Review Article Greener Approach towards Corrosion Inhibition

Neha Patni, Shruti Agarwal, and Pallav Shah

Department of Chemical Engineering, Institute of Technology, Nirma University, S. G. Highway, Ahmedabad, Gujarat 382481, India

Correspondence should be addressed to Neha Patni; neha.patni@nirmauni.ac.in

Received 24 June 2013; Accepted 30 July 2013

Academic Editors: C. Mantell and A. J. Ragauskas

Copyright © 2013 Neha Patni et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Corrosion control of metals is technically, economically, environmentally, and aesthetically important. The best option is to use inhibitors for protecting metals and alloys against corrosion. As organic corrosion inhibitors are toxic in nature, so green inhibitors which are biodegradable, without any heavy metals and other toxic compounds, are promoted. Also plant products are inexpensive, renewable, and readily available. Tannins, organic amino acids, alkaloids, and organic dyes of plant origin have good corrosion-inhibiting abilities. Plant extracts contain many organic compounds, having polar atoms such as O, P, S, and N. These are adsorbed on the metal surface by these polar atoms, and protective films are formed, and various adsorption isotherms are obeyed. Various types of green inhibitors and their effect on different metals are mentioned in the paper.

1. Introduction

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete, and wood, but generally refers to metals. The most widely used metal is iron (usually as steel). Corrosion can cause disastrous damage to metal and alloy structures causing economic consequences in terms of repair, replacement, product losses, safety, and environmental pollution. Due to these harmful effects, corrosion is an undesirable phenomenon that ought to be prevented [1]. There are several ways of preventing corrosion and the rates at which it can propagate with a view of improving the lifetime of metallic and alloy materials. The use of inhibitors for the control of corrosion of metals and alloys which are in contact with aggressive environment is one among the acceptable practices used to reduce and/or prevent corrosion. A corrosion inhibitor is a substance which, when added in small concentration to an environment, effectively reduces the corrosion rate of a metal exposed to that environment.

Corrosion inhibitors can be divided into two broad categories, namely, those that enhance the formation of a protective oxide film through an oxidizing effect and those that inhibit corrosion by selectively adsorbing on the metal surface and creating a barrier that prevents access of corrosive agents to the metal surface [1]. Almost all organic molecules containing heteroatoms such as nitrogen, sulphur, phosphorous, and oxygen show significant inhibition efficiency. Despite these promising findings about possible corrosion inhibitors, most of these substances are not only expensive but also toxic nonbiodegradable thus causing pollution problems. Hence, these deficiencies have prompted the search for their replacement.

Plants are sources of naturally occurring compounds, some with complex molecular structures and having different chemical, biological, and physical properties. The naturally occurring compounds are mostly used because they are environmentally acceptable, cost effective, and have abundant availability. These advantages are the reason for use of extracts of plants and their products as corrosion inhibitors for metals and alloys under different environment.

Different plant extracts can be used as corrosion inhibitors commonly known as green corrosion inhibitors. Some of them are the following.

Tannins and their derivatives can be used to protect steel, iron, and other tools from corrosion. To protect mild steel in 2 M HCl solutions from corrosion, extracts from leaves can be used. Extracts of tobacco from twigs, stems, and leaves can protect steel and aluminium in saline solutions and strong pickling acids [1, 2]. Extracts from leaves were investigated

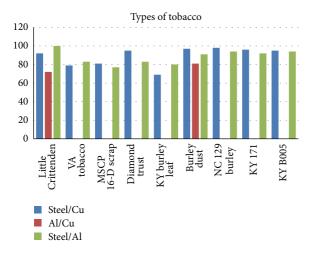


FIGURE 1: Inhibition efficiency of tobacco extracts for steel/Cu, Al/Cu, and steel/Al galvanic couples in 3.5% NaCl solution as measured by a zero resistance ammeter (ZRA) [1, 2].

and found to be effective corrosion inhibitors for mild steel in 2 M HCl solutions. Results for the same are shown in Figure 1.

It was found that maximum inhibition efficiency is 96% with only 0.01% tobacco concentration (100 ppm). Tobacco extracts contain high concentrations of chemical compounds such as alcohols, polyphenols, nitrogen-containing compounds, terpenes, carboxylic acids, and alkaloids that may exhibit electrochemical activity such as corrosion inhibition [1, 2].

Black pepper, Acacia gum, castor seed, and lignin are also good corrosion inhibitors for steel in acidic media [1, 3]. Mango peel extract is the most effective corrosion inhibitor for Al and Zn, and pomegranate fruit shells extract is most suitable for Cu. It was found that all extracts were more efficiently corrosion inhibitors in HCl solution as compared to H_2SO_4 solution [1, 4]. Aqueous extracts of *Eucalyptus* leaves protect mild steel and copper in 1 M HCl solution from corrosion [1, 5]. Inhibition efficiency of plant extracts can be tested by various methods such as galvanostatic polarization, mass loss measurements, and surface characterization techniques. SEM studies provide the confirmatory evidence for the protection of mild steel by the inhibitor.

It was found that inhibition efficiency increases with increase in concentration of extract and decreases with increase in temperature.

Extract of leaves of Henna (*Lawsonia*) acts as a good corrosion inhibitor for carbon steel, nickel, and zinc in acidic, neutral, and alkaline solutions [1, 6]. The degree of inhibition depends on nature of metal and type of medium. For steel and nickel, the inhibition efficiency increased in the order: alkaline < neutral < acidic, while in case of zinc, it increased in the order: acid < alkaline < neutral, thereby reconciling with the observed concept of the *Lawsonia* extract being a mixed inhibitor [1, 6].

One among the crucial factors for the determination of the inhibition mechanism as well as the performance of the corrosion inhibitor is the solution pH. Most of the inhibitors are pH selective which depends on the molecular structure of the inhibitor, the metal corroding, the active species present in the solution, and the composition of the inhibitor.

Extract of *Hibiscus sabdariffa* can be used as corrosion inhibitor for mild steel in 2 M HCl and 1 M H_2SO_4 solution [1, 7]. Temperature changes do not affect inhibition performance of *Hibiscus sabdariffa* in 1 M H_2SO_4 solution.

The application of the acid extract of leaves of *Citrus aurantifolia* plant on the corrosion inhibition of mild steel in 1 M HCl solution was investigated using weight loss measurement and electrochemical studies [1, 8]. Inhibitive action of the same was tested on adsorption isotherms, and it was found to fit all the models tested, that is, Langmuir, Temkin, Freundlich, Frukin, and Flory - Huggins. This extract also acts as mixed-type inhibitor. A list of various plant materials that have been used as corrosion inhibitors is given in Table 1.

Tannins, organic amino acids, alkaloids, and organic dyes of plant origin have good corrosion-inhibiting abilities. Plant extracts contain many organic compounds, having polar atoms such as O, P, S, and N. These are adsorbed on the metal surface by these polar atoms, and protective films are formed and various adsorption isotherms are obeyed.

The paper incorporates various types of green corrosion inhibitors and their effect on metals. Some important inhibitors in HCl solution, H_2SO_4 solutions, and water solution and effect of temperature and concentration of inhibitors on the process are discussed.

2. HCl Solution as Medium

2.1. Grape Pomace for Carbon Steel. Acid solutions are widely used in industry, and some of the most important fields of application are acid pickling, chemical cleaning and processing, ore production, and oil well acidification [43–45]. Csteel is one of the most important alloys being used in a wide range of industrial applications. Corrosion problems arise as a result of the interaction between the aqueous solutions and C-steel, especially during the pickling process in which the alloy is brought in contact with highly concentrated acids. This process can lead to economic losses due to the corrosion of the alloy [43, 46]. The use of green inhibitors is one of the most practical ways possible for protecting carbon steel from corrosion.

Grape pomace is an industrial waste from wine and juice processing, and it primarily consists of grape seeds, skin and stems (~18–20 kg/100 kg of grapes) [43, 47–49]. It was found that grape pomace can effectively protect carbon steel from corrosion in 1 M HCl solution [43].

The inhibition efficiency of C-steel in $1 \text{ mol } \text{L}^{-1}$ HCl increased with the concentration of crude and concentrated grape pomace extracts and was inversely associated with temperature. Presumably, the inhibitory effect was performed via the adsorption of compounds present in the grape pomace extracts onto the steel surface. Flavonoids are good candidates to explain the corrosion inhibition effects observed for grape pomace extracts. The adsorption of the grape pomace extracts followed a Langmuir adsorption isotherm. The Ea of C-steel dissolution increased in presence of the grape pomace extracts.

Doformer	Kelerence	nship [10]	rm [11]	[12]	mical [13]	ion [14]	s the [15] srm	n [16]	[17]	rm [18]	[61]	nuir [20]	the [21] ate.	
Dindingo	Finungs	A first-order kinetics relationship	Chemical adsorption isotherm	Anticorrosive materials	Mechanical and physic-chemical properties	Cathodic inhibitor, adsorption isotherm	Mixed-type inhibitor. Obeys the Langmuir adsorption isotherm	Controls the anodic reaction	Temkin isotherm	Langmuir adsorption isotherm	The standard free energy of adsorption confirms a spontaneous chemical adsorption isotherm step	Mixed-type inhibitor Langmuir Mixed-type inhibitor Langmuir icotharm	The adsorbed molecules of the alloy, lowers the corrosion rate.	
TOSION INNIDICOTS [9]. Mathad	Melliou	Langmuir adsorption isotherm Infrared spectrophotometer,	thermodynamic adsorption theories and gasometric (hydrogen evolution) methods. The study was conducted at 303 and 333 K	Weight loss method	Galvanostatic polarization technique	Weight loss measurements, electrochemical polarization, and EIS methods	Weight loss electrochemical techniques. AFM and ESCA Weight loss, potentiodynamic	polarisation, electrochemical impedance, and Raman spectroscopy	Weight loss and gasometric techniques	Electrochemical impedance, spectroscopy, potentiodynamic polarization curves, weight loss measurements, and surface analysis	, Voltammograms, Tafel plots, and EIS	Electrochemical measurements	Weight loss measurements	
IABLE I: Flaint materials used as corrosion infinitors [7]. Table I: Plaint materials Addition		Aloe vera —	Aloe vera	Banana plant juice taken from paradica and maghraby banana pseudostem	Magrabe banana stem	Pennyroyal mint	Justicia gendarussa extract (JGPE)	Caffeic acid	Combination of leaves and seeds (LVSD) extracts of <i>phyllanthus amarus</i>	Aqueous extracts of mango, orange, passion fruit, and cashew peels	Caffeine	Hibiscus sabdariffa leaves	HibiscusTeterifa	
Modium	Medium	2 M HCl	H_2SO_4	10 or 23 per cent sodium hydroxide		1 M HCl	1 M HCl	$0.1\mathrm{M}\mathrm{H}_2\mathrm{SO}_4$	1 M HCl and H ₂ SO ₄	1 M HCl	Ethanol	0.5 M NaOH	0.5 M NaOH	
Matal	INICIAL	Zinc	Mild steel	Concrete steel surface	Concrete steel surface	Mild steel	Mild steel	Mild steel	Mild steel	Carbon steel	Carbon steel	Al	Al-Zn-Mg alloy	
0 2 2 C	o. 110.	1	0	ŝ	4	IJ	9		×	6	10	11	12	

Chinese Journal of Engineering

			T_{ℓ}	TABLE 1: Continued	ŗd.		
S. no.	Metal	Medium	Inhibitor	Additive	Method	Findings	Reference
14	Mild steel		Eucalyptus, hibiscus, and agaricus		Weight loss and polarization methods	Langmuir, Freundlich adsorption isotherm. Agaricus extract was found to be a cathodic inhibitor while extracts of eucalyptus and hibiscus were found to be mixed inhibitors	[23]
15	Mild steel	$1\mathrm{M}\mathrm{HC}$ and $0.5\mathrm{M}\mathrm{H}_2\mathrm{SO}_4$	Murraya Koenigii leaves		Weight loss, EIS, linear polarization, and potentiodynamic polarization	Langmuir adsorption isotherm $(Q, \Delta H^*, and \Delta S^*)$	[24]
16	Mild steel	1N HCl	Murraya Koenigii		Weight loss, gasometric studies, electrochemical polarization, AC impedance measurements, and SEM studies (30–80°C)	The protective film formed on the surface	[25]
17	Al	2 M HCl	Chromolaena odorata L.		Gasometric and thermometric techniques (30–60°C)	Langmuir adsorption isotherm	[26]
18	Mild steel	$\mathrm{H_2SO_4}$	Ethanol extract of ITHeinsia crinata/IT		Weight loss, thermometric, hydrogen evolution techniques, and IR spectroscopy	Adsorption inhibitor Temkin and Frumkin adsorption	[27]
19	Mild steel	1 M HCl 0.5 H ₂ SO ₄	Dacryodis edulis (DE)		Gravimetric and electrochemical techniques	DE extract was found to inhibit the uniform and localised corrosion of carbon steel in the acidic madia	[28]
20	AI	HCI			Weight loss and hydrogen evolution methods	Langmuir adsorption isotherm, activation energies (E_a) , activation enthalpy, and activation entropy	[29]
21	Al	0.5 M HCl	Azadirachta indica (AZI) plant	Iodide ions	Potentiodynamic polarization and impedance techniques	Freundlich adsorption isotherm	[30]
22	Mild steel	(60 ppm of Cl ⁻)	Aqueous extract of rhizome (Curcuma longa L.) powder	Zn^{2+}	Weight loss method, FTIR, UV fluorescence, and Electrochemical studies	Forms synergistic effect, protective film consists of a Fe^{2+} -curcumin complex and zinc hydroxide $(Zn[OH]_2)$	[31]
23	Al	HCI	Peepal (Ficus religiosa).		Mass loss and thermometric methods	IE dependent upon the concentrations of the inhibitor and the acid	[32]
25	Mild steel	0.1 M HCl	TL and BR inhibitors from green tea and rice bran		Weight loss method, polarization techniques	Cathodic inhibitor	[33]
26	Mild steel	0.2 M HCl	Bark and leaf solution extracts of mango (Mangifera indica)	Ambient temperature	Weight loss method	At 1.0 mL/100 mL of 0.2 M dilute sulphuric acid concentration gives good IE	[34]
27	Mild steel	HCI	Acid extract of Andrographis paniculata		Mass loss method, Tafel polarization method, and impedance studies	Plant extract has the potential to serve as corrosion inhibitor	[35]

4

	Reference	[36]	[37]	[38]	[39]	[40]	[41]	[42]
	Findings	Suitable adsorption isotherms were tested graphically	Frumkin adsorption isotherm Kinetic parameters calculated, used in chemical cleaning and pickling	IE 93.1% at 30°C at 50% v/v concentration of ginseng Freundlich adsorption isotherm, thermodynamic parameters calculated	Freundlich and Temkin adsorption isotherms	Langmuir adsorption isotherm, IE increases with increasing extract concentration and decreases with temperature	Langmuir adsorption isotherm, olive extract decreases the charge density in the transpassive region	IE 70–82%
ied.	Method	loss and polarization Les rimetric and hydrogen n measurements. Temp		Weight loss techniques. Temp 30–60°C	Weight loss techniques electrochemical studies. Temp 30 and 60°C	Electrochemical impedance spectroscopy, potentiodynamic polarization curves, weight loss measurements, and surface analysis	Weight loss measurements, Tafel polarization, and cyclic voltammetry	Weight loss measurements
TABLE 1: Continued.	Additive							
	Inhibitor	Ambient temperature	Combretum bracteosum	Root of ginseng	Vigna unguiculata (VU) extract	Mango, orange, passion fruit, and cashew peels	olive (<i>Olea europaea</i> L.) leaves	Both aqueous and alcoholic extracts of seven aloe plants
	Medium	Abrus precatorius H ₂ SO ₄		1 M HCl	$0.5 \mathrm{M}$ NaOH and $\mathrm{H_2SO_4}$	1M HCl	2 M HCl	5% HCl
	Metal	Al NaOH	Mild steel	Al	Al	Mild steel	Mild steel	Mild steel
	S. no.	28	29	30	31	32	33	34

SEM revealed the persistence of a smooth surface on Csteel when grape pomace extracts were added, possibly due to the formation of an adsorptive film of phenolic compounds with electrostatic character [43].

2.2. Tannin for Mild Steel. Rhizophora racemosa is in abundance in the Mangrove forests of southern Nigeria. The bark of its stem is rich in tannins which can be described as any group of naturally occurring phenolic compounds. Their basic structure consists of garlic acid residues which are linked to glucose via glycosidic bonds [50, 51]. Thus tannins have an array of hydroxyl and carboxyl groups through which the molecules can adsorb on corroding metallic surfaces.

Ferrous materials, especially mild steel, on the other hand are largely used in acidic media in most industries including oil/gas exploration and ancillary activities. During such activities, inhibited hydrochloric acid is widely used in pickling, descaling, and stimulation of oil wells in order to increase oil and gas flow [50]. Tannins from Rhizophora Racemosa was found to be the most effective corrosion inhibitor for mild steel.

Studies on the corrosion behaviour of mild steel electrodes in inhibited hydrochloric acid are described. Conventional weight loss measurements show that a maximum concentration of 140 ppm of tannin from Rhizophora racemosa is required to achieve 72% corrosion inhibition. Similar concentration of tannin: H₃PO₄ in ratio 1:1 gave 61% inhibition efficiency, whereas efficiency obtained for phosphoric acid as inhibitor in the same environment was 55%. Corrosion rates obtained over six hours of exposure in 1 M HCl solution at inhibitor concentrations of 140 ppm are 2 mA/cm², 2.4 mA/cm², 2.6 mA/cm², and 6 mA/cm² for tannin, tannin/H₃PO₄, and H₃PO₄-inhibited and -uninhibited specimens respectively. Natural atmospheric exposure studies revealed that specimens treated in H₃PO₄ resisted corrosion for three weeks, while tannin-treated specimens suffered corrosion attack after one week of exposure tests [50].

2.3. Polyalthia longifolia for Mild Steel. Mild steel finds a lot of application in industries like metal finishing, boiler scale removal, pickling baths, and so forth. It gets rusted when it comes in contact with any acid. Acid solution, mostly HCl, is used to remove any undesirable scale or rust. Corrosion inhibitors are used to prevent the effect of corrosion in such cases. Use of hazardous chemical inhibitors is totally reduced because of environmental regulations. Chromates, phosphates, molybdates, and so forth and a variety of organic compounds containing heteroatoms like nitrogen, sulphur, and oxygen have been investigated as corrosion inhibitors [52–58].

The study shows that acid extract of *Polyalthia longifolia* (PL) is a good inhibitor for the corrosion of mild steel in HCl. The inhibition efficiency increases with the increase in inhibitor concentration and thus increases the protective action of the inhibitor on mild steel. The compound seems to function as inhibitor by being adsorbed on the metal surface. The inhibitor showed maximum inhibition efficiency of 87.79% at 1.5% v/v inhibitor concentration for an immersion

period of 12 hours at 303 K. The % inhibition efficiency increases with increase in temperature, which confirms that PL acts as an effective inhibitor at high temperature also. The adsorption of acid extract of (PL) on the surface of mild steel is spontaneous, endothermic, and consistent with the isotherm models of Langmuir, Temkin, and Freundlich [52].

2.4. Flavin Mononucleotide (FMN) for Hot Rolled Steel. Heterocyclic compounds display potential properties for use as corrosion inhibitors due to the presence of nitrogen, oxygen, and sulphur in their ring structure [59–62]. In addition, planarity due to the presence of π electrons and lone pairs of electrons on the heteroatoms contribute to their efficiency as inhibitors.

Flavin mononucleotide (7, 8-dimethyl-10-ribityl-isoalloxazine-5' phosphate monosodium salt dihydrate) is a phosphate monosodium dihydrated salt of Vitamin B2 (Riboflavin). It consists of a heterocyclic isoalloxazine ring attached to the sugar alcohol, ribitol, which is derived from a D(-)pentose sugar (ribose) that contains three antisymmetric carbons and a phosphate monosodium salt [59].

It was found that FMN is a potential inhibitor for corrosion of hot rolled steel in acidic medium. The inhibition efficiency of FMN increases with both concentration and temperature. The inhibitor follows Frumkin isotherm with negative values of ΔG_{ads}° , which signifies that the adsorption is a spontaneous process. High ΔG_{ads}° values indicate that the adsorption takes place by chemisorption at all temperatures except at the lowest temperature, where comprehensive adsorption exists. The Ea values for various concentrations of FMN are lower than Ea for acid, further confirming the role of chemisorption in the adsorption of FMN is mainly concentrated around the isoalloxazine ring [59].

3. Water Solutions as Medium

3.1. Gum Exudates from Acacia Species (A. drepanolobium and A. senegal) for Mild Steel. Corrosion is a major destructive process affecting the performance of metallic materials in applications in many construction sectors. Corrosion is a naturally occurring phenomenon commonly defined as deterioration of metal surfaces caused by the reaction with the surrounding environmental conditions [63]. The use of the gum exudate from Acacia seyal var seyal as corrosion inhibitor for mild steel in fresh water has been reported [63, 64].

The study shows that gum exudates, from *Acacia drepanolobium* and *Acacia senegal* trees, which are natural products, inhibit the corrosion of mild steel in fresh water with *A. senegal* gum exhibiting better inhibition characteristics compared to *Acacia drepanolobium*. It was found that the inhibition performances of the *Acacia* gum exudates are insignificantly affected by temperature rise. Potentiodynamic polarization studies reveal that the gum exudates are mixed-type inhibitors of mild steel corrosion in fresh water with significant reduction of anodic current densities [63].

3.2. Asafoetida Extract (ASF) for Mild Steel in Sea Water. Asafoetida is an ingredient of a plant mixture reported to have antidiabetic properties in rats [65, 66]. Asafoetida has a broad range of uses in traditional medicine as an antimicrobial, antiepileptic, used for treating chronic bronchitis and whooping cough [65, 67, 68].

It was found that the formulation consisting of 4 mL of ASF and 25 ppm of Zn^{2+} offers 98% inhibition efficiency to carbon steel immersed in sea water. When immersion period increases, corrosion rate also increases. Polarization study reveals that this system formulation acts as a mixed type of inhibitor. The FTIR spectra reveal that the protecting film consists of Fe²⁺ Asafoetida (active ingredient) complex. AFM studies confirm that the surface is smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe²⁺ ASF complex on the metal surface thereby inhibiting the corrosion of carbon steel [65].

3.3. Ginger Extract for Steel in Sulfide-Polluted Salt Water. Low-grade gram flour, natural honey, onion, potato, gelatin, plant roots, leaves, seeds, and flower gums are some of the good inhibitors. However, most of them have been tested on steel and nickel sheets. Although some studies have been performed on aluminum sheets, the corrosion effect is seen in very mild acidic or basic solutions (mill molar solutions) [69]. It was found that ginger can be effectively used to prevent corrosion of steel in sulphide-polluted salt water. Biological effect of ginger on *Escherichia coli* was also tested.

Ginger is suggested that it has oxygen donor atoms attached with the proteins and lipids on the bacterial tissues surface making a little activity for it. So it was observed that this inhibitor has no toxicity on the bacterial activity and can be applied on the waste water plants safely without any problems in treating waste water operations [69].

It was found that this extract inhibits the acid-induced corrosion of steel by virtue of adsorption of its components onto the metal surface. The inhibition process is a function of temperature, inhibitor concentration, and the metal as well as inhibitor adsorption abilities which is so much dependent on the number of adsorption sites. The mode of adsorption depends on the type of adsorption (physisorption and chemisorption) observed and could be attributed to the fact that this extract contains many different chemical compounds some of which can adsorb chemically and others adsorb physically. It may be due to the fact that adsorbed organic molecules can influence the behaviour of electrochemical reactions involved in corrosion processes in several ways [69].

Thus it was found that ginger acts as an inhibitor for corrosion of steel in sulfide-polluted salt water. The inhibition efficiency increases with increase in the concentration of the inhibitor. The inhibition is due to the adsorption of the inhibitor molecule on the metal surface by charge transfer or by the diffusion of the inhibitor molecules. The adsorption of these compounds on the metal surface follows Temkin adsorption isotherm. This inhibitor has no biological effect on the activity of *Escherichia coli*, and can be applied safely on waste water treatment plants.

4. H₂SO₄ Solution as Medium

4.1. Tannin Extract of Chamaerops humilis (LF-Ch) Plant for Mild Steel. Tafel polarization curves and electrochemical impedance spectroscopy (EIS) approve that LF-Ch extract is an effective corrosion inhibitor for mild steel in 0.5 M sulfuric acid solution +5% EtOH. The inhibition efficiency improved with the increase of LF-Ch extract concentration, whether LF-Ch extract was used alone or in combination with KI. The increase in inhibitor efficiency is generated by the addition of KI to LF-Ch extract. The Tafel polarization curves indicate that both LF-Ch extract is mixed anodic-cathodic type inhibitors. The addition of 0.025% KI to the solution leads to reduction in the essential usage of LF-Ch extract to achieve desirable inhibition efficiency. The values of the inhibition efficiency increased with the immersion time and leads to the formation of a protective film which grows with increasing exposure time [70]. An inhibitor is usually added in small amount in order to slow down the rate of corrosion through the mechanism of adsorption [70-72].

4.2. Tryptamine (TA) as a Green Corrosion Inhibitor in Deaerated Sulfuric Acid. Tryptamine (TA), a derivative of the tryptophan, is relatively cheap, nontoxic and easy to produce in purity greater than 99% [73]. TA, a cheap molecule with a very low environmental impact, was found effective in inhibiting ARMCO iron corrosion in deaerated 0.5 M sulphuric acid in the 25–55°C temperature range. Results obtained from potentiodynamic polarisation and electrochemical impedance spectroscopy indicated that TA in the more concentrated solution and at 55°C also chemisorbs. EIS long-time tests (72 h and more) demonstrated that only the 10^{-2} M TA solution attained the maximum protection efficiency both at 25 and 55°C: IP ranged from about 95% to 98% [73].

4.3. Essential Oil of Salvia aucheri mesatlantica for Steel. Essential oil of aerial parts of Salvia aucheri Boiss. var. mesatlantica was obtained by hydrodistillation and analyzed by GC and GC/MS. The oil was predominated by camphor (49.59%). The inhibitory effect of this essential oil was estimated on the corrosion of steel in 0.5 M H₂SO₄ using electrochemical polarization and weight loss measurements. The corrosion rate of steel is decreased in the presence of natural oil [74]. Chemical analysis shows that camphor can be the major component of S. aucheri mesatlantica oil. Salvia aucheri mesatlantica oil mainly acts as good inhibitor for the corrosion of steel in 0.5 M H₂SO₄. Inhibition efficiency increases with both the concentration of inhibitor and the temperature. The natural oil acts on steel surface as anodic inhibitor. Inhibition efficiency on steel may occur by action of camphor [74].

5. Conclusions

Corrosion control of metals is technically, economically, environmentally, and aesthetically important. Corrosion of metals is the major problem in industries. Considering environmental and ecological reasons, green inhibitors are found to be effective. As organic corrosion inhibitors are toxic in nature, so green inhibitors which are biodegradable, without any heavy metals and other toxic compounds, are promoted. Also plant products are inexpensive, renewable, and readily available. The paper discusses some of the important inhibitors in HCl, water, and H₂SO₄ medium and effect of temperature and concentration of inhibitors on the process. Tannins, organic amino acids, alkaloids, and organic dyes of plant origin have good corrosion-inhibiting abilities. Plant extracts contain many organic compounds, having polar atoms such as O, P, S, and N. These are adsorbed on the metal surface by these polar atoms, and protective films are formed, and various adsorption isotherms are obeyed. Corrosion inhibitors can be divided into two broad categories, namely, those that enhance the formation of a protective oxide film through an oxidizing effect and those that inhibit corrosion by selectively adsorbing on the metal surface and creating a barrier that prevents access of corrosive agents to the metal surface. Inhibition efficiency depends on temperature and concentration of inhibitor. Some of the inhibitors are mixed-type inhibitors.

Acknowledgment

The authors thank the Chemical Engineering Department of Institute of Technology, Nirma University, to provide infrastructure and ample resources needed for the work done.

References

- J. Buchweishaija, "Phytochemicals as green corrosion inhibitors in various corrosive media a review," Chemistry Department, College of Natural and Applied Sciences, University of Dares Salaam.
- [2] G. D. Davis, Anthony Von Fraunhofer J, Krebs LA and Dacres CM, 1558, The use of Tobacco extracts as corrosion inhibitors. CORROSION, 2001.
- [3] K. Srivastava and P. Srivastava, "Studies on plant materials as corrosion inhibitors," *British Corrosion Journal*, vol. 16, no. 4, pp. 221–223, 1981.
- [4] R. M. Saleh, A. A. Ismail, and A. A. El Hosary, "Corrosion inhibition by naturally occurring substances. The effect of aqueous extracts of some leaves and fruit peels on the corrosion of steel, aluminum, zinc and copper in acids," *British Corrosion Journal*, vol. 17, no. 3, pp. 131–135, 1982.
- [5] K. Pravinar, A. Hussein, G. Varkey, and G. Singh, "Inhibition effect of aqueous extracts of *Eucalyptus* leaves on the acid corrosion of mild steel and copper," *Transaction of the SAEST*, vol. 28, no. 1, pp. 8–12, 1993.
- [6] A. Y. El-Etre, M. Abdallah, and Z. E. El-Tantawy, "Corrosion inhibition of some metals using *Lawsonia* extract," *Corrosion Science*, vol. 47, no. 2, pp. 385–395, 2005.
- [7] E. E. Oguzie, "Corrosion inhibitive effect and adsorption behaviour of *Hibiscus sabdariffa* extract on mild steel in acidic media," *Portugaliae Electrochimica Acta*, vol. 26, no. 3, pp. 303– 314, 2008.
- [8] R. Saratha, S. V. Priya, and P. Thilagavathy, "Investigation of *Citrus aurantiifolia* leaves extract as corrosion inhibitor for mild

steel in 1 M HCL," *E-Journal of Chemistry*, vol. 6, no. 3, pp. 785–795, 2009.

- [9] M. Sangeetha, S. Rajendran, T. S. Muthumegala, and A. Krishnaveni, Green corrosion inhibitors-An Overview.
- [10] O. K. Abiola and A. O. James, "The effects of *Aloe vera* extract on corrosion and kinetics of corrosion process of zinc in HCl solution," *Corrosion Science*, vol. 52, no. 2, pp. 661–664, 2010.
- [11] N. O. Eddy and S. A. Odoemelam, "Inhibition of corrosion of mild steel in acidic medium using ethanol extract of *Aloe vera*," *Pigment and Resin Technology*, vol. 38, no. 2, pp. 111–115, 2009.
- [12] M. El-Sayed, O. Y. Mansour, I. Z. Selim, and M. M. Ibrahim, "Identification and utilization of banana plant juice and its pulping liquor as anti-corrosive materials," *Journal of Scientific* and Industrial Research, vol. 60, no. 9, pp. 738–747, 2001.
- [13] S. H. Tantawi and I. Z. Selim, "Improvement of concrete properties and reinforcing steel inhibition using a natural product admixture," *Journal of Materials Science and Technology*, vol. 12, no. 2, pp. 95–99, 1996.
- [14] A. Bouyanzer, B. Hammouti, and L. Majidi, "Pennyroyal oil from *Mentha pulegium* as corrosion inhibitor for steel in 1 M HCl," *Materials Letters*, vol. 60, no. 23, pp. 2840–2843, 2006.
- [15] A. K. Satapathy, G. Gunasekaran, S. C. Sahoo, K. Amit, and P. V. Rodrigues, "Corrosion inhibition by *Justicia gendarussa* plant extract in hydrochloric acid solution," *Corrosion Science*, vol. 51, no. 12, pp. 2848–2856, 2009.
- [16] F. S. de Souza and A. Spinelli, "Caffeic acid as a green corrosion inhibitor for mild steel," *Corrosion Science*, vol. 51, no. 3, pp. 642–649, 2009.
- [17] P. C. Okafor, M. E. Ikpi, I. E. Uwah, E. E. Ebenso, U. J. Ekpe, and S. A. Umoren, "Inhibitory action of *Phyllanthus amarus* extracts on the corrosion of mild steel in acidic media," *Corrosion Science*, vol. 50, no. 8, pp. 2310–2317, 2008.
- [18] J. C. da Rocha, J. A. da Cunha Ponciano Gomes, and E. D'Elia, "Corrosion inhibition of carbon steel in hydrochloric acid solution by fruit peel aqueous extracts," *Corrosion Science*, vol. 52, no. 7, pp. 2341–2348, 2010.
- [19] L. G. da Trindade and R. S. Gonçalves, "Evidence of caffeine adsorption on a low-carbon steel surface in ethanol," *Corrosion Science*, vol. 51, no. 8, pp. 1578–1583, 2009.
- [20] E. A. Noor, "Potential of aqueous extract of *Hibiscus sabdariffa* leaves for inhibiting the corrosion of aluminum in alkaline solutions," *Journal of Applied Electrochemistry*, vol. 39, no. 9, pp. 1465–1475, 2009.
- [21] F. A. Ayeni, V. S. Aigbodion, and S. A. Yaro, "Non-toxic plant extract as corrosion inhibitor for chill cast Al-Zn-Mg alloy in caustic soda solution," *Eurasian Chemico-Technological Journal*, vol. 9, no. 2, pp. 91–96, 2007.
- [22] E. Khamis and N. Alandis, "Herbs as new type of green inhibitors for acidic corrosion of steel," *Materialwissenschaf Tund Werkstoffiechnik*, vol. 33, no. 9, pp. 550–554, 2002.
- [23] A. Minhaj, P. A. Saini, M. A. Quraishi, and I. H. Farooqi, "A study of natural compounds as corrosion inhibitors for industrial cooling systems," *Corrosion Prevention and Control*, vol. 46, no. 2, pp. 32–38, 1999.
- [24] M. A. Quraishi, A. Singh, V. K. Singh, D. K. Yadav, and A. K. Singh, "Green approach to corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by the extract of *Murraya koenigii* leaves," *Materials Chemistry and Physics*, vol. 122, no. 1, pp. 114–122, 2010.
- [25] A. Sharmila, A. A. Prema, and P. A. Sahayaraj, "Influence of *Murraya koenigii* (curry leaves) extract on the corrosion

inhibition of carbon steel in HCL solution," *Rasayan Journal of Chemistry*, vol. 3, no. 1, pp. 74–81, 2010.

- [26] I. B. Obot and N. O. Obi-Egbedi, "An interesting and efficient green corrosion inhibitor for aluminium from extracts of *Chlomolaena odorata* L. in acidic solution," *Journal of Applied Electrochemistry*, vol. 40, no. 11, pp. 1977–1984, 2010.
- [27] N. O. Eddy and A. O. Odiongenyi, "Corrosion inhibition and adsorption properties of ethanol extract of ITHeinsia crinata/IT on mild steel in H₂SO₄," *Pigment and Resin Technology*, vol. 39, no. 5, pp. 288–295, 2010.
- [28] E. E. Oguzie, C. K. Enenebeaku, C. O. Akalezi, S. C. Okoro, A. A. Ayuk, and E. N. Ejike, "Adsorption and corrosion-inhibiting effect of *Dacryodis edulis* extract on low-carbon-steel corrosion in acidic media," *Journal of Colloid and Interface Science*, vol. 349, no. 1, pp. 283–292, 2010.
- [29] E. I. Ating, S. A. Umoren, I. I. Udousoro, E. E. Ebenso, and A. P. Udoh, "Leaves extract of ananas sativum as green corrosion inhibitor for aluminium in hydrochloric acid solutions," *Green Chemistry Letters and Reviews*, vol. 3, no. 2, pp. 61–68, 2010.
- [30] S. T. Arab, A. M. Al-Turkustani, and R. H. Al-Dhahiri, "Synergistic effect of Azadirachta Indica extract and iodide ions on the corrosion inhibition of aluminium in acid media," *Journal of the Korean Chemical Society*, vol. 52, no. 3, pp. 281–294, 2008.
- [31] S. Rajendran, S. Shanmugapriya, T. Rajalakshmi, and A. J. Amal Raj, "Corrosion inhibition by an aqueous extract of rhizome powder," *Corrosion*, vol. 61, no. 7, pp. 685–692, 2005.
- [32] T. Jain, R. Chowdhary, P. Arora, and S. P. Mathur, "Corrosion inhibition of aluminum in hydrochloric acid solutions by peepal (Ficus *Religeosa*) extracts," *Bulletin of Electrochemistry*, vol. 21, no. 1, pp. 23–27, 2005.
- [33] Z. Liu and G.-L. Xiong, "Preparation and application of plant inhibitors," *Corrosion and Protection*, vol. 24, no. 4, pp. 146–150, 2003.
- [34] C. A. Loto, "The effect of mango bark and leaf extract solution additives on the corrosion inhibition of mild steel in dilute sulphuric acid—part I," *Corrosion Prevention and Control*, vol. 48, no. 1, pp. 38–41, 2001.
- [35] S. P. Ramesh, K. P. Vinod Kumar, and M. G. Sethuraman, "Extract of andrographis paniculata as corrosion inhibitor of mild steel in acid medium," *Bulletin of Electrochemistry*, vol. 17, no. 3, pp. 141–144, 2001.
- [36] R. Rajalakshmi, S. Subhashini, M. Nanthini, and M. Srimathi, "Inhibiting effect of seed extract of *Abrus precatorius* on corrosion of aluminium in sodium hydroxide," *Oriental Journal of Chemistry*, vol. 25, no. 2, pp. 313–318, 2009.
- [37] P. C. Okafor, I. E. Uwah, O. O. Ekerenam, and U. J. Ekpe, "Combretum bracteosum extracts as eco-friendly corrosion inhibitor for mild steel in acidic medium," *Pigment and Resin Technology*, vol. 38, no. 4, pp. 236–241, 2009.
- [38] I. B. Obot and N. O. Obi-Egbedi, "Ginseng root: a new efficient and effective eco-friendly corrosion inhibitor for aluminium alloy of type AA 1060 in hydrochloric acid solution," *International Journal of Electrochemical Science*, vol. 4, no. 9, pp. 1277– 1288, 2009.
- [39] S. A. Umoren, I. B. Obot, L. E. Akpabio, and S. E. Etuk, "Adsorption and corrosive inhibitive properties of Vigna unguiculata in alkaline and acidic media," *Pigment and Resin Technology*, vol. 37, no. 2, pp. 98–105, 2008.
- [40] J. C. da Rocha, J. A. da Cunha Ponciano Gomes, and E. D'Elia, "Corrosion inhibition of carbon steel in hydrochloric acid solution by fruit peel aqueous extracts," *Corrosion Science*, vol. 52, no. 7, pp. 2341–2348, 2010.

- [41] A. Y. El-Etre, "Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves," *Journal of Colloid and Interface Science*, vol. 314, no. 2, pp. 578–583, 2007.
- [42] R. M. Saleh, M. A. Abd El Alim, and A. A. El Hosary, "Corrosion inhibition by naturally occurring substances: constitution and inhibiting property of Aloe plants," *Corrosion Prevention and Control*, vol. 30, no. 1, pp. 9–10, 1983.
- [43] J. C. Da Rocha, G. J. A. Ponciano C, E. D. Elia et al., "Grape pomace extracts as green corrosion inhibitors for carbon steel in hydrochloric acid solutions," *International Journal of Electrochemical Science*, vol. 7, pp. 11941–11956.
- [44] X.-H. Li, S.-D. Deng, and H. Fu, "Inhibition by Jasminum nudiflorum Lindl. leaves extract of the corrosion of cold rolled steel in hydrochloric acid solution," Journal of Applied Electrochemistry, vol. 40, no. 9, pp. 1641–1649, 2010.
- [45] A. U. Ezeoke, O. G. Adeyemi, O. A. Akerele, and N. O. Obi-Egbedi, "Computational and experimental studies of 4aminoantipyrine as corrosion inhibitor for mild steel in sulphuric acid solution," *International Journal of Electrochemical Science*, vol. 7, no. 1, pp. 534–553, 2012.
- [46] A. Y. El-Etre, "Inhibition of C-steel corrosion in acidic solution using the aqueous extract of zallouh root," *Materials Chemistry* and Physics, vol. 108, no. 2-3, pp. 278–282, 2008.
- [47] L. M. A. S. de Campos, F. V. Leimann, R. C. Pedrosa, and S. R. S. Ferreira, "Free radical scavenging of grape pomace extracts from Cabernet sauvingnon (*Vitis vinifera*)," *Bioresource Technology*, vol. 99, no. 17, pp. 8413–8420, 2008.
- [48] M. Spanghero, A. Z. M. Salem, and P. H. Robinson, "Chemical composition, including secondary metabolites, and rumen fermentability of seeds and pulp of Californian (USA) and Italian grape pomaces," *Animal Feed Science and Technology*, vol. 152, no. 3-4, pp. 243–255, 2009.
- [49] M. A. Bustamante, R. Moral, C. Paredes, A. Pérez-Espinosa, J. Moreno-Caselles, and M. D. Pérez-Murcia, *Waste Management*, 2008.
- [50] M. Oki, E. Charles, C. Alaka, and T. K. Oki, Corrosion Inhibition of Mild Steel in Hydrochloric Acid By Tannins From Rhizophora Racemosa Materials Sciences and Applications, vol. 2, 2011.
- [51] G. I. Nonaka, "The isolation and structure elucidation of tannins," *Pure and Applied Chemistry*, vol. 6, no. 3, pp. 357–360, 1989.
- [52] V. G. Vasudha and K. Shanmuga Priya, "Polyalthia longifolia as a corrosion inhibitor for mild steel in HCl solution," Research Journal of Chemical Sciences, vol. 3, no. 1, pp. 21–26, 2013.
- [53] S. A. M. Refaey, "Inhibition of steel pitting corrosion in HCl by some inorganic anions," *Applied Surface Science*, vol. 240, no. 1–4, pp. 396–404, 2005.
- [54] M. A. Quraishi and H. K. Sharma, "Thiazoles as corrosion inhibitors for mild steel in formic and acetic acid solutions," *Journal of Applied Electrochemistry*, vol. 35, no. 1, pp. 33–39, 2005.
- [55] H. Ashassi-Sorkhabi, B. Shaabani, and D. Seifzadeh, "Corrosion inhibition of mild steel by some schiff base compounds in hydrochloric acid," *Applied Surface Science*, vol. 239, no. 2, pp. 154–164, 2005.
- [56] M. Bouklah, A. Ouassini, B. Hammouti, and A. El Idrissi, "Corrosion inhibition of steel in sulphuric acid by pyrrolidine derivatives," *Applied Surface Science*, vol. 252, no. 6, pp. 2178– 2185, 2006.
- [57] E. E. Oguzie, B. N. Okolue, E. E. Ebenso, G. N. Onuoha, and A. I. Onuchukwu, "Evaluation of the inhibitory effect of methylene

Chinese Journal of Engineering

blue dye on the corrosion of aluminium in hydrochloric acid," *Materials Chemistry and Physics*, vol. 87, no. 2-3, pp. 394–401, 2004.

- [58] S. A. Ali, M. T. Saeed, and S. U. Rahman, "The isoxazolidines: a new class of corrosion inhibitors of mild steel in acidic medium," *Corrosion Science*, vol. 45, no. 2, pp. 253–266, 2003.
- [59] S. M. Bhola, G. Singh, and B. Mishra, "Flavin mononucleotide as a corrosion inhibitor for hot rolled steel in hydrochloric acid," *International Journal of Electrochemical Science*, vol. 8, pp. 5635– 5642, 2013.
- [60] M. A. Quraishi and R. Sardar, "Dithiazolidines—a new class of heterocyclic inhibitors for prevention of mild steel corrosion in hydrochloric acid solution," *Corrosion*, vol. 58, no. 2, pp. 103– 107, 2002.
- [61] S. L. Granese, B. M. Rosales, C. Oviedo, and J. O. Zerbino, "The inhibition action of heterocyclic nitrogen organic compounds on Fe and steel in HCl media," *Corrosion Science*, vol. 33, no. 9, pp. 1439–1453, 1992.
- [62] S. N. Banerjee and S. Misra, "1,10,-phenanthroline as corrosion inhibitor for mild steel in sulfuric acid solution," *Corrosion*, vol. 45, no. 9, pp. 780–783, 1989.
- [63] J. Buchweishaija, Plants As a Source of Green Corrosion Inhibitors: The Case of Gum Exudates From Acacia Species, Chemistry Department, College of Natural and Applied Science.
- [64] J. Buchweishaija and G. S. Mhinzi, "Natural products as a source of environmentally friendly corrosion inhibitors: the case of gum exudate from *Acacia seyal* var. *seyal*," *Portugaliae Electrochimica Acta*, vol. 26, no. 3, pp. 257–265, 2008.
- [65] M. Sangeetha, S. Rajendran, J. Sathiyabama, and P. Prabhakar, "Asafoetida extract (ASF) as green corrosion inhibitor for mild steel in sea water," *International Research Journal of Environment Sciences*, vol. 1, no. 5, pp. 14–21, 2012.
- [66] F. M. Al-Awadi, M. A. Khattar, and K. A. Gumaa, "On the mechanism of the hypoglycaemic effect of a plant extract," *Diabetologia*, vol. 28, no. 7, pp. 432–434, 1985.
- [67] K. Srinivasan, "Role of spices beyond food flavoring: nutraceuticals with multiple health effects," *Food Reviews International*, vol. 21, no. 2, pp. 167–188, 2005.
- [68] M. Z. Abdin and Y. P. Abdin, *Abrol*, ISBN 81-7319-707-5, Published Alpha Science Int'L Ltd. Traditional Systems of Medicine, 2005.
- [69] A. E. -A. S. Fouda, A. A. Nazeer, M. Ibrahim, and M. Fakih, "Ginger extract as green corrosion inhibitor for steel in sulfide polluted salt water," *Journal of the Korean Chemical Society*, vol. 57, no. 2, pp. 272–278, 2013.
- [70] O. Benali, H. Benmehdi, O. Hasnaoui, C. Selles, and R. Salghi, "Green corrosion inhibitor: inhibitive action of tannin extract of *Chamaerops humilis* plant for the corrosion of mild steel in 0. 5M H₂SO₄," *Journal of Materials and Environmental Science*, vol. 4, no. 1, pp. 127–138, 2013.
- [71] N. O. Eddy, "Inhibitive and adsorption properties of ethanol extract of *Colocasia esculenta* leaves for the corrosion of mild steel in H₂SO₄," *International Journal of Physical Sciences*, vol. 4, no. 4, pp. 165–171, 2009.
- [72] A. Bouyanzer and B. Hammouti, "A study of anti-corrosive effects of Artemisia oil on steel," *Pigment and Resin Technology*, vol. 33, no. 5, pp. 287–292, 2004.
- [73] G. Moretti, F. Guidi, and G. Grion, "Tryptamine as a green iron corrosion inhibitor in 0.5 M deaerated sulphuric acid," *Corrosion Science*, vol. 46, no. 2, pp. 387–403, 2004.

[74] M. Znini, L. Majidi, A. Bouyanzer et al., "Essential oil of Salvia aucheri mesatlantica as a green inhibitor for the corrosion of steel in 0.5 M H₂SO₄," Arabian Journal of Chemistry, vol. 5, no. 4, pp. 467–474, 2010.