption at room temperature. At elevated temperatures, inhibition occurs mainly through chemisorption. On prolonged exposure of the green inhibitor towards the corrosive environment, inhibitor gains or losses its effectiveness during the process of corrosion inhibition. The evaluation of the effect of increased time on the inhibition efficiency lends information about the stability of inhibitive behavior of the green inhibitor on time scale. In most of the cases, the effectiveness of the inhibitor decreases upon increasing the time, which means that the adsorption of the inhibitor molecules on the metal surface occurs predominantly via physical interactions [10-16, 22, 23, 58-60, 67-81].

There are few reports that show an increase of inhibition efficiency of the green inhibitor on time scale. For example, investigations on the leaf extract of *Clematis gouriana* for acid corrosion of mild steel revealed that the inhibition efficiency increases on increasing the immersion time of the steel specimen in the acid solution containing 400 ppm concentration of the inhibitor [10]. This was attributed to the stability and persistence of the adsorbed inhibitor layer on the steel surface. Singh et al [81] has reported the trend of an increase of inhibition efficiency along with time, which was also observed for a synthetic natural product 2,3-dihydroxyflavanone [11].

It is important to consider the concentration of the inhibitor to achieve maximum efficiency. Though the compositions and sources are different for the inhibitors, with respect to the reaction conditions, the inhibition efficiencies of the plant extract of *Justicia gendarussa* [21] and Pennyroyal oil from *Mentha pulegium* [24] can be compared. 93% of inhibition efficiency was achieved for 150 ppm of *Justicia gendarussa* plant extract, whereas 2.76 g/L (approximately 2760 ppm) is needed to attain 80% of inhibition efficiency for Pennyroyal oil. In such a case, consideration of the effect of synergism is

valuable. For example, Oguzie [74] reported the synergistic effect of halide derivatives on inhibition of acid corrosion of mild steel by plant extracts. The synergistic effects of KCl, KBr and KI increased the inhibition potential of 10 (v/v) % of *Occimum viridis* from 69% to 87%, 88% and 95%, respectively. While comparing the green inhibitors with non-green inhibitors, the latter show better inhibition efficiency. For example, benzimidazole and triazole derivatives are well known corrosion inhibitors that showed more than 97% of inhibition against acid corrosion of mild steel [82, 83] but they are also known for their toxicity [84, 85, 86, 87].

Though the inhibitors of biological origin are presumably eco-friendly, it is highly preferable to be familiar with the EC50 (Effective Concentration 50) and LD50 (Lethal Dose 50) for the inhibitors with irrespective of their origins. These cytotoxicity experiments can give a solid evidence for the biocompatibility of the inhibitors.

An Overview on Selectivity of Green Inhibitors

A thorough examination of the available literatures revealed that a universal eco-friendly corrosion inhibitor that is applicable to most of the metals is yet to be discovered or invented. There are few reports that compare the efficacy of the inhibitors for different metals against various corrosive environments [69-73]. Rehan has investigated the water extracts of leaves of date palm, *phoenix dactylifera*, henna, *lawsonia inermis*, and corn, *zea mays* against the acidic and basic corrosion of steel, aluminium, copper and brass [69]. The results showed that the inhibition action was purely dependant on the metal type and the composition of solution. For example, 1% solutions of henna extracts showed no inhibition for aluminium in 0.2 M hydrochloric acid solutions; whereas 86% of inhibition was observed for the corrosion of steel. Meanwhile, 96% inhibition of corrosion was observed against the alkaline corrosion of aluminium, which indicated that the inhibition efficacy of an inhibitor is greatly affected not only by the type of metal but also by the corrosive medium.

El-Etre et al reported the versatility of lawsonia extract for acidic, neutral and alkaline corrosion of C-steel, nickel and zinc [70]. For C-steel and nickel better inhibition was observed in acid solutions with the inhibitor. On the other hand, lawsonia extract potentially inhibited the corrosion of zinc in neutral solutions.

Conclusions

Generally green inhibitors are excellent inhibitors under a variety of corrosive environments for most of the metals. The non-toxicity and biodegradability are the major advantages for these inhibitors. However, they do have performance boundaries. Although a number of publications are witnessing the green inhibitors as a potential candidate against corrosion at different environments, further research efforts are needed to employ the green inhibitors widely at an industrial level.

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