Green solution to corrosion problems – at a glance

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Abstract

Extracts of natural products are used as corrosion inhibitors since they are non toxic and environmentally friendly. Especially the extracts of leaves have attracted the attention of many researchers. Usually weight loss methods are adopted to measure the corrosion inhibition efficiencies. The mechanistic aspects have been investigated by electrochemical studies such as polarization study and AC impedance spectra. Sometimes noise measurement has also been used. The protective films formed on the metal surface have been analysed by surface analysis techniques such as SEM, EDAX, FTIR and AFM. Experiments have been carried out at various temperatures also. Various adsorption isotherms have been proposed. Of all the metals and alloys used, mild steel has been extensively used. The experiments have been carried out in acid medium and neutral medium (sodium chloride). The extracts of the leaves contain many ingredients which have polar groups such as N, O, S and P atoms. The lone pair of electrons present on these atoms are pumped on to the metal surface. This controls the corrosion process.

Key words: *green inhibitors, corrosion inhibition, electrochemical studies, isotherms, SEM, AFM.*

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1. Introduction

When materials come in contact with environment, they decay. This decaying process is termed as corrosion. Even though most of the materials such as ceramics and glass also decay, usually, the term corrosion is concerned with metals. Corrosion is the expression of desire of the metals to go back to their original state of ores. Corrosion is a natural process, spontaneous and thermodynamically stable process favoured by nature. So no one can prevent corrosion. However the rate of corrosion can be controlled, just like postponing death. There are many methods to control corrosion. Anyhow the use of inhibitors in small quantities is a common process. Once chromates were used as corrosion inhibitors effectively. Yet, environmental scientists point out the health hazards caused by chromium(VI) ions. Hence corrosion scientists go for environmentally friendly non-toxic natural products extracts as corrosion inhibitors.

Many active principles are present in the extracts of plant materials. Usually they contain electron rich polar atoms such as oxygen, nitrogen, sulphur and phosphorus. These lone pair of electrons is pumped on to the metal surfaces. This prevents the metallic corrosion, because, loss of electrons by metals is prevented, by the pumped electrons. The recent trends in the use of green inhibitors are presented in this section. Many parts of the plant materials such as, flowers, barks, seeds and leaves can be used as corrosion inhibitors. The use of extracts of leaves as corrosion inhibitors is discussed. Several research papers have been published in this regard [1–104].

2. Methods

For evaluation of corrosion inhibition efficiencies of the extracts, methods such as weight loss methods [21, 22, 28, 31, 33, 35, 41, 42, 90] have been employed.

3. Metals

The corrosion of various metals such as mild steel [2, 21, 22, 25, 26, 27, 28, 31, 32, 35, 36, 40, 41, 42, 47, 53, 90, 92], stainless steel [24, 28, 29, 81], aluminium [3, 38, 44, 87], copper [33, 59], zinc [37], steel-copper [33], pipeline steel API 5L X52 [34], AM60 magnesium alloy [100] has been controlled by the extracts of leaves.

4. Media

The inhibition efficiencies of metals in various media such as acidic [2, 3, 21, 22, 26, 27, 29, 31, 32, 34, 35, 36, 37, 38, 39, 42, 44, 47, 53, 81, 87, 90, 92], basic [88], neutral [25, 40, 41, 59, 100] and sea water [103] have been investigated.

5. Leaves

Leaves such as *Urtica dioica* leaves extract [2], almond (*Prunus amygdalus*) fruit leaves [3], *Xanthium strumarium* leaves [21], *Piper guineense* (uziza leaf) [22], Olive leaves [24], *Glycyrrhiza glabra* [26], extract of *ginkgo biloba* [28], extract of *Prunus persica* (*P. persica*) [29], *Murraya koenigii* (curry) leaves [32], *Ziziyphus* leaves [33], *Aloe vera L.* [35, 81], *Gongronema latifolium* [36], Areca palm leaves [38], *Chaenomeles sinensis* (*C. sinensis*) leaves [39], *Ficus carica* (*Fig tree*) leaves [40], Mangrove (*Rhizophora apiculata*) bark and leaf [42], *Urtica Dioica* leaves [43], *Murraya koenigii* leaves [44], *Bauhinia tomentosa* leaves extract [47], Schreabera swietenioids leaves [53], camellia sinensis [87], leaves of *Pistacia lentiscus* from Saidia Morocco [90], leaves of *Hibiscus sabdariffa* [92], have been used as corrosion inhibitors.

6. Mechanism of corrosion inhibition

Mechanism of corrosion inhibition has been established by electrochemical studies such as polarization study [24, 27, 29, 35, 41, 42, 44, 59, 90], AC impedance spectra [24, 25, 27, 29, 35, 38, 42, 44, 59, 81, 90] electrochemical noise method [81]. The extracts can act as anodic inhibitors [44], cathodic inhibitors [29] and mixed type of inhibitors [29, 34, 42, 53].

7. Surface analysis

The protective films formed on the metal surface have been analysed by FTIR [24, 25, 31, 47, 53] spectra, SEM [2, 24, 28, 31, 38, 47, 53, 59, 81], EDAX [25], X-ray [32] and AFM [2, 26, 38, 47].

8. Temperature

Experiments have been carried out at various temperatures [3, 44, 47] also.

9. Isotherms

The active principles of the extracts are adsorbed on the metal surface. The adsorption obeys Langmuir isotherm [37, 42, 44, 93], Freundlich isotherm [37, 93], Temkin [37], Frumkin [93], Florry–Huggins [93].

The outcomes of the study are summarized in Tables 1–5.

Table 1. The outcomes of the study

No.	Metal / Medium	Inhibitor / Additives	Methods	Findings	Ref.
1	Mild steel / acidic media	Parsley (*Petroselinum Sativum*) extract (PSL)	Weight loss, potentiodynamic polarization, impedance spectroscopy and SEM	PSL acts as a mixed type inhibitor. 92.39% inhibition efficiency (IE)	1
2	Mild steel corrosion in 1 M HCl solution	*Urtica dioica* leaves extract	EIS, polarization test, SEM, AFM and computational approaches	adsorption of green inhibitors on the steel substrate, the density functional theory calculations suggested the inhibitors adsorption via electronic donor–acceptor interactions. 92% IE	2
3	Aluminium corrosion in HCl acidic medium	Almond (*Prunus amygdalus*) fruit leaves extract as green inhibitor	Optimisation and modeling, effect of temperature, Response Surface	97.9% IE	3

No.	Metal / Medium	Inhibitor / Additives	Methods	Findings	Ref.
			Methodology (RSM)		
4	Steel in chloride solutions	Olive leaf extract	Polarization, EIS	80% IE for ethanol extracted inhibitor at 300 ppm	4
5	Aluminium corrosion in 1 M HCl	Orange seed extract	Weight loss measurement and phytochemical analysis, temperature study	38.37% IE. Orange seed extract is a good corrosion inhibitor	5
6	Steel corrosion	Silver nanoparticles (AgNPs) doped palm oil leaf	Linear polarization resistance (LPR), potentiodynamic polarisation, half-cell potential (HCP) and electrical resistivity	Maximum inhibition efficiency was recorded to be as much as 94.74%	6
7	Benzo-triazole uptake and removal in vegetated biofilter mesocosms planted with *Carex praegracilis*	1*H*-Benzotriazole is a persistent, recalcitrant trace organic contaminant commonly used as a corrosion inhibitor in airplane deicing processes, automobile liquids, and engine coolants.	Removal of 1*H*-benzotriazole from stormwater using bench-scale biofilter mesocosms planted with California native sedge, *Carex praegracilis*, over a series of three storm events and succeeding monitoring period.	This study suggests that vegetation may increase the operating lifespan of bioretention basins by enhancing the degradation of dissolved trace organic contaminants, thus increasing the sorption capacity of the geomedia.	
8	Mild steel	Zinc acetylacetonate	Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), UV-Vis analysis, thermal gravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS) techniques	Pigment showed mixed corrosion inhibition properties.	7
9	Mild steel in	*Elaeis guineensis*	Weight loss	EG leaves is a potential metal	8

No.	Metal / Medium	Inhibitor / Additives	Methods	Findings	Ref.
	hydrochloric acid	leaves extracts	measurement, Adsorption, SEM and EDX analyses	corrosion inhibitor in acidic condition	
10	Mild steel in sea water	*Azadirachta indica L.* extracts	Weight loss, electrochemical impedance spectroscopy (EIS), linear polarization and potentiodynamic polarization techniques	98% IE	9
11	E 24 steel in a neutral solution NaCl 3.5%	Methanolic extract	Scanning electron microscope (SEM) coupled with the EDS	Inhibitors act as a mixed type	10
12	Austenitic stainless steel (304SS corrosion in conc. HCl)	*Psidium guajava* leaves	Polarization potentiodynamic measurements	Inhibition efficiency up to 91.81%.	11
13	Metals and alloys in aggressive corrosive media	Green inhibition strategies	–	Plant extract as corrosion inhibitors for metals and alloys in aggressive aqueous solutions	12
14	Cu in Nitric acid solutions	Berry leaves	Electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PP), electrochemical frequency modulation (EFM), and weight loss techniques	Mixed-type inhibitor	
15	Mild steel in 1 M hydrochloric acid	*Holoptelea integrifolia* leaf extract (HILE)	weight loss, surface, electrochemical, and DFT methods, SEM and AFM	93.91% IE	14

No.	Metal / Medium	Inhibitor / Additives	Methods	Findings	Ref.
16	304L stainless steel	*Cistus ladanifer* leaves extract	Electrochemical measurements and surface analysis techniques	99.36% IE	15
17	Mild steel in 1 N sulfuric acid medium	*Pongamia Pinnata*	Weight loss method, potentiodynamic polarization method and electrochemical impedance spectroscopy (EIS) technique, Fourier transform infrared spectroscopy (FTIR) and gas chromatography-mass spectrometry (GCMS) analysis	Maximum inhibition efficiency was attained at 100 ppm of the leaf extract	16
18	Steel dissolution in acidic medium	Glycine max, *Cuscuta reflexa* and *Spirogyra* extracts	Electrochemical, surface and density functional theory (DFT) methods	IE: GMLE > CRRE > SGAE. 73.60%, 81.92% and 94.05%	17
19	Mild steel against acid activation	Novel *Elaeis Guineensis* and silver nanoparticles	FESEM, EDX, AFM, XRD, weight loss, polarization and electrochemical impedance measurements , TEM, XRD, and EDX analyses	94.1% IE	18
20	316L stainless steel	Green inhibitors (leaf extracts of *Musa spp*. (MS) and *Jatropha curcas* (JC))	Current transients and potentiodynamic polarization	Cathodic inhibitor	19

Table 2. Outcomes of the study

No.	Metal / Medium	Inhibitor / Additives	Methods	Findings	Ref.
21	Low carbon steel in HCl	*Xanthium strumarium* leaves	Weight loss method	The inhibition efficiency was found to increases with increase in inhibitor	21

No.	Metal / Medium	Inhibitor / Additives	Methods	Findings	Ref.
				concentration and temperature	
22	Mild steel in a 2 M H_2SO_4 medium	*Piper guineense* (uziza leaf) extract	Weight loss method	Corrosion inhibition increases with increasing concentrations of *Piper guineense* extract	22
23	Metals when exposed to acidic environment	Synthetic polymers			23
24	Stainless steel grade 316L (SS316L)	Olive leaves extract (OLE)	Scanning electron microscope (SEM), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. The Fourier Transform Infrared (FTIR) spectroscopy	OLE as anticorrosion coating for control of stainless steel in marine application.	24
25	Mild steel corrosion in 3.5% NaCl solution	Green Nettle leaves extract	Molecular dynamics (MD) simulations and quantum mechanics (QM) methods, (EIS), (FT-IR), (EDS)	MD simulations demonstrated the adsorption ability of organic-inorganic inhibitors onto steel substrate.	25
26	Mild steel 1 M HCl solution	*Glycyrrhiza glabra* extract	Atomic force microscopy test	All corrosion inhibiting materials exist in *Glycyrrhiza glabra* adsorbed to steel surface, and thereby form a corrosion-protective film over the steel surface.	26
27	Mild steel in 0.5 M H_2SO_4	Dried marjoram leaves (DML)	Anodic and cathodic polarization and electrochemical impedance spectroscopy (EIS) measurements	The protection efficiency increases with increasing concentration of DML and decreasing temperatures.	27
28	N80 steel in 5% HCl solution	Extract of *ginkgo biloba*	(SEM) and weight loss	The surface topography of the steels before and after being corrupted showed that the extracts offer good protection	28

No.	Metal / Medium	Inhibitor / Additives	Methods	Findings	Ref.
29	AISI 1018 steel in 0.5 M H_2SO_4 at 25°C.	Extract of *Prunus persica* (*P. persica*) leaves	(CIE), (PPC), (EIS)	The analysis of the electrochemical parameters from the polarizations curves confirmed that the *P. persica* extract behaved as a mixed-type GCI with cathodic predominance.	29
30	Antimicrobial actions	Silver nanoparticles (Ag-NPs) using *Sida acuta* extract	X-ray diffraction and transmission electron microscopy (TEM)	The infrared spectra confirmed the bio-fabrication of the Ag-NPs displayed the existence of conceivable functional groups responsible for the bio-reduction and capping.	30
31	Mild steel in 0.1 M of hydrochloric acid (HCl)	Black tea extract containing compounds such as catechin, caffeine and tannins	Corrosion weight loss measurement, FTIR, SEM	Loss in weight of mild steel reduces as the concentration of inhibitor increases.	31
32	Mild steel (MS) in nitric acid medium	*Murraya koenigii* (curry) leaves extract	Adsorption isotherm studies and the thermodynamic analysis, X-ray spectroscopy	Mild steel corrosion inhibition efficiency of 62% is obtained with 600 ppm of extract in 0.1 N HNO_3.	32
33	Steel–copper	*Ziziphus* leaves extract	Weight loss technique	Inhibition efficiency increases with increase in inhibitor concentration but decrease with rise in temperature.	33
34	Pipeline steel API 5L X52 in hydrochloric acid solution	Extract from the leaves of *Ruta Chalepensis* (LERC)		LERC inhibitor affects both the anodic and cathodic corrosion reactions.	34
35	Mild steel in 5.0 M hydrochloric acid	*Aloe vera L.* extract	Weight loss, gasometric, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques	97% corrosion inhibition efficiency was shown by 4 g/L of *Aloe vera L.* in 5 M HCl solution for mild steel.	35

No.	Metal / Medium	Inhibitor / Additives	Methods	Findings	Ref.
36	Mild steel in acid media	Extracted from *Gongronema latifolium* (SEGL)	Hydrogen evolution technique	Inhibition efficiency depends on the concentration of the plant extract, temperature and the period of immersion.	36
37	Zinc corrosion in acidic mediated	Neem and Hibiscus, as a green inhibitor	Analysis adsorption	The Freundlich, Langmuir and Temkin models are employed to analysis adsorption occurred in the experiment.	37
38	Aluminium corrosion inhibition in hydrochloric acid (0.5 M) medium	Areca palm leaves (AL) extract	Scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques	Impedance method indicates that the Al dissolution in hydrochloric acid environment was fully hindered by charge transfer process.	38
39	Acid corrosion of low carbon steel	*Chaenomeles sinensis* (*C. sinensis*) leaves	Phytochemical characterization	Efficiency increased remarkably in the presence of inhibitor and found as concentration dependent.	39
40	Mild steel 3.5% sodium chloride solution	*Ficus carica* (*Fig tree*) leaves extract	Electrochemical techniques	Among the four major *Ficus carica* leaves extract constituent investigated, Caffeoylmalic acid was found to make the most contribution to the overall inhibition action of *Ficus carica* leaves extract.	40

Table 3. Outcomes of the study

No.	Metal / Medium	Inhibitor / Additives	Methods	Findings	Ref.
41	Carbon steel in NaCl solution	Key lime (*Citrus Aurantiifolia*) leaves and seeds at pH=7	Weight loss method, polarisation study	Good inhibition efficiency.	41
42	Mild steel in 1 M HCl	Mangrove (*Rhizophora apiculata*) bark and leaf	Gravimetric measurement (weight loss), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization	Mixed type inhibitor, Langmuir model.	42

No.	Metal / Medium	Inhibitor / Additives	Methods	Findings	Ref.
			techniques		
43	Graphene oxide (GO) nanosheets	*Urtica Dioica* leaves	Fourier transform infrared spectroscopy, high resolution-Transmission electron microscopy, field-emission scanning electron microscopy, UV-visible spectroscopy, and thermal gravimetric analysis	Physisorption mechanism, intermolecular H-bonds.	43
44	Aluminum in hydrochloric acid	*Murraya koenigii* leaves extract of pH=3 at 303°K to 323°K.	Tafel polarization and electrochemical impedance spectroscopy techniques	Anodic type of inhibitor, Langmuir adsorption isotherm.	44
45	Stainless steel 304 (SS304) in 2 m hydrochloric acid	*Tectona grandis* leaf extract	Potentiodynamic polarization studies, Fourier transform infrared spectroscopy	Mixed type inhibitor, physisorption and chemisorptions processes.	45
46	Mild steel in 3.5% NaCl	*Glycyrrhiza glabra* leaf extract	Polarization measurements, UV, IR and SEM study	Mixed type of inhibitor	46
47	Mild Steel in 1 M HCl	*Bauhinia tomentosa* leaves extract , 308–333°K	weight-loss method and electrochemical techniques, FT-IR, UV, SEM and AFM techniques	Mixed-type inhibitor, Langmuir adsorption isotherm.	47
48	Aluminium in 1 M H_2SO_4	*Dryopteris cochleata* leaf extracts	Weight loss, electrochemical measurements, X-ray diffraction and scanning electron microscopy	Mixed type inhibitor	48
49	Stainless steel 304 in acidic	*Thymus vulgaris* leaf extracts	Electrochemical impedance spectroscopy,	Positive corrosion inhibiting properties.	49

No.	Metal / Medium	Inhibitor / Additives	Methods	Findings	Ref.
	solution		electrochemical noise analysis and density functional theory		
50	Carbon steel in acidic media	*Tetraclinis articulata* (Vahl) masters leaves	Electrochemical polarization method	Mixed type inhibitor	50
51	Monel 400 in hydrochloric solution	Green leaves of *Mespilus japonica*, *Ricinus communis and Vitis vinifera*	Electrochemical impedance spectroscopy and potentiodynamic polarization	Langmiur isotherm, good corrosion inhibitors.	51
52	–	Aqueous extract of leaves of *Pancratium Foetidum Pom*	Potentiodynamic polarization, electrochemical impedance spectroscopy and weight loss studies	Inhibition efficiency increases with the increase in inhibitor concentration	52
53	Mild steel in 1 N HCl	*Schrebera swietenioids* leaves	Mass loss method, polarization measurements and electrochemical impedance spectroscopy, SEM analysis, FTIR studies	Mixed type inhibitor.	53
54	Aluminium in hydrochloric acid	*Delonix regia* (Gulmohar) extract	Weight loss, Potentiodynamic Polarization, Electrochemical Impedance Spectroscopic (EIS) techniques	Langmuir adsorption isotherm, Thermodynamic parameters were calculated	54
55	J55 steel in 3.5 % NaCl solution saturated with CO_2	*Ilex kudingcha* C.J. Tseng (Kudingcha) leaves extract	Fourier transform infrared spectroscopy (FTIR), potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning	Langmuir, Frumkin and Temkin isotherms, mixed type inhibitor.	55

No.	Metal / Medium	Inhibitor / Additives	Methods	Findings	Ref.
			electron microscopy (SEM) methods		
56	Mild steel in aqueous hydrochloric acid solution	*Jatropha Curcas* leaves	Gravimetric and thermometric techniques	Langmuir isotherm model	56
57	Low-alloy steel in acidic medium	*Aloe Vera* leaves extract	Gravimetric analysis, potentiostatic polarization measurements, electrochemical impedance spectroscopy and quantum analysis	Langmuir adsorption isotherm, Dubinin-Radushkevich isotherm, Mixed type inhibitor	57
58	API 5L Carbon steel in 0.5 M H_2SO_4	Thyme leaves hydroalcoholic extract	Tafel polarization and electrochemical impedance spectroscopy	Mixed type inhibitor	58
59	Copper in neutral medium	*Azadirachta indica* leaves extract	Electrochemical impedance spectroscopy, potentiodynamic polarization studies, scanning electron microscopy	Good corrosion inhibiting properties	59
60	Aluminium in 2 M phosphoric acid	*Mentha pulegium* leaves	Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS)	Cathodic inhibitor	60

Table 4. Outcomes of the study

No.	Metal / medium	Inhibitor / Additives	Methods	Findings	Ref.
61	Steel in 1 M HCl	*Morus Alba Pendula* leaves extract (MAPLE)	Electrochemical impedance spectroscopy (EIS) and polarization test, (AFM), (FT-IR), UV-visible analysis	High inhibition efficiency value of 93%. A synergistic effect was observed between KI and MAPLE with optimum concentration of 0.4 g/L MAPLE + 10 mM KI. Adsorption of extract on the	61

No.	Metal / medium	Inhibitor / Additives	Methods	Findings	Ref.
				steel surface.	
62	Carbon steel in 1 M HCl	*Ziziphus jujuba* leaves extract	Weight loss measurements, gasometric method, potentiodynamic polarization curves and electrochemical impedance spectroscopy methods	Inhibition efficiency increased with extracts concentration. The maximum inhibition efficiency of 82.2% was obtained. ZJL extract acts as a mixed-type. Langmuir adsorption isotherm.	62
63	Carbon steel in 1 M HCl and 0.5 M H_2SO_4	*Coriandrum sativum* leaves extract (CSL)	Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), weight loss techniques and scanning electron microscopy analysis	The inhibition efficiency increased with the increase of the concentration of the extract and decreased with the increase in temperature. Langmuir adsorption isotherm model.	63
64	Mild steel in 1 N HCl medium	*Balsamodendron Caudatum* (BC) leaves	Weight loss, potentiodynamic polarization methods and EIS, FTIR	Inhibition efficiency (% IE) was proportional to inhibitor concentration. Mixed type inhibitors. The surface morphology was determined by Scanning Electron Microscopy.	64
65	Copper in nitric acid solution	Lawsonia extract	Weight loss, potentiodynamic polarization and electrochemical impedance spectroscopic methods	Inhibition efficiency is enhanced with increase of inhibitor concentration and decrease with increase in temperature. Langmuir adsorption isotherm in all tested systems. Mixed type inhibitor. Inhibition efficiency was obtained up to 98%.	65
66	Mild steel in 1 M H_2SO_4	*Rhus verniciflua*	Fourier transform infrared spectroscopy, electrochemical impedance spectroscopy, and potentiodynamic polarization measurements. SEM,	The inhibition efficiency was found to increase with an increase in the inhibitor concentration. On the other hand, the inhibition efficiency decreased with an increase in the temperature. Langmuir, Temkin, and El-Awady isotherms.	66

No.	Metal / medium	Inhibitor / Additives	Methods	Findings	Ref.
			EDAX		
67	Mild steel in HCl solution	*Aquilaria malaccensis*	Gravimetric and electrochemical methods	Inhibit corrosion by as much as 94.49% at the concentration of 1500 ppm. The leaf extract acted as a mixed-type, but predominantly cathodic inhibitor for the potentiodynamic polarization measurement. Langmuir adsorption isotherm model.	67
68	Steel-rebar in H_2SO_4	*Anthocleista djalonensis* and $Na_2Cr_2O_7$	Steel-reinforced concrete samples immersed in the test-system, from which macrocell corrosion measurements were obtained and analysed as per ASTM G109-99a	Results showed that only the 3.33 g/L *Anthocleista djalonensis*, among the equal-mass models of leaf extract and the chemical admixtures, was outperformed by the 3.33 g/L $Na_2Cr_2O_7$ in total corrosion reduction effects. In the study, 5.00 g/L Anthocleista djalonensis exhibited optimal effectiveness, n = 93.77%, on the total-corrosion effect of concrete steel-reinforcement.	68
69	Mild steel in H_2SO_4 medium	*Tribulus terrestris* extracts	Mass loss, EIS and polarization, SEM	Good corrosion inhibition efficiency, Langmuir adsorption isotherm	69
70	Mild steel in 8% H_2SO_4	*Withania somnifera* extract	By using polarization measurements, UV, IR and weight loss study	Plant extract acts as better inhibitor on increasing its concentration.	70
71	Mild steel in 0.5 M H_2SO_4 solution	*Thymus Algeriensis*	Investigated by electrochemical studies	Investigated by electrochemical studies in the presence of different concentrations of TAE & TAO ranging from 0.25 g/L to 2 g/L. TAE and TAO behave as mixed type inhibitors.	71
72	Mild steel in 2 M H_2SO_4 solution	By *Nicotiana tabacum* extract	Studied by weight loss method	The inhibition efficiency (%IE) and surface coverage (θ) of *N. tabacum* extract increased with increase in inhibitor	72

No.	Metal / medium	Inhibitor / Additives	Methods	Findings	Ref.
				concentration but decreased with increasing the temperature. Langmuir's adsorption isotherm. The free energy value (ΔG_{ads}) indicated that the adsorption of inhibitor molecules was typical of physisorption. Quantum chemical parameters such as highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), dipole moment (μ) and Mulliken charges were calculated. Quantum chemical calculations	
73	Carbon steel in 1 M sulphuric acid	*Eucalyptus globulus* Leaves Cultivated in Tunisia Arid Zones	Weight loss measurements and different electrochemical methods.	This compound acts as a mixed-type inhibitor. As the inhibitor concentration increased, the charge transfer resistance of carbon steel increased and double layer capacitance decreased. The results of weight loss measurements were in good agreement with other electrochemical methods results. adsorption obeys the Langmuir isotherm.	73
74	Aluminium in hydrochloric acid	*Delonix regia* (Gulmohor) extract	Weight loss, polarization, EIS	As inhibitor concentration increases corrosion rate decreases while percentage of inhibition efficiency (IE) increases. Obeys Langmuir adsorption isotherm. inhibitor acts as mixed type.	74
75	Steel in 1 M HCl	Extracts of *Diospyros kaki L.f.* (persimmon) leaves	Investigated, by using weight loss and potentiodynamic polarisation techniques	The highest efficiency was 94.3%. The extracts inhibit corrosion mainly by an adsorption mechanism. Mixed-type inhibitors. In addition, the extracts were screened for antibacterial activity against oil	75

No.	Metal / medium	Inhibitor / Additives	Methods	Findings	Ref.
				field microorganisms, and they showed good to moderate activity against SRB, IB, and TGB	
76	Steel materials in hydrochloric acid	*Michelia alba* leaves extract	Investigated by potentiodynamic polarization, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and quantum chemical calculations	The results showed that MALE acted as a highly-efficient mixed-type inhibitor for all steels and increasing temperatures benefited its corrosion inhibition. The adsorption of MALE on steel surfaces obeyed a Langmuir adsorption isotherm. Quantum chemical calculation results provided reasonable theoretical explanation for the inhibition property of MALE.	76
77	Mild steel in aqueous medium	*Citrus sinensis L.* leaf extract	Using weight loss method, pH, UV–Vis, and FT-IR. To prepare the extract, the shade-dried leaf of *Citrus sinensis L.* FT-IR and UV	*Citrus sinensis L.* leaf extract have several bioactive compounds, can be used as corrosion inhibitor and such rare morphovariant should be conserved in nature.	77
78	Mild steel in phosphoric acid	*Psidium guajava* leaf extract	Investigated by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy techniques	Inhibition efficiency increases with inhibitor concentration up to 800 ppm and decreases slightly at 1200 ppm. The adsorption obeys both the Langmuir and the Temkin adsorption isotherm equations. the inhibitor acted as a mixed-type inhibitor.	78
79	Steel in brine solution saturated with CO_2	Olive leaf extract		Olive leaf extract acts as good green inhibitor.	79

No.	Metal / medium	Inhibitor / Additives	Methods	Findings	Ref.
80	Carbon steel in 1 M hydrochloric acid	Date palm (*Phoenix dactylifera*) leaf extract	Investigated using weight loss measurements, linear and potentiodynamic polarization curves, electrochemical impedance spectroscopy and scanning electron microscopy	The inhibition efficiency increased with increase in the concentration of the inhibitor but decreased with increase in temperature. Inhibition efficiency also was found to increase as immersion time increased. Langmuir isotherm. Practical implications – Date palm leaf extract (DPLE) is an effective inhibitor at room temperature and can be used to protect plain carbon steel from corrosion in HCl solution. Originality/value – This study provides new information on the inhibiting characteristics of DPLE under specified conditions. The environmentally friendly inhibitor could find possible applications in metal surface anodizing and acid pickling processes.	80

Table 5. Outcomes of the study

No.	Metal / medium	Inhibitor / Additives	Methods	Findings	Ref.
81	Stainless steel in 1 M H_2SO_4	*Aloe Vera* leaf extract	Electrochemical techniques, electrochemical noise (EN), scanning electron microscope	The results of linear polarization and electrochemical impedance spectroscopy proved the effectiveness of *Aloe Vera* extract as concentration increased. Employing EN, different aspects like transient analysis, noise resistant and characteristic charge were characterized.	81
82	Mild steel in 1 M hydrochloric	*Pistacia lentiscus L.* leaves essential oil	Weight loss, Electrochemical Impedance	Inhibition was found to increase with increasing concentration of *P. lentiscus*	82

No.	Metal / medium	Inhibitor / Additives	Methods	Findings	Ref.
	acid solution		Spectroscopy (EIS) and Tafel polarization curves	essential oil to attain 90.8% at 2.56 g/L of (PLL) at 303 K. The effect of temperature on the system followed the kinetic/thermodynamic model of El-Awady et al. in the temperature range from 303 to 333 K. The calculated ΔG°adsvalue showed that the corrosion inhibition of the carbon steel in 1 M HCl is mainly controlled by a physisorption process.	
83	Mild steel in 2.0 M HCl and 1.0 M H_2SO_4 solutions	*Gundelia tournefortii*	Weight loss measurement, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS)	The inhibition efficiency was found to increase with increase of the inhibitor concentrations due to the adsorption of the inhibitor molecules on the metal surface. In addition, it was established the Langmuir adsorption isotherm fits well with the experimental data. The inhibition efficiency was found to be 93% and 90% at 150 ppm in 2.0 M HCl and 1.0 M H_2SO_4 respectively. Cathodic and anodic polarization curves show that *G. tournefortii* extract is a mixed-type inhibitor in both acidic media. EIS showed that the charge transfer controls the corrosion process. The effect of temperature on the inhibition efficiency was studied.	83
84	Cast iron surface in 1 M HCl medium	*Eleusine aegyptiaca* and *Croton rottleri* leaf extracts	Weight loss and Tafel polarization and electrochemical impedance spectroscopy, FT-IR, UV-vis, Wide-angle X-ray diffraction and SEM	The inhibition efficiency increased with inhibitor concentrations. It was found that the extracts acted as mixed-type inhibitors. The addition of halide additives (KCl, KBr, and KI) on the inhibition efficiency has also	84

No.	Metal / medium	Inhibitor / Additives	Methods	Findings	Ref.
				been investigated. The adsorption of the inhibitors on cast iron surface both in the presence and absence of halides follows the Langmuir adsorption isotherm model. The inhibiting nature of the inhibitors was supported by FT-IR, UV-vis, Wide-angle X-ray diffraction and SEM methods.	
85	Water permeability resistance and microstructure of reinforced concrete treated with *Bambusa arundinacea* as green corrosion inhibitor	*Bambusa Arundinacea* leaves compared with that of calcium nitrite and ethanolamine	Compressive strength test, durability (permeability using initial surface absorption test (ISAT) and field emission scanning electron microscopy (FESEM)) for 360 days exposure.	Water absorption values of steel reinforced concrete in the presence of *Bambusa arundinacea* inhibitor were generally less than 0.25, 0.17, 0.1 and 0.07 mL/m^2 s after 10 min, 30 min, 1 h and 2 h, *i.e.*, as required by ISAT standard for low permeability concrete. This might possibly be due to the presence of residual alkalinity of potassium hydroxide (KOH) in the concrete. KOH is adequate for passivation and reduction of permeability, which serves as a chemical water barrier or hydrophobic agent that stabilizes calcium silicate hydrates.	85
86	Mild steel in 1 M HCl	*Artemisia Mesatlantica* essential oil (AMEO)	Weight loss measurements	The obtained results showed that inhibition efficiency increases with increasing inhibitor concentration to attain 91% at 2.76 g/L of AMEO at 303 K. Physical adsorption is proposed for the corrosion inhibition mechanism and the process followed the kinetic/thermodynamic model of El-Awady *et. al.* in the temperature range from 303 to 343 K. The adsorption and	86

No.	Metal / medium	Inhibitor / Additives	Methods	Findings	Ref.
				kinetic parameters for mild steel/AMEO/1 M HCl system were calculated from experimental gravimetric data and the interpretation of the results are given.	
87	Aluminium alloy in tea extract in H_2SO_4	*Camellia sinensis*	Weight loss/corrosion rate and potential measurement techniques	The extracts gave appreciable corrosion inhibition performance of aluminium at 20 and 40% concentrations with the weight loss of 236 mg (0.236 g) and 265 mg (0.265 g) respectively. ANOVA test confirmed the results at 95% confidence, and further showed that concentration of green tea extract had greater effect on potential and weight loss measurements. The value of Gibb's free energy of adsorption obtained signified that the mechanism of adsorption of plant extract molecules on the metal surface was by physiosorption.	87
88	Aluminium in 1 N NaOH solution	*Vitex negundo* (VNL) leaves extract	Chemical and electrochemical measurements, SEM	It was found that the inhibition efficiency increased with increase of VNL extract and reached the maximum of 72.6% at 900 ppm of VNL extract. The results obtained from chemical and electrochemical measurements were in good agreement. The potentiodynamic polarization studies reveal that the VNL extract act as mixed type inhibitor. Adsorption of VNL extract on the surface of aluminium follows Langmuir adsorption isotherm. The surface characteristics of inhibited and uninhibited aluminium were investigated	88

No.	Metal / medium	Inhibitor / Additives	Methods	Findings	Ref.
				by scanning electron microscope studies.	
89	Mild steel in 1 M HCl medium	*Aquilaria crassna* leaves extracts	Gravimetric method (weight loss method), electrochemical methods (electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation) and scanning electron microscope (SEM)	The extracts were shown to have good inhibition efficiencies for the gravimetric and electrochemical methods. EIS analysis revealed that increase in concentration increases the charge transfer resistance, thus increased inhibition efficiency. The potentiodynamic polarisation measurements showed the extracts acted as mixed-type inhibitors with predominantly cathodic effectiveness. SEM techniques supported the success of corrosion inhibition with the presence of inhibitors and the methanol extract best fitted the Temkin adsorption isotherm while the aqueous extract best fitted the Langmuir and Temkin adsorption isotherms. The adsorption mechanisms for both extracts were mainly physisorption.	89
90	Mild steel in hydrochloric acid: the case of oil extract of leaves of *Pistacia lentiscus* from Saidia Morocco	Plants as a source of green corrosion inhibitors: extract of leaves of *Pistacia lentiscus* from Saidia Morocco	Gravimetric, electrochemical polarization and EIS methods	The inhibition efficiency increases with increased organic oil and extract concentration to attain a maximum value of 96.34 % and 86.59% at 1g/L for oil and extract respectively. The study reveals that oil, was dominated by monoterpene hydrocarbons (44.99%) followed by oxygenated monoterpenes (13.66%) and Sesquiterpene hydrocarbons (16.59%). Among them, limonene (18.92%), α-pinene (13.94%), β-caryo phyllene (6.93%) and terpinen-4-ol (5.57%) were	90

No.	Metal / medium	Inhibitor / Additives	Methods	Findings	Ref.
				identified as major components. The Pistacia lentiscus oil and extract acts a mixed inhibitor and showed a result of the growth in the compactness of the protecting film dressing. The organic oil and extract adsorbs on the mild steel surface according to a Langmuir isotherm adsorption model.	
91	Mild steel in HCl medium	Methanol leaf extract of *Manihot esculenta* as green corrosion inhibitor	The weight loss method	The best fit adsorption isotherm model for methanol leaf extract of *Manihot esculenta* as green corrosion inhibitor of corrosion of mild steel in 2 M HCl medium was determined with the help of the Adejo-Ekwenchi adsorption isotherm. The inhibition efficiency, %IE, of the extract was found to increase with increase in both concentration and temperature, suggestive chemisorption. Going by the values of %IE, R^2 and ΔG_{ads} this adsorption process would have been thought to be chemisorption and well fitted into Langmuir, Freundlich and Temkin isotherm models. However, from the information obtained through the Adejo-Ekwenchi isotherm model the adsorption process was unambiguously resolved to be physisorption and best fitted into the Langmuir isotherm model.	91
92	Mild steel in sulfuric acid solution	*Kleinia grandiflora* leaf extract as a green corrosion inhibitor	Mass-loss analysis, potentiodynamic polarization measurements, electrochemical	The effect of temperature on the corrosion behavior of mild steel was studied in the range of 308 to 328 K. The inhibition efficiency was observed to	92

No.	Metal / medium	Inhibitor / Additives	Methods	Findings	Ref.
			impedance spectroscopy, Fourier-transform infrared spectroscopy, scanning electron microscopy, UV-visible spectroscopy, and X-ray diffraction analysis	increase with increasing concentration of the extract. Polarization curves revealed that the *Kleinia grandiflora* leaf extract is a mixed inhibitor. Impedance diagrams revealed that an increase of *Kleinia grandiflora* leaf extract concentration increased the charge transfer resistance and decreased the double-layer capacitance. The adsorption process obeys Langmuir's model, with a standard free energy of adsorption (ΔG_{ads}) of −18.62 kJ/mol. The obtained results indicate that the *Kleinia grandiflora* leaf extract can serve as an effective inhibitor for the corrosion of mild steel in a sulfuric acid medium.	
93	Mild steel in acidic bath (1.2 N HCl and 1.2 N H_2SO_4)	Leaves of *Hibiscus sabdariffa*		The results of the present study show that this compound has decent inhibiting property for mild steel corrosion in 1.2 N H_2SO_4 than 1.2 N HCl. Four sorption isotherms are tested for the data, namely Langmuir, Frumkin, Florry–Huggins, and Langmuir–Freundlich isotherms; of these the Langmuir isotherm fits the data well having correlation coefficient over 0.99 in both the acid environments.	93
94	Steel in 1 M HCl solution	Extract of *Mentha rotundifolia* leaves (EMRL)	Electrochemical impedance spectroscopy, Tafel polarization methods, and weight loss measurements	The results obtained revealed that the inhibitor tested differently reduced the kinetics of the corrosion process of steel. Its efficiency increases with the concentration and attained 92.87% at 35%. The effect of temperature on the corrosion behavior of steel in	94

No.	**Metal / medium**	**Inhibitor / Additives**	**Methods**	**Findings**	**Ref.**
				1 M HCl was also studied in the range 298 and 338 K. The thermodynamic data of activation were determined. *Mentha rotundifolia* extract is adsorbed on the steel surface according to a Langmuir adsorption model.	
95	Mild steel in HCl solution	UAE *Rhazya stricta* Decne extract	Weight loss measurements	The aqueous *Rhazya stricta* Decne leaves extract was found to be a highly efficient inhibitor for mild steel in 1.0 M HCl solution, reaching about 90 per cent at 2.0 g/L and 303 K, a concentration considered to be very moderate. Even with one-tenth of that concentration, 0.2 g/L, an inhibition of about 82 per cent was obtained at 303 K. The rate of corrosion of the mild steel in 1.0 M HCl is a function of the concentration of the *Rhazya stricta* Decne extract. This rate increases as the concentration of the *Rhazya stricta* Decne extract is increased. The percentage of inhibition in the presence of this inhibitor was decreased with temperature which indicates that physical adsorption was the predominant inhibition mechanism because the quantity of adsorbed inhibitor decreases with increasing temperature.	95
96	Carbon steel in acidic media	*Opuntia ficus* extract	Weight loss determinations, surface studies, electrochemical impedance spectroscopy and	It was observed that *Opuntia ficus-indica* extract can decrease the corrosion rate of CS, and its efficiency increases with increasing concentration up to 1,000 ppm and with time,	96

No.	Metal / medium	Inhibitor / Additives	Methods	Findings	Ref.
			potentiodynamic polarization	but decreases with increasing the temperature from 25 to 600°C. The inhibitory activity is due to the presence of phenolic compounds in its chemical structure. Research limitations/implications: The work was done under static conditions, whereas in acid cleaning conditions, there is a dynamic system. However, the findings may apply to both the systems.	
97	Mild steel in 0.5 M HCl solution	Silver nanoparticles from *Artemisia annua* and *Sida acuta* leaves extract	UV-visible spectrophotometer	Antifungal activity was studied against *Candida albicans*. The results of the antimicrobial studies showed good inhibitory effect against *Staphylococcus aureus*, *Escherichia coli* and *Candida albican*. Also, anti-corrosion activity of these silver nanoparticles on the corrosion of mild steel in 0.5 M HCl solution was studied by potentiodynamic polarization curves and the results show that they are good inhibitors. The antioxidant activity of both the extracts and synthesized AgNP's was analyzed by 1,1-diphenyl-2-picryl-hydrazyl (DPPH) radical scavenging assay using ascorbic acid as control and they were all found to exhibit good antioxidant activity especially at lower concentrations.	97
98	Mild steel in 1 M hydrochloric acid	*Salvia officinalis* essential oil	Principal component analysis (PCA), weight loss measurements, potentiodynamic polarization,	Tafel polarization study revealed that extract of *S. officinalis* acts as a mixed type inhibitor. Inhibition was found to increase with increasing concentration of the essential	98

No.	Metal / medium	Inhibitor / Additives	Methods	Findings	Ref.
			electrochemical impedance spectroscopy (EIS)	oil and extract of *S. Officinalis*. Values of inhibition efficiency calculated from weight loss, Tafel polarization curves, and EIS are in good agreement. The effect of temperature on the corrosion behaviour of mild steel in 1 M HCl with addition of essential oil and extract was also studied and thermodynamic parameters were determined and discussed.	
99	Aluminium alloy in HCI	Adsorption and inhibitive properties of *Camellia sinensis*	Weight loss/corrosion rate and potential measurement techniques	The results obtained showed effective corrosion inhibition of the extract on the aluminium alloy test specimens in the different concentrations of hydrochloric acid used. The extracts gave appreciable corrosion inhibition performance of aluminium at 100 and 80% concentrations with the weight loss of 652 mg (0.652 g) and 674 mg (0.674 g) respectively. ANOVA test confirmed the results at 95% confidence, and further showed that concentration of green tea extract had greater effect on potential measurements whereas test exposure time had greater influence on weight loss measurements. The value of Gibb's free energy of adsorption obtained signified that the mechanism of adsorption of plant extract molecules on the metal surface was by physiosorption. The adsorption of *Camellia sinensis* extract on the surface of aluminium obeys the Freundlich isotherm model.	99

No.	Metal / medium	Inhibitor / Additives	Methods	Findings	Ref.
100	Mild steel in acidic environment	*Asteraceae* family – *Parthenium hysterophorus* plant leaves extract	Weight loss measurements, Tafel polarization and electrochemical impedancespectrosc opy techniques	The maximum potential of the extract was obtained at 1100 mg L-1 with 84% efficiency. It was found that adsorption of *Parthenium hysterophorus* extract follows Langmuir isotherm model. Mechanism of corrosion inhibition is explored with the help of UV-vis spectra and SEM images.	100

10. Some studies in detail

Rajendran *et al*. have done extensive work in the field of using green inhibitors [101–104].

10.1 Corrosion inhibition of carbons steel in chloride medium by extract of Henna leaves

An aqueous extract of leaves of Henna (*Lawsonia inermis L.*) powder has been used as a corrosion inhibitor in controlling corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^-. Weight loss method has been used to calculate the inhibition efficiency. The experiments were carried out in the absence and presence of Zn^{2+}. It is well known that the main constituent of this plant extract is Lawsone. It is observed that it has good inhibition efficiency (IE) and shows excellent IE at pH 6, 8 and 12. Interestingly in the presence of Zn^{2+} a synergistic effect is noticed. Synergism parameters have been calculated to evaluate the synergistic effect. Analysis of variance (F-test) reveals that the synergistic effect existing between henna extract and Zn^{2+} in statistically significant. The protective film has been analyzed using Fourier transform infrared (FTIR) spectroscopy. The film consists of Fe^{2+}-Lawsone complex and zinc hydroxide .It is found to be UV-fluorescent. Electro chemical studies such as potentiodynamic polarization and alternating current (AC) impedance have been used to find the mechanistic aspects of corrosion inhibition [101].

10.2 Use of extracts of Henna leaves in prevention of concrete corrosion

Green inhibitors have been used in concrete technology also. The corrosion resistance of mild steel in simulated concrete pore solution (SCPS) prepared in seawater has been investigated. Weight loss method, polarization study and AC impedance spectra have been used in this study. The influence of green inhibitor extracted from henna leaves has also been investigated in the absence and the presence of Zn^{2+} ions. It is noted that, in presence of this environmentally friendly green inhibitor (henna extract) the corrosion resistance of mild steel increases. This formulation may find application in concrete technology especially in marine environment because the experiments have been carried out in sea water. While constructing bridge in seas this findings may be taken into consideration [102].

10.3 Inhibition of corrosion of carbon steel in sea water by extracts of Henna leaves

The inhibition efficiency (IE) of an aqueous extract of henna leaves in controlling corrosion of carbon steel in seawater has been evaluated by weight-loss method. It is observed that the formulation consisting of 8 ml of henna extract (HE) and 25 ppm of Zn^{2+} has 94% inhibition efficiency in controlling corrosion of carbon steel in sea water. Polarization study reveals that HE and Zn^{2+} system functions as mixed type inhibitor. AC impedance spectra reveal that protective film is formed on the metal surface. The nature of the metal surface has been analysed by FTIR spectra, SEM, and AFM analysis [103].

10.4 Inhibition of corrosion of mild steel in well water by an aqueous extract of Adhatoda vasica leaves

The inhibition of corrosion of mild steel in well water by an aqueous extract of *Adhatoda vasica* leaves has been investigated. The findings are discussed in this sections.

Adhatoda vasica leaves were shade dried. 50 g of the dried leaves were boiled in double distilled water. The suspended impurities were removed by filtration. The solution was made up to 100 ml and used in the present study as inhibitor solution.

10.4.1. Weight loss method

The inhibition efficiency of an aqueous extract of *Adhatoda vasica* leaves in controlling corrosion of mild steel in well water has been evaluated by weight loss method. The results are summarized in Table 6.

It is observed from the Table 6 that as the concentration of *Adhatoda vasica* leaves extract increases, the corrosion inhibition efficiency also increases. The active principle of *Adhatoda vasica* leaves extract, namely vasicine, vasicinone has coordinated with Fe^{2+} ions on the metal surface and forms a protective film consisting of Fe^{2+}-vasicine and/or Fe^{2+}-vasicinone complex. Thus the anodic reaction of metal dissolution is prevented. 92% inhibition is offered by 10 ml of the extract.

Table 6: Corrosion inhibition efficiency of *Adhatoda vasica* leaves extract in controlling corrosion of mild steel in well water.

Volume of *Adhatoda vasica* leaves extract, mL	Corrosion rate (CR), mdd	IE%
0	32.68	–
2	17.64	46
4	14.05	57
6	9.80	70
8	6.2	81
10	2.61	92

10.4. 2. Polarization study

Polarization study is useful in confirming the formation of protective film formed on the metal surface. If a protective film is formed, the linear polarization resistance increases and the corrosion current value decreases. The polarization curves of mild steel immersed in various test solutions are shown in Figure 1.

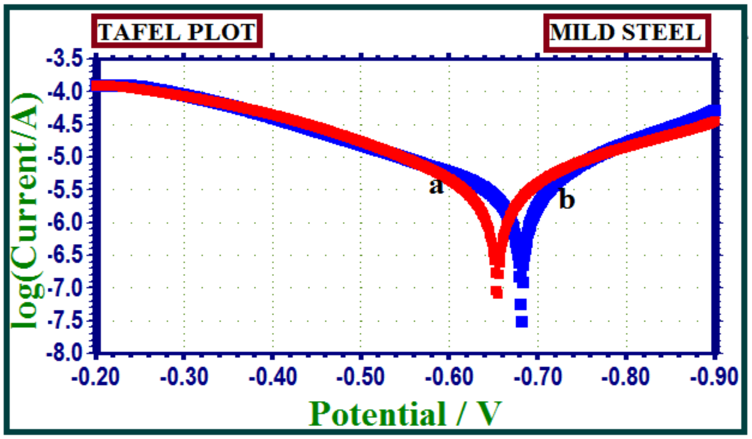


Figure 1. Polarization curves of mild steel immersed in various test solutions. (a) well water, (b) well water + 10 ml of *Adhatoda vasica* leaves extract.

The corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), linear polarization resistance (LPR) and Tafel slopes (b_c = cathodic; b_a = anodic) are given in Table 7.

It is observed from Table 7, that when mild steel is immersed in well water, the corrosion potential is –654 mV *vs.* SCE. The corrosion current is $9.447 \cdot 10^{-6}$ A/cm^2. The LPR value is 4022.1 Ohm·cm^2. In the presence of inhibitor, the corrosion potential is shifted from –654 to –682 mV *vs*. SCE. This is a cathodic shift. It suggests that the cathodic reaction is controlled predominantly. The shift is only in small range. Hence anodic and cathodic reactions are controlled to an equal extent. The LPR value increases from 4022.1 to 11108.3 Ohm·cm^2. The corrosion current decreases from $9.447 \cdot 10^{-6}$ to $3.61 \cdot 10^{-6}$ A/cm^2. These observations confirm that a protective film is formed on the metal surface. This controls the corrosion of metal.

Table 7. Corrosion parameters of mild steel immersed in well water in the absence and presence of an aqueous extract of *Adhatoda vasica* leaves (Polarization study)

No.	System	E_{corr} mV *vs.* SCE	I_{corr} A/cm^2	LPR Ohm cm^2	b_c mV/decade	b_a mV/decade
1	Well water	–654	$9.447 \cdot 10^{-6}$	4022.1	181.6	168.4
2	Well water + *Adhatoda* leaves extract	–682	$3.61 \cdot 10^{-6}$	11108.3	155.9	225.8

10.4.3. AC impedance spectra

AC impedance spectra are useful in confirming the formation of protective film formed on the metal surface. If a protective film is formed on the metal surface, the charge transfer resistance (R_t) value increases; double layer capacitance value (C_{dl}) decreases and the impedance [log (*Z*/Ohm)] value increases. The AC impedance spectra of mild steel immersed in well water in presence of inhibitor system are shown in the Figure 2 and Figure 3. The Nyquist plots are shown in the Figure 2. The Bode plots are shown in Figure 3a and Figure 3b. The corrosion parameters, namely, R_t, C_{dl} and impedance values are given in Table 8.

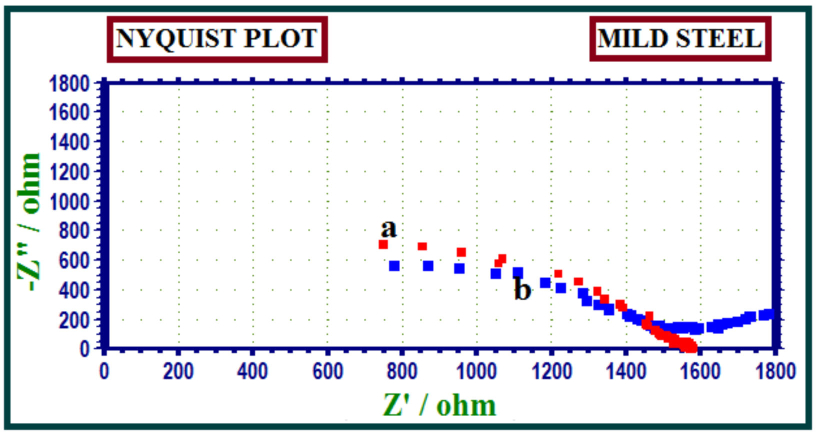


Figure 2. AC impedance spectra of mild steel immersed in various test solution (Nyquist Plot) (a) Well water (b) Well water + 10 mL of *Adhatoda vasica* leaves extract.

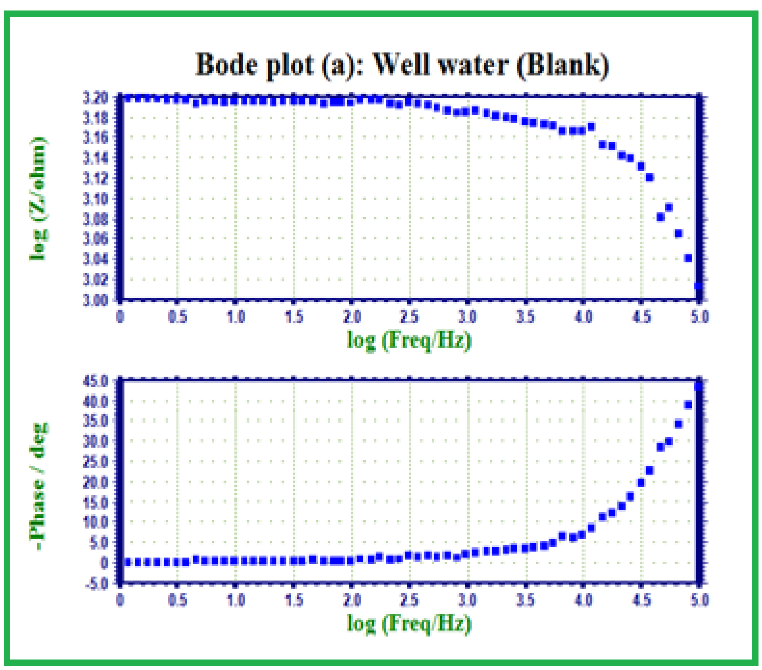


Figure 3a. AC impedance spectra of mild steel immersed in well water (Bode Plot).

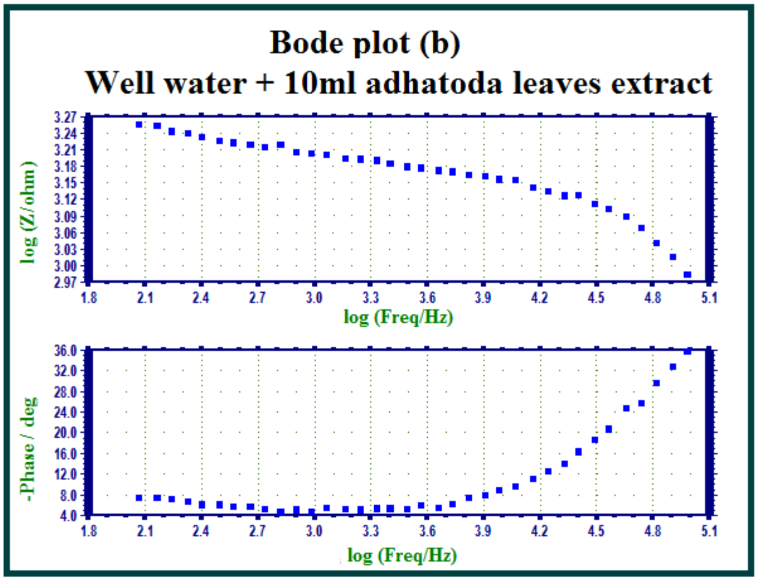


Figure 3b. AC impedance spectra of mild steel immersed in well water + 10 mL of *Adhatoda vasica* leaves extract (Bode Plot).

It is observed from Table 8 that when mild steel is immersed in well water, the charge transfer resistance is 286.7 Ohm cm^2. The double layer capacitance is $17.739 \cdot 10^{-9}$ F cm^{-2}. The impedance value is 2.721. In the presence of inhibitor (10 ml of *Adhatoda vasica* leaves extract), the charge transfer resistance value (R_t) increases from 286.7 Ohm cm^2 to 921 Ohm cm^2. The double layer capacitance value (C_{dl}) decreases from $17.739 \cdot 10^{-9}$ F cm^{-2} to $5.428 \cdot 10^{-9}$ F cm^{-2}. The impedance log (Z/Ohm) increases from 2.721 to 3.201.

Table 8. Corrosion parameters of mild steel immersed in well water in presence of adhatoda vasica leaves extract obtained from AC impedance spectra.

System	**Nyquist plot**		**Bode plot**
	R_t **Ohm cm^2**	C_{dl} **F cm^{-2}**	**Impedance log (Z/ohm)**
Well water (blank)	286.7	$17.739 \cdot 10^{-9}$	2.721
Well water + 10 ml of *Adhatoda vasica* leaves extract	921	$5.428 \cdot 10^{-9}$	3.201

These observations confirm that a protective film is formed on the metal surface. This prevents the transfer of electrons from the metal to the solution medium. Thus corrosion of mild steel is prevented.

10.4.4. AFM (Atomic Force Microscopy) studies

The 2D AFM images of polished metal surface, corroded surface (immersed in well water) and the film protected metal (well water +inhibitor solution) are shown in Figure 4a, Figure 4b and Figure 4c. The corresponding 3D images are shown in Figure 5a, Figure 5b and Figure 5c. The AFM parameters RMS (R_q) roughness (nm), Average (R_a) roughness (nm) and maximum peak-to-valley height (nm) were calculated. These values are given in Table 9 for polished mild steel, mild steel immersed in well water and mild steel immersed in inhibitor system.

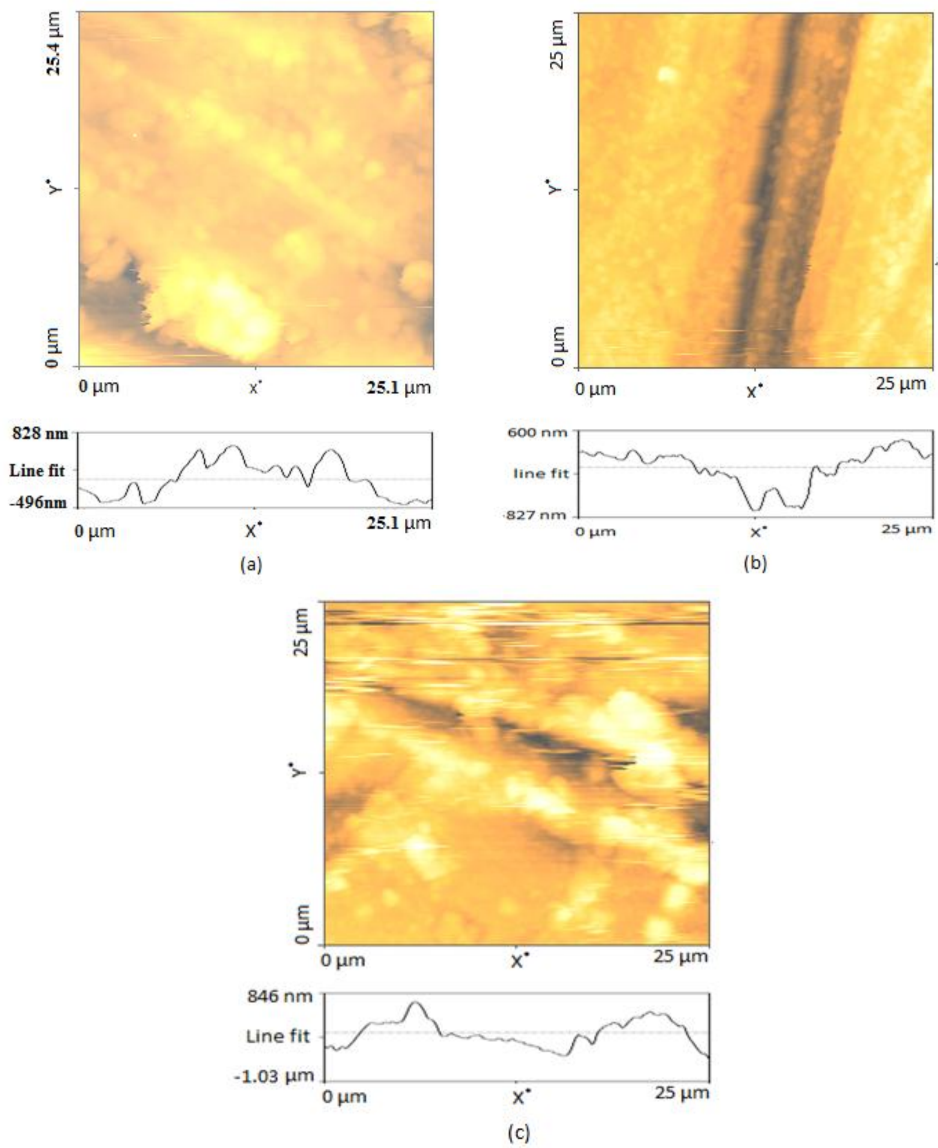
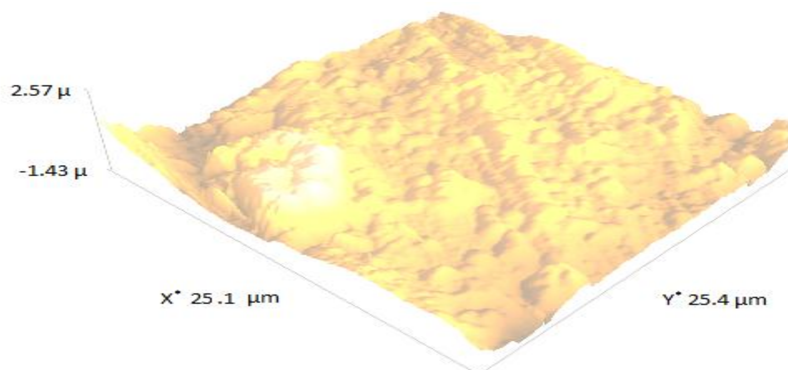


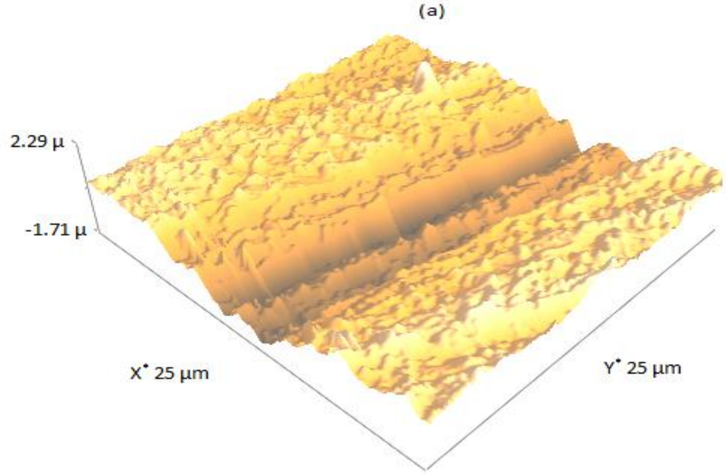
Figure 4. 2D AFM images of surface (a) polished metal, (b) mild steel immersed in well water, (c) mild steel immersed in well water containing adhatoda vasica leaves extract.

Table 8. AFM parameters of mild steel surface in the presence and absence of inhibitor (*Adhatoda vasica* leaves system).

Sample	RMS (R_q) Roughness (nm)	Average (R_a) Roughness (nm)	Maximum peak-to-valley height (nm)
Polished metal	135.9	172.84	806.9
Mild steel immersed in well water (Blank)	513.53	637.27	2885.3
Mild steel immersed in well water and 10 mL of *Adhatoda vasica* leaves extract	203.86	265.82	1152.6



(a)



(b)

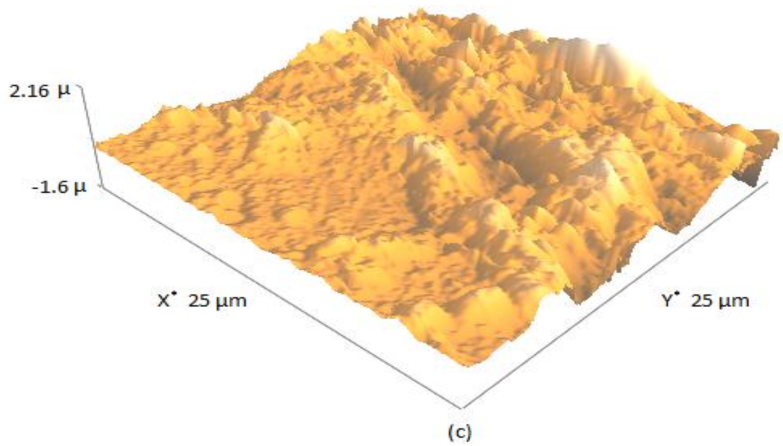


Figure 5. 3D AFM images of surface (a) polished metal, (b) mild steel immersed in well water, (c) mild steel immersed in well water containing adhatoda vasica leaves extract

It is observed from the Table 8 that the RMS roughness of polished mild steel is 135.9 nm. The average roughness is 172.84 nm. The maximum peak-to-valley height is 806.9 nm. Analysis of Table 8 reveals that the RMS roughness value of mild steel immersed in well water is higher than that of the polished mild steel. This indicates that due to corrosion, thick nanofilm is formed on the metal surface. Similar is in the case of average roughness and maximum peak-to-valley height. For the metal immersed in inhibitor system, the RMS roughness is higher than that of the polished metal, but lower than that of the metal immersed in corrosive medium. Similar is the case in the case of average roughness and maximum peak-to-valley height. This indicates that a protective film of nano scale is formed on the metal surface. This film protects the metal from corrosion.

Thus the above section explains how weight loss method, electrochemical studies and AFM spectra are used in green inhibitor study.

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