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NATURAL PRODUCTS AS CORROSION INHIBITORS - A REVIEW

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ABSTRACT

The corrosion of metals and alloys are controlled by inhibitors. Instead of toxic organic inhibitors, recently environmental friendly inhibitors have attracted several researchers. Natural products are non-toxic, biodegradable and readily available renewable sources. They have been widely used as inhibitors. Investigation of corrosion inhibition potential by natural products are particularly interesting because they are non-expensive, ecologically friendly, acceptable and possess no threat to the environment. Most of the earlier studies on inhibition of corrosion of metals in different media have been related to the performance of organic compounds containing Nitrogen, Oxygen and Sulphur groups. This article provides a wide data of green inhibitors which are used as corrosion inhibitors for different metals and alloys in aggressive media.

KEYWORDS: Natural products, Green inhibitors, Mild steel, Corrosion, Inhibition.

INTRODUCTION

Decomposition or corrosion is a spontaneous and thermodynamically encouraging process. There are many methods used to control corrosion process. Use of some organic inhibitors, such as phosphates, chromates have been prohibited because of they create hazards to the atmosphere. Hence there is an attempt to make use of environmental friendly, non-toxic/less toxic, extracts of naturally occurring plant materials as corrosion inhibitors. Plant extracts contain a wide variety of organic compounds. Most of them contain hetero atoms such as P, N, S, O. These atoms coordinate with the corroding metal atom (their ions), through their electrons. Adsorption of inhibitor molecules on metal surface, shielding films are formed on the metal exterior and hence corrosion is banned. A variety of extracts of plant materials have been used to prevent a variety of metals immersed in different medium at various

temperatures in presence and absence of many additives.[1-33] Many methods have been employed (such as weight loss method, electrochemical studies and gasometric techniques etc.,) to estimate corrosion inhibition efficiencies of inhibitors. The adsorption and protective film formation have been analyzed by various surface morphology techniques (such as FT-IR, UV-Visible, SEM and AFM etc.).

1.0 Metals: Extracts of natural products have been used to prevent corrosion of various metals and alloys such as mild steel,[1,2,5,6,7,8,9,14,17,23,24,25,32] stainless steel,[15] carbon steel,[4,11,13,16,19,20,26] copper,[22] zinc,[30] aluminium[3,10,12,] and concrete steel rebar.[18,21,29]

2.0 Plant materials: Extracts of various parts of the plant have been used as corrosion inhibitors. Peels,[9,15] leaves,[6,13,17,18,21,23,32] roots[17] and seeds,[3,12,24] stem,[4,17] oil[10,11,14] have been used as corrosion inhibitors.

3.0 Medium: The inhibition study have been done to prevent corrosion of metals and alloys immersed in various medium such as acidic medium,[1,2,4,5,6,7,8,12,13,14,16,17,19,20, 22,23,24,25,26,32] basic medium,[3] Neutral medium, [5,29] NaCl[9,11,18,21,30] and in Na_2CO_3.[10]

4.0 Synergistic effect: Additives mixture of inhibitors shows better inhibition efficiency than individual members. This is called Synergistic effect. For this purpose many additives have been used to improve the inhibition efficiency of plant extracts. For this purpose Methylene dichloride and n-butanolic extract,[16] Sodium dichromate[18] is added.

5.0 Methods: To evaluate the corrosion inhibition efficiency of inhibitor, several methods such as Weight loss method,[2,3,4,5,6,7,8,9,10,11,12,13,14,16,17,19,23,32] Electrochemical studies (such as polarization,[1,2,3,4,5,6,7,8,9,10,11,13,14,15,16,17,18,19,20,21,22,23,24,25,26,30,32] AC impedance spectra,[1,2,3,4,5,6,7,8,9,10,11,13,14,16,17,18,19,20,22,23,24,25,26,30,32]) Gasometric method[17,32] and Hydrogen permeation method[1] have been employed.

6.0 Surface morphology of protective film: The protective films formed on metal surfaces have been analyzed by various surface analysis techniques such as FT-IR spectroscopy,[5,12,19] UV-Visible spectroscopy,[5] Raman Spectroscopy,[5,20] X-ray diffraction,[5,11] Energy dispersive X-ray spectroscopy,[5,11] SEM,[1,5,8,11,12,13,16,19,20,27] FESEM,[2] GC-MS,[9] POM analyses,[14] ANOVA test[23] and XPS.[26]

7.0 Adsorption isotherm: The protective layer formed on the metal surface by adsorption of active compounds of different plant extracts on the metal surface. The adsorption isotherms are such as Freundlich adsorption isotherms,[16] Temkin adsorption isotherm,[22,25] Langmuir adsorption isotherm[1,2,6,7,8,9,10,12,19,20,21] and Frumkin adsorption isotherm.[7]

8.0 Thermodynamic parameters: From the adsorption isotherms various thermodynamic parameters such as changes in free energy,[3,5,9,10,14,16,20,22,23] entropy,[5,9,10,14,16,22] enthalpy,[5,9,10,14,16,22] equillibrium constant,[20] heat of adsorption[20] and activation energy[3,6,9,10,13,14,16,20,22] have been calculated.

9.0 Advantages and Drawbacks: Natural product extracts are eco-friendly, non-toxic, low cost and easily bio-degradable. But those are simply infected by microbes. The putrefaction of plant extracts can be barred by adding up of biocides such as sodium dodecyl sulphate and N-acetyl-N,N,N-trimethyl ammonium bromide.[34-44]

10.0 View of plant scientists: If plant materials are used as corrosion inhibitors, the various plants will be slowly extinct.

A list of plant materials that have been used as corrosion inhibitors is given in Table 1.

Table 1: Plant materials as corrosion inhibitors.

S. No	Metal Used	Medium	Inhibitor + Plant Name	Methods Used	Findings	Ref. No.
1.	Mild Steel	HCl	Adathoda vasica, Eclipta alba and Centella asiatica	Polarization method, Impedance method, Scanning Electron Microscopy, Hydrogen permeation method	Mixed type inhibitor, obeys Langmuir adsorption isotherm. Increasing inhibition efficiency in the order: Eclipta alba > Adathoda vasica > Centella asiatica.	1
2.	Mild Steel	HCl	Hexane extract of Alpinia galanga rhizome, 1'-acetochavicol acetate	Weight loss, Electrochemical and Quantum chemical methods, FESEM	Mixed type inhibitor. The highest inhibition efficiency of 90.2% was achieved for crude hexane extract while 84.6% was obtained for 1'-acetochavicol acetate. Obeys Langmuir adsorption isotherm.	2
3.	Aluminium	1 M NaOH	Piper longum seed extracts	Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) methods, and weight loss measurements	Mixed Inhibitor. Activation energy and free energy of adsorption were calculated.	3
4.	Carbon Steel	HCl	Stem of Mangifera indica L.	Weight loss test, electrochemical techniques	Mangiferin shows inhibitory action on the corrosion process.	4
5.	Mild Steel	1 M HCl	Tragia plukenetii extract	Weight loss calculation, electrochemical impedance spectroscopy, and Tafel polarization, UV-Visible, FT-IR, Raman spectroscopy, and	Good mixed-type inhibitor, maximum corrosion inhibition efficiency was found to be 88 % at 500 ppm, change in enthalpy, entropy, and free energy, Decreased dissolution of Fe in the presence of	5

				Wide-angle X-ray diffraction studies, Scanning electron microscopy and energy-dispersive X-ray spectroscopy	the plant extract, Surface analysis.	
6.	Mild Steel	1 M HCl	Chrysophyllum albidum leaves extract	Weight loss, Potentiodynamic polarization and Electrochemical impedance techniques at 303 K	The effect of immersion time and temperature, Inhibition was found to decrease with increasing time and temperature, Mixed type inhibitor, Follow Langmuir adsorption isotherm, Adsorption process is exothermic.	6
7.	Mild Steel	1.0 N H_2SO_4, 1.0 N HCl	Ethanol extracts of Acacia Nilotica	Weight loss method and Polarization techniques between 303 K and 333K,	The corrosion rate enhanced with increase in temperature and minimized with increase in concentration of inhibitor, Obeys Langmuir and Frumkin adsorption isotherms, Mixed Inhibitor.	7
8.	Mild Steel	1.0 M HCl	Kimbiolongo extract	Gravimetric, Potentiodynamic polarization measurements and Electrochemical impedance spectroscopy, (EIS)	Inhibition efficiency increases with concentration and maximum value was obtained at 100 ppm concentration, Obeys Langmuir adsorption isotherm.	8
9.	Mild Steel	1.5 M NaCl	Theobroma cacao peels extract	Weight loss, Potentiodynamic polarization (Tafel) and Electrochemical impedance spectroscopy (EIS) methods. Infrared spectra and GC-MS, SEM-EDX	Gibbs energy (ΔG), enthalpy (ΔH), entropy (ΔS) and activation energy (E_a) were calculated to elaborate the mechanism of corrosion inhibition, Obeys Langmuir isotherm. Corrosion inhibition efficiency of 91.93 (weight loss) and 85.90% (Tafel), 90.19% (Rp) and 75.23% (EIS) were at a concentration of 2.5% extract.	9
10.	Aluminium	Na_2CO_3	Eugenol oil	Weight loss and Electrochemical techniques	Thermodynamic, kinetic parameters was calculated, Obeys Langmuir adsorption isotherm.	10
11.	Low Carbon Steel	In distilled water and 3.5% NaCl	Palm oil and Corn oil	Immersion and electrochemical tests, Scanning Electron Microscopy, Energy Dispersive Spectroscopy and X-Ray diffractometer	Corn oil inhibitor in distilled water shows the highest inhibition efficiency. Its inhibition efficiency is 93.9%, which is slightly higher than palm oil (91.5%) in similar environment.	11
12.	Aluminum	0.5 N HCl	Ethanol extracts of psidium guajava seeds	Conventional weight loss, FTIR spectroscopy and SEM analysis techniques	Inhibition mechanism was by adsorption process, Inhibition efficiency decreased with the temperature rise, Langmuir model was found to be the best fit.	12
13.	C-steel	1.0 M HCl	Leaf extract of Khaya senegalensis (Mahogany)	Weight loss measurements, Scanning electronic microscope, Polarization curves and Electrochemical impedance spectroscopy	Mixed-sort inhibitor with a major cathodic effectiveness, Activation parameters were calculated.	13
14.	Mild Steel	1.0 M HCl	Pelargonium extract and oil	Weight loss, Electrochemical Impedance spectroscopy (EIS) and Tafel polarization curves, POM analyses	The effect of temperature on the corrosion behavior, Thermodynamic parameters were determined, Essential oil and extract of Pelargonium behave as mixed type inhibitors in HCl.	14
15.	st37 steel	Geothermal fluid	Quercus robur and pomegranate peels	Tafel polarization method	250 ppm of Quercus robur oak extract was seen to have 90%	15

			extracts		corrosion inhibition efficiency, increasing pH level more than 5 indicates that corrosion constructive aggressive ions (H+) decrease, decrease of conductivity values as a result of the decrease of inhibitor concentration shows that corrosion slows down, Ryznar and Langelier Indexes are calculated for AF11 well, reinjection and collected pools.	
16.	carbon steel	HCl	Methylene dichloride and Butanolic extracts of Reutera lutea (Desf.) Maire (Apiaceae)	Weight loss and Potentiodynamic polarization measurements, Electrochemical Impedance spectroscopy, and Scanning electron microscopy techniques	The effect of temperature on the corrosion behavior of CS, The extracts behaved as mixed-type corrosion inhibitors Obeys Freundlich isotherm. The free energies, enthalpies, and entropies for the adsorption process and the apparent energies, enthalpies, and entropies of the dissolution process are explained	16
17.	Mild Steel	H_2SO_4	Ethanol extracts of leaves (LV), stems (ST) and roots (RT) of Rotula aquatica plant.	Weight loss, Gasometric techniques, Electrochemical polarizations and Electrochemical impedance spectroscopy.	Inhibition efficiencies of the extracts follows the trend RT > LV > ST, Mixed type corrosion inhibitors.	17
18.	Concrete steel-rebar	3.5% NaCl medium (Saline/ marine simulating-environment)	Solanum aethiopicum leaf-extract and sodium-dichromate effects	Electrochemical test-measurements	0.083% sodium-dichromate admixture outperformed the 0.083% Solanum aethiopicum leaf-extract in corrosion-inhibition effectiveness, The 0.25% Solanum aethiopicum leaf-extract exhibited optimal performance, $\eta = 98.28\%$.	18
19.	Carbon Steel	1 M HCl	Opuntia ficus-indica extract	Weight loss tests, potentiodynamic polarization curves, and electrochemical impedance spectroscopy measurements, scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR) analysis	Inhibitor acted as a cathodic-type inhibitor, Follows the Langmuir adsorption isotherm, indicating monolayer adsorption, The presence of hetero atoms such as C, N, and O and OH groups were responsible for the corrosion inhibition.	19
20.	Q235 carbon steels	1 M HCl	Capsella bursa-pastoris extracts	Electrochemical methods, Environmental scanning electron microscopy (SEM) and Raman microscopy analysis.	CBE serves as an effective, mixed-type inhibitor, The highest inhibition efficiency can reach 97% when adding 60 mg·L- 1 CBE, Obeys the Langmuir adsorption isotherm, Thermodynamic and kinetic parameters for the adsorption process are calculated, Formation of a CBE inhibition film on the metal surface.	20
21.	Concrete Steel rebar	3.5% NaCl, for simulating saline/ marine environment.	Morinda lucida leaf extract	Corrosion potential as per ASTM C876-95 R99, corrosion current by zero resistance ammeter and corrosion rate from linear polarization resistance instrument, Electrochemical noise resistance	Electrochemical test data showed that excellent correlation, of R = 98.07%, Nash-Sutcliffe Efficiency = 96.18% and ANOVA p-value = 0.0456, exists between the corrosion rate as a function of the plant extract concentration and the noise resistance, 3.333 g/L Morinda lucida exhibited optimal inhibition efficiency, $\eta = 90.59 \pm 2.52$, Obeys Langmuir isotherm.	21

22.	Copper	0.1 M HCl	Egyptian licorice extract	DC polarization, AC impedance techniques	Obeys Temkin isotherm, Mixed-type inhibitor. The values of activation energy for copper corrosion and various thermodynamic parameters were calculated.	22
23.	Mild Steel	0.5 M HCl and 0.8 M H_2SO_4	Camellia Sinensis (green tea) extract	Weight loss/corrosion rate and potential measurement techniques, ANOVA test	In 0.5 M HCl, 100% green tea gave the optimal performance with weight loss and corrosion rate of 246mg and 0.63 mm/yr , 0.8 M H_2SO_4 where 100% green tea gave the best results of 1226 mg weight loss and 3 mm/yr corrosion rate. Gibb's free adsorption energy signified physisorption in HCl and chemisorption in H_2SO_4.	23
24.	Mild Steel	HCl	Aqueous extract of seeds of Nigella sativa	Different electrochemical techniques	Nigella sativa offers a good protection and its efficiency increases with the concentration.	24
25.	Steel	1 M HCl	Mentha pulegium extract (MPE)	Potentiodynamic polarisation and electrochemical impedance spectroscopy	The inhibition efficiency of MPE, reached 88% at 33%, extract acted as a mixed inhibitor, Obeys Temkin isotherm.	25
26.	C38 steel	1 M HCl	Aniba rosaeodora alkaloidic extract	Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques, XPS	To determine the parameter of CPE (α, Q), Total alkaloids extract shows that it contains the anibine as the major alkaloid, Formation of inhibitor layer containing the Aniba rosaeodora alkaloidic extract and the anibine molecules.	26
27.	Tectona grandis based Fe-nanoparticle material		Tectona grandis (Teak)	(SEM+EDS)	Positive prospect on the suitability of Fe bio-nanoparticle for corrosion inhibition applications for the protection of metals against microbiological corrosion influencing environment.	27
28.	Various Metals	Different media	Plant extracts as green corrosion inhibitors	Gravimetric, Electrochemical and Surface Analysis Techniques	Type of inhibitors, Mechanism of corrosion, Thermodynamic, kinetic properties.	28
29.	Corrosion-Fatigue Fracture of Steels	Fresh Water	The oak-bark extract	Evaluation Methods	This enables to recommend the inhibitor based on the oak-bark extract not only for the retardation of corrosion processes but also for the inhibition of corrosion-fatigue fracture.	29
30.	Zinc	NaCl	Ethanol extract of Mansoa alliacea	Polarization and electrochemical impedance spectroscopy (EIS)	Mixed type inhibitor, To determine the parameter of CPE (α, Q).	30
31.	Steel	HCl, H_2SO_4	Plant Extracts	Evaluation Methods	Properties, Adsoption modes and Mechanisms of inhibition.	31
32	Mild Steel	H_2SO_4	Phyllanthus fraternus leaves extract	Conventional weight loss, Gasometric techniques, Electrochemical polarizations and Electrochemical impedance spectroscopy	Mixed Type Inhibitor.	32
33	Various metals and alloys	Different acid media	Natural products	Evaluation Methods	Properties, adsorption and inhibition mechanism and the efficiencies of natural products.	33

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