The Efficacy of Plant Inhibitors as Used against Structural Mild Steel Corrosion: A Review

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Abstract

MS acceptability for nowadays structural construction is premised on its availability and low cost. However, due to MS poor corrosion resistance, most especially in acidic and alkaline environments, there have been increasing concerns about its use. The use of inhibitors, as proposed by different researchers, mitigates MS CR, thus reducing the economic losses experienced by all chief users of this alloy. In recent years, scientists have focused on green inhibitors obtained from plant, fruit and vegetable extracts, and essential oils. Besides being environmentally friendly, in terms of corrosion resistance, plant extracts are becoming increasingly important, due to their low cost and toxicity, and high availability. Additionally, they are rich in organic compounds with polar atoms, such as O, P, S and N, containing multiple bonds in their molecules, through which they can adsorb onto the metal surface, forming a protective film, by various adsorption isotherms. This paper provides a review on research works done so far on MS corrosion control by naturally occurring plant extracts as corrosion inhibitors, in both acidic and alkaline environments, where this alloy is mainly applied.

Keywords: plant extracts; CR; inhibition; MS; adsorption isotherms; environments.

Introduction•

Steel is an indispensable alloy of Fe and C, but does not exclude other elements [1]. CS is classified as MS (0.10 to 0.3% C), medium CS (0.3 to 0.6% C) and high CS (0.6% to 1.7% C) [2]. Although MS is the cheapest among the steel grades, and it is mostly used for construction purposes, due to its availability and good mechanical properties, it is very susceptible to corrosion, especially when exposed to atmospheric

[•] The abbreviations list is in pages 387-388.

O in humid environments [3]. Other known options, which are readily available for metals protection against corrosion attack, include painting, anodic/cathodic protection and electroplating [4-13]. However, the use of inhibitors has gained general acceptance as one of the most efficient means of corrosion protection [5,14, 15]. Due to MS high susceptibility to dissolution, many researches have been done using different plant extracts to investigate the corrosion behaviour of this material in various media, such as HCl, H₂SO₄, NaCl and NaOH [16-21], among others. A corrosion inhibitor is an organic or inorganic chemical substance, which can have an anodic, cathodic or mixed behaviour, by adsorbing itself onto a dissolving metal surface, when added to an aggressive medium, thereby controlling and reducing CR [19, 22-30]. Most inorganic inhibitors are harmful to the environment, due to the presence of heavy metals. This has increased the search for green corrosion inhibitors that can be biodegradable, eco-friendly, cheap, easy to find and renewable, without containing heavy metals [6, 7, 16, 17, 31-44].

All metals are widely used in human activities, but MS is the most used among them [45, 46]. It is applied to a high degree in food, oil, chemical, energy and fabrication industries, due to its excellent mechanical properties. Therefore, MS is accorded the highest preference in all solutions to metals corrosion problems. Since the high costs associated with replacing rusted metals due to their dissolution can be reduced through the use of corrosion inhibitors [47, 48], a periodic review of related research done in this field, mostly targeting MS, is always required. This justifies and emphasizes the need for this review, on which premise it is based.

Metallic corrosion

Corrosion is a reversible process that converts pure metal into its oxides, hydroxides and so on [49]. At the present time, corrosion is viewed as a costly science and engineering materials problem. Metallic corrosion has been a great concern, since the first use of common metals [50]. As stated by Bardal E. [51], the cost caused by corrosion damage in industrialized countries is about 34% of the total GDP. Third world countries spend 10 times more than the above estimate in their fight against corrosion. In order to give credibility to this claim, a survey was conducted in 2003, in the United States, which is the most technologically advanced country in the world, for investigating corrosion costs. As a result, it was found that the United States spent about 13 times (about \$41.9 billion) the total productivity of Nigeria in fighting this menace. Corrosion costs are mostly related to equipment, structures and attempts to embellish structures. Partly due to direct replacement and maintenance costs, there are associated losses due to plant interruptions, and additional expenditures related to the use of expensive products and other protection precautions [52]. Besides causing economic losses, corrosion also shortens structural steel life span, thus posing a safety problem to humans, who continuously use these products [49, 52].

Fig. 1 shows that metallic corrosion can be divided into three broad groups, as stated by [51]. Its morphological categorization [50] is general corrosion. Under this class

are uniform, quasi-, non-uniform and galvanic corrosion. Localized corrosion involves crevice, pitting and filiform corrosion types. Then, there is microbiological corrosion. Metallurgically influenced corrosion includes sensitization, exfoliation, intergranular corrosion and dealloying. Environmentally induced cracking examples are high-temperature H attack, damage and induced cracking, hot-cracking, stresscorrosion, hydride formation, embrittlement, and solid and liquid metal-induced embrittlement. Mechanically assisted wear comprehends erosion, wear and fatigue corrosion.

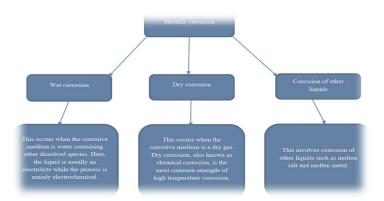


Figure 1. Forms of metallic corrosion.

Anticorrosion measures

Corrosion prevention aims to eliminate or reduce the effects of one or more of the conditions that may cause corrosion, through the following means (Fig. 2) [51]:

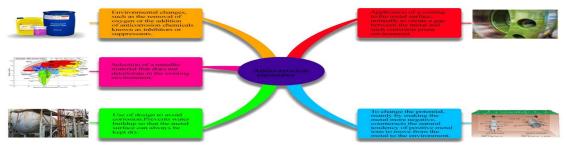


Figure 2. Anticorrosion measures.

Corrosion inhibition

Generally, any process that can cause corrosion delay is seen as inhibition. Corrosion prevention with inhibitors is achieved by adding a compound that suppresses metal oxidation. The chemical inhibitors added to the system can be in the form of liquids and/or vapors [50].

Plant extracts as MS corrosion inhibitors

Table 1 a and b show recent studies, by various authors, on the structural MS corrosion inhibition by plant extracts.

	Plant	Corrosive medium	Technique(s) used	IE _{max} (%)	Adsorption isotherm	Ref.
$\begin{array}{c} Azatmentia nataca \\ and HNO, \\ Cryptocarry anigra HCI \\ PDP, EIS, SEM, EDX, \\ 91.05 \\ Fr, L and T \\ 571 \\ \hline Molasses \\ HCI \\ PDP, EIS, SEM, EDX, \\ 90 \\ - \\ 1851 \\ \hline Mnalesses \\ HCI \\ PDP, DEIS and GM \\ 90 \\ - \\ 1851 \\ \hline Mnalesses \\ HCI \\ PDP, DEIS and GM \\ 90 \\ - \\ 1851 \\ \hline Mnalesses \\ HCI \\ PDP, WL EIS, PT-R, \\ 88 \\ L \\ 199 \\ \hline Licathyna \\ HCI \\ WL, PDP and EIS \\ 88 \\ L \\ 199 \\ \hline Licathyna \\ HCI \\ WL, EIS, PDP, GC-MS, \\ 90 \\ - \\ 162 \\ \hline Casto seed \\ HCI \\ WL, EIS, EDX, and SEM \\ 91.2 \\ L \\ 162 \\ \hline Casto seed \\ HCI \\ WL, EIS, EDX, GC-MS, \\ 90 \\ - \\ 162 \\ \hline Rescherghold \\ HCI \\ WL, EIS, EDX, and SEM \\ 91.2 \\ L \\ 162 \\ \hline Rescherghold \\ HCI \\ WL, EIS, EDX and SEM \\ 90.79 \\ L \\ 1651 \\ \hline Rescherghold \\ HCI \\ WL, EIS, EDX and SEM \\ 90.79 \\ L \\ 1651 \\ \hline Rescherghold \\ HCI \\ WL, EIS, EDX and SEM \\ 90.79 \\ L \\ 1651 \\ \hline Rescherghold \\ HCI \\ WL, EIS, EDX and SEM \\ 90.79 \\ L \\ 1651 \\ \hline Rescherghold \\ HCI \\ WL, EIS, PDP, GC-MS, \\ 90.79 \\ L \\ 1651 \\ \hline Rescherghold \\ HCI \\ WL, EIS, PDP, GC-MS, \\ 90.79 \\ L \\ 1651 \\ \hline Rescherghold \\ HCI \\ WL, EIS, PDP, RM and ANS \\ 90.79 \\ L \\ 1651 \\ \hline Rescherghold \\ HCI \\ WL, GM, ACI and SEM \\ 94.2 \\ - \\ 1711 \\ Rescherghold \\ HCI \\ WL, ACI, PDP \\ and GM \\ 98.8 \\ - \\ 1711 \\ Rescherghold \\ HCI \\ WL and SEM \\ 94.2 \\ - \\ 1711 \\ Rescherghold \\ HCI \\ WL and PDP \\ 95.71 \\ - \\ 1712 \\ Rescherghold \\ HCI \\ WL and PDP \\ 95.71 \\ - \\ 1712 \\ Rescherghold \\ HCI \\ WL and PDP \\ 93.71 \\ - \\ 1712 \\ Rescherghold \\ HCI \\ WL and PDP \\ 93.71 \\ - \\ 1711 \\ Rescherghold \\ HCI \\ WL and PDP \\ 93.71 \\ - \\ 1712 \\ Rescherghold \\ HCI \\ WL and PDP \\ 93.71 \\ - \\ 1712 \\ Rescherghold \\ HCI \\ WL and PDP \\ 93.71 \\ - \\ 1712 \\ Rescherghold \\ HCI \\ WL and PDP \\ 93.71 \\ - \\ 1712 \\ Rescherghold \\ HCI \\ WL and PDP \\ 93.71 \\ - \\ 1712 \\ Rescherghold \\ HCI \\ WL and PDP \\ 93.71 \\ - \\ 1712 \\ Rescherghold \\ HCI \\ WL and PDP \\ 93.71 \\ - \\ 1712 \\ Rescherghold \\ HCI \\ WL and PDP \\ 93.71 \\ - \\ 1712 \\ Rescherghold \\ HCI \\ WL and PDP \\ 93.71 \\ - \\ 1712 \\ Rescherghold \\ HCI \\ WL and PDP \\ 93.71 \\ - \\ 1712 \\ Rescherghold \\ HCI \\ WL \\ 96. \\ 171$	Citrus aurantium		WL and SEM	89	L	[18]
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Molasses HCI PDP, DEIS and GM 90 - 581 Timme HCI PDP, WL, EIS, FT-IR, 88 L 1601 Castor seed HCI WL PDP, WL, EIS, FT-IR, 88 L 1601 Perioloham hexapetalum HCI WL, EIS, SDA, SMA, SDA, SDA, SDA, SDA, SDA, SDA, SDA, SD	Cryptocarya nigra	HCl	PDP, EIS, SEM, EDX,	91.05	Fr, L and T	[56]
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	Ficus hispida	HCl		90	L	[63]
Rosemarius officialis I. HCl WL, PDP 98.33 - fef6 Euphorbia heterophylia I. HCl WL, GM, ACI and SEM 84.6 L, Fr, F-H, EI-A, F and [67] Murraya koenigi HCl EIS, PDP, FTIR, AFM and MDS 98.8 - [69] Pherocarpus sovuci HCl WL 96.48 T and F [70] Pherocarpus sovuci HCl WL 96.48 T and F [70] Jaglans regia NaCl PDP, EIS, FRIR, SEM and EDX 94.2 - [72] Brooknikulan pinnatam HCl WL and SEM 94.27 L [73] Poncicana publicherini and HCl WL and PDP 96.94 - [75] Cassia occidentalis HCl WL and PDP 93.71 - [76] Splanthes alignosa HCl WL and PDP, SEM, FTIR 94.3 - [76] Splanthes alignosa HCl WL 98.3 L [78] Alcorpio turkiale HSO4 WL, PDP, FTIR and UV-Vis 90 <t< td=""><td></td><td></td><td></td><td></td><td>L and T</td><td></td></t<>					L and T	
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		HCl	WL and PDP	93.71	-	[75]
	Imperrata cylindrica	H_2SO_4	WL	76	-	[23]
				94.3	-	[76]
	Spilanthes uliginosa	HCl	WL, PDP, FTIR and UV-Vis	90	-	[77]
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						[107]
<u>Gnetum africana</u> HCl WL and FTIR 92.42 L and T [13]					2	
	Gnetum africana	HCl	WL and FTIR	92.42	L and T	[13]

Table 1a. Plant extracts as MS corrosion inhibitors in various electrochemical media.

Spirulina platensis	HCl and H ₂ SO ₄	WL, PDP, EIS and SEM	74.15, 82.65	Т	[32]
Myristica fragrans	H ₂ SO ₄	WL, EIS, SEM, UV-Vis,	87.81	L	[8]
Olea europaea l.	H ₂ SO ₄	PDP, EIS, SEM and FTIR	99	Т	[40]
Thapsia villosa	H_2SO_4	WL, PDP and EIS	74.09	L, T and F	[108]
Zenthoxylum alatum	HCl	WL, EIS, SEM, XPS, FT-IR and GC-MS	91	L	[109]
Mollugo cerviana	HCl	PDP, EIS, WL and SEM	96.95	L	[110]
Thymus vulgar l.	NaCl	WL and PDP	80.49	Т	[111]
Lawsonia inermis	HCl	PDP, SEM and EDX	92.06	L	[112]
Nauclea latifolia	H ₂ SO ₄	WL and GM	94.26	El-A	[113]
Stylosanthes gracilis	H ₂ SO ₄	WL and PDP	94.23	-	[114]
Wormin mebendazole	H2SO4	PDP and SEM	99.53	L	[115]

Table 1b. Plant extracts as MS corrosion inhibitors in various electrochemical media.

Adsorption isotherms- El-A: El-Awary; F: Freundlich; F-H: Flory-Huggins; Fr: Frumkin; L: Langmuir; T: Temkin

Green corrosion inhibitors adsorption onto a metal surface is controlled by many factors, such as metal type, test medium, inhibitor chemical structure, type of substituents and additives that it contains, solution temperature and concentration [53, 54]. Some leaf extracts have been used as effective inhibitors against MS corrosion, in various electrochemical media.

Leaf extracts as corrosion inhibitors in selected weak acids

Researchers have added some plant extracts to weak acids, such as H₃O₄P, HCO₂H, CH₃COOH and HCOOH, as corrosion media. Some of the applied techniques are herein presented as pertaining to MS. Ameer and Fekry [116] studied *Thymo* inhibition property against MS corrosion in a H₃PO₄ solution, using different electrochemical techniques, such as PDP and EIS measurements. It was confirmed that higher Thymo concentrations increased its IE(%) against MS corrosion. The obtained PDP and EIS results were in good agreement with each other, while the surface inspection was done by SEM. Chaudhari and Vashi [117] studied Lawsonia inermis leaf extract, as a green inhibitor against structural MS corrosion in a CH₃COOH solution, by WL, ACI and PDP methods. The investigation indicated that, with higher acid concentrations, CR increased. However, corrosion IE(%) was also found to increase with higher extract concentrations, and the results obeyed Langmuir's adsorption isotherm. Psidium guajava leaf extract was investigated, by Noyel et al., as a green inhibitor against MS corrosion in a H₃PO₄ solution [118], using WL, ACI and PDP techniques. In that study, it was observed that IE(%) increased with higher inhibitor concentrations. The results obeyed Langmuir's and Temkin's adsorption isotherms. PDP results indicated that the extract reacted as a mixed-type corrosion inhibitor. The obtained $IE_{max}(\%)$ was 89%, while SEM and FTIR analysis were also conducted for the surface examination. The study of Dendrocalamus brandisii leaf extract IE(%), against MS corrosion in a Cl₃CCOOH solution, was carried out by Xianghong et al. [119], using WL, EIS and AFM. The compounds adsorption mode followed Langmuir's isotherm. The results proved that the plant extract was a good corrosion inhibitor, since IE_{max} (%) was 97.2%. Singh and Gupta [120] have studied structural MS corrosion with various HCOOH concentrations, using WL and electrochemical techniques. It was found that MS CR was a function of the acid concentrations and of temperature. Maximum CR was observed in a 20% HCOOH solution, with both techniques. The anodic polarization curve showed MS active corrosion over the entire potential range, at any concentrations and temperatures. Cathodic polarization curves were almost the same and did not depend on the HCOOH solution concentration.

Active compounds present in green inhibitors for structural MS corrosion

Plant extracts have the prospects of filling the role of inorganic and synthetic organic inhibitors, due to their proven track record in the literature. Since the plant extracts mechanism of action relies on their active ingredients structure, many researchers have devised several theories to illustrate this phenomenon [54, 121]. The plant extracts IE(%) is due to their phytochemical constituents [49], which contain some heteroatoms, such as N, O, and S compounds [122]. For instance, Glycyrrhiza glabra phytochemical analysis showed that its main constituents are glycyrrhizin, flavonoids, liquiritigenin, isoflavonoids, glabridin and licochalcone [123]. Nypa fruticans wurmb leaf extract contains phenols and flavonoids [74]. The chemical ingredients found, via GC-MS, in Ficus hispida leaf extract, in varying percentages, are stigmasterol, 2-(benzyloxyme thyl)-5-methylfuran, 5-(hydroxylmethyl)-2-furan car-boxaldehyde, 2,3-dihydro-3,5-dihydroxy-6-methyl-pyran-4-one, neophytadiene, phytol, palmitic acid, sitosterols and ethyl linoleate [63]. The methanolic phytochemical examination of Pterolobium hexapetalum and Celosia argentea plants extracts showed the presence of flavonoids, tannins and phenolic compounds. Steroids, antraquinones and triterpenes were found only in Pterolobium hexapetalum extract, and saponins and amino acids were detected in Celosia argentea extract [62]. These plants inhibitors are all capable of reducing or even blocking structural MS corrosion [49].

Conclusion and future outlook

Following the examined previous literature, it was concluded that plants extracts are right choice candidates to replace the already known conventional, expensive and highly toxic inorganic and synthetic organic corrosion inhibitors. Therefore, this article has proved that the use of such green inhibitors is the only way to find a safer and more environmentally friendly protection against metallic corrosion, which has a huge impact on the worldwide economy. In fact, plant extracts have numerous phytochemical constituents that are capable to easily be adsorbed onto metals, and thus inhibit their corrosion. This paper has pinpointed and summarized the types of corrosion, different plant extracts and techniques used for combating corrosion in practical terms, in the industries where structural MS is applied in acidic (H₂SO₄, HCl, HNO₃, CH₃COOH, HCOOH, HCO₂H and H₃PO₄), basic (NaOH) and neutral (NaCl, and Na₂SO₄) media. It also was concluded that most of the reviewed studies focused more on strong acidic media, such HCl and H₂SO₄, than on other weak acidic environments, like CH₃COOH, HCOOH, HCO₂H and H₃PO₄, while there were less studies on basic (NaOH) and neutral (NaCl and Na₂SO₄) media. Hence, it is encouraged that more studies soon be done, using basic, neutral and week acidic media.

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Conflict of interest

The authors declare that there are no conflicts of interest.

Authors' contributions

Uzoma Samuel Nwigwe: gave minor contributions to the conception and design of the analysis; collected the data; contributed with data or analysis tools; performed the analysis of the outcomes; wrote the paper as the lead author; proofread the work. **Chukwuka Ikechukwu Nwoye**: gave substantial contributions to the conception/technical guidance of the analysis; contributed with data or analysis tools, providing intellectual support; helped with the data analysis and interpretation; proofread the manuscript, made editions where necessary, and gave the final approval of the version to be published.

Abbreviations

AAS: atomic absorption spectroscopy **ACI**: AC impedance AFM: atomic force microscope ATR: attenuated total reflection spectroscopy CH₃COOH: acetic acid Cl₃CCOOH: trichloroacetic acid **CR**: corrosion rate CS: carbon steel **DEIS**: dynamic electrochemical impedance spectroscopy **DFT**: density functional theory **EDX**: energy-dispersive X-ray spectroscopy **EIS**: electrochemical impedance spectroscope FTIR: Fourier-transform infrared spectroscope **GC-MS**: gas chromatography mass spectrometry **GDP**: gross domestic product **GM**: gasometry H₂SO₄: sulfuric acid H₃PO₄: phosphoric acid HCI: hvdrochloric acid HCO₂H: methanoic acid HCOOH: formic acid HE: hydrogen evolution HNO₃: nitric acid **IE**_{max}(%): maximum inhibition efficiency **LC-MS**: liquid chromatography-mass spectrometry **MDS**: molecular dynamics simulation MS: mild steel Na₂SO₄: sodium sulfate NaCl: sodium chloride NaOH: sodium hydroxide **OPM**: optical microscopy **PDP**: potentiodynamic polarization

SEM: scanning electron microscopy

UV-vis: ultraviolet-visible spectroscope or ultraviolet-visible spectrophotometry WL: weight loss

XPS: X-ray photoelectron spectroscopy

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