Chapter 1

Current Status, Opportunities and Challenges of Green Corrosion Inhibitors

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Abstract

The term ‘Corrosion’ is associated with the deterioration of materials. To get rid of this problem corrosion inhibitors are commonly used. Though many conventional corrosion inhibitors can efficiently reduce corrosion, their disposal often adversely affects the environment. However, there are many natural products that have the potential of reducing corrosion and they are referred to as green corrosion inhibitors. They are much safer to use and most importantly cost-effective. This chapter deals with the current development of the use of green corrosion inhibitors, their opportunities and challenges.

Keywords

Corrosion, Inhibition, Natural Products, Environment Friendly

Contents

Current Status, Opportunities and Challenges of Green Corrosion Inhibitors	1
1. Introduction.....	2
2. Different forms of corrosion	3
2.1 General corrosion.....	3
2.2 Metallurgical influenced corrosion.....	3
2.3 Mechanically assisted corrosion.....	3

2.4	Localized corrosion	3
2.5	Microbiological corrosion	3
2.6	Environmentally induced corrosion	4
3.	Corrosion inhibition	4
4.	PARCOM guidelines for corrosion inhibition	5
4.1	Toxicity	5
4.2	Biodegradation.....	5
4.3	Bioaccumulation	6
5.	Theory of green corrosion inhibitors.....	7
6.	Some Works on The Corrosion Prevention Using Green Corrosion Inhibitors	8
7.	Opportunities	16
8.	Challenges.....	18
	Conclusion.....	19
	References	19

1. Introduction

The term “corrosion” originated from the Latin word *corrodere* meaning “gnawing to pieces”. It is a very common detrimental issue of concern in our daily life [1]. In accordance with ASTM standard corrosion can be defined as the process of putrefaction of materials generally metals by chemical or electrochemical reactions between the materials and their adjacent environment [2]. From the time of industrial revolution i.e. late eighteenth century corrosion became a severe problem as most of the metals in application are exposed to environmental moisture, which leads to the moist environmental corrosion [3]. The modern corrosion science was pillared by Wanger and Traud in 1938 where they concluded that the mechanism of corrosion mostly occurred in the boundary region of metals and electrodes [4].

2. Different forms of corrosion

2.1 General corrosion

General corrosion is a very habitual term which occurs when a metal is exposed to an environment where chemically or electrochemically the outer layer of the metal becomes thin and hence is corroded. This type of corrosion can be prevented by choosing of proper materials of construction [5].

2.2 Metallurgical influenced corrosion

The fatigue strength of corrosion depends on the internal structure of the construction of materials. It includes intergranular corrosion (comparatively little grain corrosion occurred at the boundaries of the grain which results in defragmentation of the alloy and the strength is lost), dealloying or selective leaching (process of removing an element from an alloy by corrosion), sensitization, exfoliation etc. [5].

2.3 Mechanically assisted corrosion

This type of corrosion includes wear corrosion, erosion corrosion and corrosion fatigue. These occur when fluctuating or cyclic stress is applied on the materials. Corrosion fatigue is greatly influenced by composition of the solution, pH, oxygen content, temperature etc. [5].

2.4 Localized corrosion

This type of corrosion can be categorized as filiform corrosion, crevice corrosion, pitting corrosion. In pitting corrosion localized penetration occurs. This autocatalytic type of corrosion requires extended initiation period. Crevice corrosion is generally found in lap joints, holes, rivets and bolts etc. This type of corrosion occurs via hydroxylation mechanism. Filiform corrosion can be found in flanges, gaskets, underlying metals coated with paints etc. [5].

2.5 Microbiological corrosion

This type of corrosion is promoted by different types of bacteria including heterotrophic and autotrophic bacteria. This corrosion leads to dealloying, pitting as well as hydrogen embrittlement [5].

2.6 Environmentally induced corrosion

This class of corrosion includes hydrogen-induced cracking, hydrogen damage, stress-corrosion cracking, embrittlement, hot-cracking, liquid metal embrittlement, formation of hydride, solid metal induced embrittlement [5].

3. Corrosion inhibition

In the context of protection of metals with their alloys lots of techniques such as using chemicals which forms a protective layer of films, passing impressed current to protect the cathodes etc. are applied. Sometimes by the virtue of auto oxidation process corrosion can also be minimized.

To prevent the corrosion phenomenon corrosion inhibitors are very much readily used. Corrosion inhibitors are the chemicals which keep down the corrosion [6]. Generally, four types of environment are considered for the use of corrosion inhibitors:

- Water in the pH range 5-9
- Aqueous acid solutions
- Oil refining environment considering primary and secondary production
- Miscellaneous environments

The classification of the inhibitors can be done according to:

- Electrode process

Three types of processes are employed viz. process based on anodes, process based on cathodes and process based on both anodes and cathodes.

Now what happens during corrosion? Actually, metals have lot of free electrons which in solution state move towards anode which acts as an active site and then they are passed to the cathodic side which acts as an electron acceptor. In this context, any oxidizing agent promotes the acceptance of electrons. The extent of corrosion can be reduced by minimizing the cathodic and anodic reactions. Inhibitors are adsorbed on the metallic surface creating a strong barrier that slower down the oxidation reactions of corrosion [7].

- The chemical nature of the environment

Vapor-phase inhibitors, alkaline inhibitors, acidic inhibitors, neutral inhibitors.

Some works on conventional corrosion is summarized in Table 1.

Table 1. Some earlier investigations on corrosion inhibition.

Observations	References
By the virtue of screening and electrochemical tests the test rate of decay by using inhibitor was observed.	8
Effect of stress-corrosion cracking on high-strength Al-alloys following the variation of mechanical properties was monitored.	9
Investigation on inhibition of aluminium-based alloys in caustic alkalis, chlorides and some mineral acidic media was performed.	10
Investigation on inhibition of copper and copper-based alloys in different media was observed.	11

4. PARCOM guidelines for corrosion inhibition

Considering environmental concern, green corrosion inhibitors can be used instead of the conventional inhibitors, yet the effects of the green inhibitors on the environment must be taken into consideration. PARCOM (Paris Commission) delegated by EEC (The European Economy Community) provide some guidelines which can be summarized as follows.

PARCOM guidelines are based on three parameters: (i) toxicity, (ii) biodegradation and (iii) bioaccumulation.

4.1 Toxicity

Toxicity is measured as LC₅₀ (Lethal Concentration that affects the population by 50%) as well as EC₅₀ (Effective Concentration of chemicals required for which the population is affected by 50%). Generally, EC₅₀ is lower than LC₅₀. Table 2 lists the standard test methods of toxicity tests with preferred species of different tropic levels [12].

Table 2. Toxicity tests on different tropic levels.

Group	Preferred species	Test
Primary producer	<i>Skeletonema costatum</i>	72-h EC ₅₀
Consumer	<i>Acartia tonsa</i>	48-h LC ₅₀
Decomposer	<i>Corophium volutator</i>	10-day LC ₅₀

4.2 Biodegradation

Biodegradation is an evaluation of the time during which a chemical persists in the vicinity of the system. This test is followed by the Organization for Economic Co-operation and Development (OECD) 301D test observing 28 days of biodegradation study.

4.3 Bioaccumulation

Bioaccumulation is measured by calculating the partition co-efficient of a chemical dispersed between two phases of 1-octanol and water. The chemical compounds present in inhibitors are examined by HPLC OECD 117 method.

A model is emerged by PARCOM which is termed as CHARM (Chemical Hazard Assessment and Risk Management) which contains four modules: Pre-screening, Hazard assessment, Risk analysis and Risk management.

Pre-screening uses a term “bad actors” which indicates the biodegradation level is less than 20% or the logarithmic value of the partition co-efficient is greater than 0.5 and the molecular weight is also greater than 700.

Hazard assessment is done by calculating the ratio of PEC (predicted environmental concentration) to NEC (no effect concentration). The eco-system will not be affected if NEC is equal or greater than PEC.

Risk analysis measures the probability of occurrence of harmful effects of the chemicals on the environment.

Risk management identifies the steps to be taken to reduce the harmful effects on the environment involving cost-effectiveness, unconventional chemicals and treatment process. It introduces two terms viz. best available technology (BAT) and best environmental practice (BEP).

The mammal toxicity LD₅₀ values of conventional corrosion inhibitors tabulated in Table 3, point out the need for green corrosion inhibitors.

Table 3. Mammal Toxicity LD₅₀ values.

Compound	LD₅₀ (mg/kg)
Propargyl alcohol	55
Hexynol	34
Cinnamaldehyde	2200
Formaldehyde	800
Dodecylpyridinium bromide	320
Naphthylmethyl quinolinium chloride	644
Nonylphenoethylene oxide surfactants	1310

The mechanism of corrosion inhibition by organic or inorganic compounds generally involves isolation of the metallic surface from its circumambient media in order to prevent/reduce the process of oxidation-reduction. Organic inhibitors form a defensive

layer to prevent corrosion on the surface of metal or alloy by adsorption. On the other hand, in case of inorganic inhibitors which generally act as anodic inhibitors a film is formed in which the atoms of the metal are bound to increase their resistance towards corrosion. The majority of the conventional corrosion inhibitors are toxic which create environmental issues after disposal. Moreover, the regulations regarding environment, limits their application also. For example, oilfield chemicals used as inhibitors that are discharged from offshore production platforms into the environment, adversely affect the marine life.

Regular corrosion inhibitors in general, are harmful for the environment. This triggered the need of the corrosion inhibitors which are eco-friendly. These anti-corrosive materials are most of the time derived from natural resources. So, these are far less hazardous to the environment upon rejection.

These inhibitors are also termed as green corrosion inhibitors which by a little dose can effectively reduce the problem of corrosion on the metals or alloys surface. During the process of adsorption of effective species i.e., naturally synthesized chemical compounds from plant extracts the rate of corrosion on metallic surface can be affected by:

- Altering the rate of reactions at the anode and/or cathode,
- Affecting the rate of diffusion of aggressive ions that interact with the metals,
- Enhancing the electrical resistance of the metallic surface by formation of a protective film.

5. Theory of green corrosion inhibitors

The corrosion process is directly related to Gibbs' free energy. Higher the Gibbs' free energy higher will be the corrosion rate. To lower down the free energy green corrosion inhibitors can be used. Inhibitors accumulate on the surface of the active sites of the corroded metals and form a barrier against corrosion. The relative rate of corrosion is also regulated by the Pilling-Bedworth ratio, by which the status of the film surface can be identified [13]. When the ratio is less than 1, i.e., the volume of the product generated by corrosion is less than that of the volume of the metal, insufficient oxide to protect the metal is produced which means the metal is rendered non-protective. When the ratio is greater than 1, i.e. the volume of the product generated by corrosion is greater than the volume of metal, the metal is protective; however too large value of the ratio may create cracking in the oxides formed. When the ratio becomes 1, there is a good spatial match between the oxide and the metal, and the oxide is rendered protective [14].

Inhibition that occurs based on the adsorption technique is affected by many factors like type of the electrolytes used, temperature, chemical compositions of the inhibitors etc. For

chemical adsorption process there is a chance of the formation of coordinate covalent bond. The green corrosion inhibition is generally done at room temperature and the inhibition efficiency is generally inversely proportional with temperature [15].

The action of the green corrosion inhibitors is also influenced by the structure of the ingredients which can be summarized as follows [16]:

- The inhibitors are generally in onium ions form which are adsorbed on the metal surface having active cathodic sites
- The plant extracts contain alkaloid bebeerines. It has O- and N- atoms carrying free electrons which facilitate to form bonds with the electrons that are freely available on the metal surfaces
- The potential cathodic process of steel can be affected by S-containing unsaturated compounds such as allyl propyl disulfide existed from many plant extracts
- In pyrrolidine, the strength of the bond between pyrrolidine and metals depends on the availability of the negative charge on the N- atoms which in turn denotes the basicity of the compounds
- The -OCH₃ group in alkaloid ricimine favors the interaction with the active metal surfaces

6. Some Works on The Corrosion Prevention Using Green Corrosion Inhibitors

Nowadays, cleaner production, biodegradability, sustainable development, pollution prevention are to be implemented in industrial unit operations, synthesis and applications.

Currently several investigations have been carried out using different plant sources as inhibitors to prevent corrosion. Onion, ficus, natural honey, khella, olive, shirsh zallouh, vanillin, many oils extracted from different parts of various plants etc. are some of the examples which have been used for this purpose. Herbal extracts have many active groups which are the key factors inhibiting corrosion. Natural products such as tannin and lignin, cinchona alkaloids, eucalyptus leaves, *Lawsonia inermis* *Swertia angustifolia*, *Calotropis gigantea* latex, *officinalis*, *Terminalia belerica*, *Sapindus trifolius*, Mahasudarshan churna, *Eugenia jambolans*, *Acacia concina* are very fruitful for preventing different forms of corrosion mentioned earlier [17].

Farooqi and Quraishi used aqueous extract of *Azadirachta indica* and *Cordia latifolia* to prevent scaling in cooling towers. Moreover, it was noticed that the hardness of water did not affect the inhibitor. The inhibition process was also in the permissible limits of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) [18]. In another

work, the coordination chemistry behind the inhibition process was shown by Agarwaala by using porphyrins as corrosion inhibitors [19]. *Aloe vera* leaves, orange and mango peels have been used by Saleh et al. to prevent corrosion on steel in acidic media whereas Srivatsava et al. used caffeine and nicotine for corrosion prevention on steel [20]. Abdel-Gaber *et al.* used the extracts of black cumin and kidney bean green corrosion inhibitors to arrest corrosion on steel in acidic media [21]. *Hibiscus sabdariffa* extract has been used by El-Hosary *et al.* to analyze corrosion inhibition of aluminum and zinc in acidic medium. The corrosion inhibition of mild steel has been thoroughly monitored by Ananda et al. using ethanolic extract of *Ricinus communis* leaves in acid media [22]. Several works have been carried out by Hammouti *et al.* using different extracts of natural products such as jojoba oil, acetyl eugenol, *Mentha pulegium* etc. to study corrosion prevention of steel. The extract of *Rosmarinus officinalis* was applied by Kliskic *et al.* as corrosion inhibitor for aluminum alloy in chloride solution [23]. The effects of reducing sugars like fructose and mannose have been observed by Muller et al. on the alkaline corrosion of zinc and aluminium [24]. Some investigations on natural products as corrosion inhibitors were done by Zucchi and Omar and it was found that *Papaia*, *Azadirachta indica*, *Calotropis procera*, *Poinciana pulcherrima* etc. can act as efficient corrosion inhibitors in acidic environment [25]. The restrain of corrosion on industrial cooling towers has been surveyed by Minhaj et al. using aqueous extract of hibiscus flower [26]. Corrosion inhibition of copper has been monitored by El-Etre using natural honey [27]. Anticorrosive activity of *T. chebula* and *Emblica officinalis* was analyzed by Sanghvi et al. [28]. Abdallah used guar gum as anticorrosive agent [29]. Prevention of corrosion in acidic medium taking low-carbon steel as a case study has been investigated by Martinez and Stern using Mimosa tannin [30]. The effect of inhibition using *Z. alatum* plant extract on mild steel corrosion in phosphoric acid medium by Weight Loss (WL) and Electrochemical Impedance Spectroscopy methods was studied by Chauhan and Gunasekaran. It was concluded that the prevention efficiency was about 88% at 70°C [31]. *Opuntia* extract and berberine from *Captis* were investigated by Li et al. and found that due to the presence of heterocyclic constituents the corrosion inhibition activity became very much high [32]. Black pepper as corrosion inhibitor has been studied by Raja and Sethuraman by conventional WL studies, electrochemical TI and EIS, as well as by scanning electron microscopic studies and it was found that this reagent can act as very good corrosion inhibitor at high temperature through adsorption process [33]. The inhibition mechanism via the investigation of activation energy change and effect of temperature was investigated by Okafor et al. They concluded that the favorable adsorption model was Temkin isotherm [34]. Ethanol extract of *Colocasia esculenta* was used as corrosion inhibitor on mild steel corrosion by Eddy and the effects of phytochemical constituents have been analyzed along with the adsorption kinetics [35]. Polarization of mixed-type inhibitor like carboxymethyl-chitosan was observed by Cheng

et al. and it has been observed that the protection efficiency of this inhibitor is inversely proportional to the rise in temperature (for a small range) [36].

The leaf extracts of *Chromolaena odorata* L. has been studied as green inhibitor for corrosion of aluminium in acidic medium by gasometric and thermometric techniques at different temperatures [37]. The feasibility study showed that this green inhibitor is biodegradable as well as cost-effective. It has a variety of applications including anodizing and surface coating in industries. Guar Arabic, a water soluble, branched, neutral natural gum is very much popular in case of corrosion inhibition. As it contains high concentration of organic components it is used as adsorptive material in mild steel and aluminium corrosion in acidic environment.

Punica granatum extract as corrosion inhibitor was monitored by Deepa et al. [38] on brass and they found that the efficiency of inhibition is directly proportional to the increase of concentration of acid. The maximum efficiency achieved was 94.52% at 1000 ppm concentration of bio-inhibitor. On the basis of these results the physisorption mechanism was also studied.

Hitherto saps of *Accacia Arabica*, *Annona squamosa*, *Ricinus communis*, *Eugenia jambolans*, *Azadirachta Indica*, *Pongamia glabra* etc. have been scrutinized for analysis of reluctance of corrosion in the acidic environment taking mild steel as a case study. In addition, it has been found that some herbs like anis, black cumin, coriander can be used as potential, new, green corrosion inhibitors [39].

The study of protection of rebar rooted into concrete from premature deterioration under high alkaline environment was reviewed by Kundu et al. in the light of green inhibitors [40]. Considering the formation of two-faced oxides the effect of hydrophobicity of *Bambusa arundinacea* influences the mechanism of these inhibitors. The study of corrosion inhibition using *Vernonia amygdalina* extract green inhibitor has been carried out by Eyu et al. using a case study of reinforcement of carbon steel in concrete in the environment enriched with chlorides [41]. Green synthesis of inhibitors has been investigated by several other researchers [42]. Table 4 lists some natural products having anti-corrosive properties.

Table 4. Different natural products and their anti-corrosive properties.

Serial No.	Metal	Medium	Inhibitor	Observations	Ref.
1	Carbon steel	NaCl (10 ppm) and $\text{Al}_2(\text{SO}_4)_3$ (35 ppm)	Propolis	Boiling water was used as solvent. Using inhibitor concentration 0.6 g/l inhibitor efficiency (IE) was achieved by 92.7% at 30°C.	43
2	Aluminium	0.5 to 2M HCl	Citrus peel	Pectin was the major constituent. At 10°C the IE was 91%.	44
3	Steel	1M HCl	Cladodes of <i>opuntia ficus indica</i>	Microwave extraction method was used which led to 94% IE.	45
4	Bronze	Simulated acid rain solution	<i>Salvia hispanica</i> seeds	Inhibition was carried out by soaking in methanol.	46
5	Mild steel	1M HCl	Leaves of henna	Boiling water was used as solvent. IE was 90.34% at 30°C.	47
6	6063 Al-alloy	1M HCl	Grains of <i>peganum harmala</i>	Methanol was used as solvent followed by acidic/alkaline extraction. Inhibitor concentration was 0.025 g/l and IE was 91.78%.	48
7	Low carbon steel	1M HCl	<i>Schinopsis lorentzii</i> tree powder	TAPPI T204 OM-8 and ASTM 1110-96 standard was followed.	49
8	C38 steel	1M HCl	<i>Geissospermum</i> leave	Acidic/alkaline extraction method was applied. IE was 90% 30°C.	50
9	Carbon steel	1M HCl	<i>Retama monosperma</i> (L.) Boiss. stems	Acidic/alkaline extraction method was applied. IE was 83% 30°C.	51

10	Mild steel	1M HCl	Bark and leaves of <i>Neolamarckia cadamba</i>	Acidic/alkaline extraction method was applied. IE was 91% 30°C.	52
11	Carbon steel	2M HCl	Dry olive leaves	Boiling water was used.	53
12	Mild steel	1M HCl	Watermelon peel, seeds and rind	Boiling in 1M HCl solution.	54
13	Tin	NaCl (2%), acetic acid (1%) and citric acid (5%) solution	Tomato peel wastes	Acidic/alkaline extraction method was applied. IE was 90% 30°C.	55
14	Mild steel	1M HCl	Pennyroyal oil from <i>Mentha pulegium</i>	Weight measurements, Loss, Electrochemical polarization and Electrochemical Impedance Spectroscopy was used.	56
15	Mild steel	0.5M H ₂ SO ₄	<i>Artemisia herba alba</i>		57
16	Mild steel and copper	NaCl and SO ₂ environment	Natural oil from <i>Cassia auriculata</i> , <i>Strychnos nuxvomica</i>		58
17	Concrete steel surface	10-23% NaOH	Magraba banana stems	Banana plant juice was used as inhibitor. Inhibition was monitored using WL method.	59
18	Mild steel	1M HCl	<i>Justicia gendarussa</i> extract	WL method, Atomic Force Microscopy, Electron Spectroscopy for chemical analysis was used which suggested that the inhibitor was mixed-type inhibitor. The isotherm was that of Langmuir.	60

19	Mild steel	0.1M H ₂ SO ₄	Caffeic acid	WL method, Raman spectroscopy, potentiodynamic polarization techniques were applied which concluded that the inhibitor controls the anodic reaction.	61
20	Carbon steel	1M HCl	Aqueous extract of passion fruits and cashew peels	WL and EIS were used. The adsorption isotherm was of Langmuir.	62
21	Chill cast An alloy of Al-Zn-Mg	0.5M NaOH	<i>Hibiscus teterifa</i>	WL method was used. The process thermodynamics was also investigated.	63
22	Mild steel	1M HCl and H ₂ SO ₄	Seeds and leaves extract of <i>Phyllanthus amarus</i>	WL and gasometric techniques were used. The Temkin isotherm fitted this process.	64
23	Mild steel	1M HCl and 0.5M H ₂ SO ₄	<i>Murraya koenigii</i> leaves	Electrochemical measurements were done. The inhibitor was of mixed type. The adsorption isotherm was followed by Langmuir and Dubinin-Radushkevich isotherm.	65
24	Mild steel	1M H ₂ SO ₄	Coriander, black cumin	WL, EIS and linear polarization were used.	66
25	Mild steel	2M H ₂ SO ₄	Ethanolic extract of <i>Medicago sativa</i>	The alternating current and direct current. electrochemical techniques were used.	67
26	Aluminium	0.5M NaOH	<i>Hibiscus sabdariffa</i> leaves	10% ethanol was used as additive. Hydrogen evolution followed by EIS, SEM, WL techniques were used.	68

27	X52 mild steel	20% H ₂ SO ₄	<i>Cotula cinerae</i> , <i>Retama retam</i> plant	WL, Electrochemical methods were used.	69
28	Aluminium	Highly basic (pH=12)	<i>Hibiscus rosasinensis</i>	The additive was Zn ²⁺ . The inhibitor was cathodic type. WL followed by AC impedance techniques were used.	70
29	Carbon steel, Nickel, Zinc	Neutral solution along with solutions containing acid as well as alkali	Lawsonia leaves	Polarization technique was used. IE order for carbon and nickel: alkaline<neutral<acid, whereas for zinc IE order: acid<alkaline<neutral	71
30	316 stainless steel	HCl (5%)	<i>Medicago polymorpha</i> Roxb.	The process was carried out at ambient temperature. Open circuit potential studies were done.	72
31	Aluminium, copper and brass	NaOH and acid chloride	Leaves of date palm and Lawsonia inermis, corn	WL and solution analysis were done. The adsorption isotherm was of Temkin isotherm.	73
32	N80 steel	15% HCl	Formaldehyde extract of different plant leaves	The synergistic effects were monitored. Thermodynamic parameters were calculated. The adsorption isotherm was of Langmuir isotherm.	74

33	An alloy of Al-2.5Mg	NaCl (3%)	Rosemary leaves extract containing phenol based compound	The analysis of curves of Potentiodynamic polarization was done. The adsorption process was followed by Freundlich isotherm. Ferulic acid was responsible for the inhibition action.	75
34	Aluminium	2M HCl	Mucilage extract of opuntia	Langmuir isotherm fitted the process. WL and hydrogen evolution techniques were used.	76
35	Aluminium	1M HCl	Roots of ginseng	WL method was followed. IE was 93.1%. The adsorption isotherm was Freundlich isotherm	77
36	Mild steel	3% NaCl	<i>Ricinus communis</i> , Coumarines plants	Galvanostatic anodic and cathodic polarization measurements were done.	78
37	Mild steel	0.2M HCl	Leaves and bark of mango plant	WL method was employed. 0.2M sulfuric acid concentration gave a good IE.	79
38	Mild steel	0.1M HCl	<i>Calotropis procera</i> plant extract	WL method was used and the polarization curves were analyzed.	80
39	Mild steel	20%, 50% and 88% H ₃ PO ₄	<i>Zenthoxylum alatum</i> plant extract	WL, EIS, XPS and FTIR abalysis was carried out. The IE was 88%.	81
40	Tin	HNO ₃	<i>Ficus carica</i> L., <i>Glycyrrhiza glabra</i> plants	Thermometric method was used.	82

Table 5 gives country wise information of the status of research on green corrosion inhibitors.

Table 5. Green corrosion inhibitors currently in use (countrywise).

Name of country	Green inhibitors (from different plants)	Findings	Ref.
Nigeria and Jeddah	Aloe vera extract	Zinc in 2M HCl; aluminum in 0.5M HCl (84% IE)	83
Somalia and Italy	Seeds of Datura stramonium, Cassia occidentalis Papaia, and Poinciana pulcherrima and sap of Auforpio turkiale, Calotropis procera B, Azydracta indica and Papaia.	Mild steel in 1N HCl (88–96% IE)	84
China	Jasminum nudiflorum Lindl. leaves extract	Mixed type of inhibitor for cold rolled steel (CRS) in 1.0 M HCl	85
India	Vitis vinifera seed and skin extract	Pure copper and one of its alloy (Cu-27Zn brass) in a natural seawater environment (92.3% IE)	86
Columbia	Tobacco extracts	Aluminum and steel in acidic medium	87
Mexico	Opuntia-Ficus-Indica (Nopal) mucilage	Steel in a concrete like environment (alkaline solutions)	88
Latin America	Zygophyllum album	X52 mild steel in 1M H ₂ SO ₄	89
Malaysia	Uncaria gambir extract	Mixed-type inhibitor for mild steel in aqueous (~70% IE)	90
Morocco, France	Rosmarinus officinalis oil	C38 steel in 2.0M H ₂ SO ₄ (~60% IE)	91
Iran	Lawsonia inermis extract	Mixed type of inhibitor for mild steel in 1M HCl (92% IE)	92
French Guiana	Annona squamosa extract	Mixed-type inhibitor for C38 steel in 1M HCl	93

7. Opportunities

Green corrosion inhibitors could be cost effective, i.e., economic feasibility is always a key factor. It is well known that many technological fields, households etc. are affected through many ways which in turn affect human beings. Several industries are running without corrosion prevention management. In 1978, National Bureau of Standards (USA)

published a list of cost items which were affected by corrosion. The list includes industrial building, product loss, different kinds of parts of many plants and machines etc. [94]. The sacking of machines and minimization of production rate are greatly affected by these. A report published by National Association of Corrosion Engineers, worldwide corrosion authority in 2013 which shows that 2.5 trillion USD was spent worldwide due to corrosion which in turn equivalence to the worldwide gross domestic products as 3.4%. In practice of corrosion inhibition, about 35% i.e., 875 billion USD annually is saved on a global basis. This point gives a giant expansion of the use of green corrosion inhibitors. Many works show the use of bio-wastes and natural products as green corrosion inhibitors can maintain the economic feasibility. The inhibition of corrosion for metals and alloys such as different types of steel by using *Phoenix clactylifera* seeds, highlight the economic aspects of the bio-waste with the reference of a one seeded berry as fruit of the said plant [95]. The inhibition efficiency of the pericarp of the food is near about 97% at a temperature of 50°C. There is another patent which reported that some antimicrobial agents which is derived from plants have powerful tendency towards corrosion inhibition in the area of corrosion in pipelines for oil transportation, water-cooling systems, different kind of storage tanks, systems for fire protection etc. The 40% of these corrosion problems are greatly affected by microbes. [96]. Considering the fact of reduction of pollution, excluding the conventional protocols of the conventional methodologies there are some eco-friendly as well as biodegradable green corrosion inhibitors viz. sweet potato stems and stalks of lettuce flower stalks and stems of sweet potato, as reported in a Chinese patent [97]. The importance of working on many wastes like seeds and skin, byproducts of mango, passion-fruit, fruit juices, cashew, and orange can play an important role in inhibition of corrosion as eco-friendly corrosion inhibitors. This study was performed by Gomes et al. [98] for prevention of steel corrosion in acid medium. Not only prevention of corrosion of steel but also of copper, aluminum and their individual alloys were investigated by another patent applying alternative formulations and method [99]. Dealing with corrosion inhibitors based on vegetable oils considering biorefinery and creating give-and-take relationship, more precisely synergistic relation between petroleum industries and natural resources and providing uniqueness in green methodologies. Versails worked and boosted the transformation of conventional sources towards the sustainable sites [100].

The field of corrosion inhibitors derived from naturally available products is scarcely applied to real-scale plants for arresting damage. The fault of using green products from vegetables, fruits or matrices as inhibitors is very much related with this aspect. These are precious as they are hard to harvest, scarce and edible. Irrespective of the source value the formulation of an extract from different natural substances can be dealt in the literature under lab-scale research. The probability of the natural extracts to be used in inhibition of

corrosion is quite high, considering that the property of corrosion inhibition is closely related to unsaturation or the presence of hetero atoms in the source materials. The extracts from natural resources generally possess these kinds of features. Instead of the question of the impact of these inhibitors on society as well as economy, it is still very important considering the final application of the products.

The benefits of green corrosion inhibitors are tabulated in Table 6.

Table 6. Benefits of green corrosion inhibitors.

Types of green corrosion inhibitors	% of efficiency	Cost	References
Plant leaves, latex, fruits	75-96%	Low	101
Plant stems, branches	87-95%	Low	102
Gum	34-46%	Low	103
Flour, yeast etc.	65-82%	Very low	104
Caffine, nicotine	80-90%	Medium	105
Tobacco	70-91%	Low	106
Vapour phase inhibitors	96%	Medium	107
Ionic liquids	79-99%	Expensive	108
Chitosan and proteins	98%	Medium	109
Leguminous seeds	34-91%	Low	110
Drugs	94-97%	Medium	111

8. Challenges

Though the words “green corrosion inhibitors” are interesting, having lots of advantages relating to the environment, there are several limitations too which encourage the potentiality of taking the challenges while using these inhibitors. Considering green corrosion inhibitors, it must be noted whether the inhibitor is still non-toxic after a period of 28 days or not. Further the bioaccumulation of the inhibitor is also to be checked. Bioaccumulation is estimated by partition coefficient method between 1-octanol and water. Higher the partition coefficient higher will be the bioaccumulation. So, the components of the inhibitor must be pre-investigated before using it to prevent corrosion. One of the major drawbacks is their longevity. Since generally they are highly biodegradable it is difficult to store these for a long time. Choice of extraction method is another important fact. During the extraction of plants fragments it must be kept in mind that the solvent used for extraction must be less harmful. Also, some process requires long processing time, high

temperatures which disfavor the green corrosion inhibition. To overcome these problems nowadays supercritical fluid extraction process is applied as alternative techniques. But the effect of physico-chemical parameters on its mechanism is currently under investigation. Moreover, the active ingredients of the inhibitors are very much less. Nowadays some pharmaceuticals drugs are used for this purpose. But Gece pointed out that as all the drugs are not biodegradable it limits the processing of dry raw materials for green corrosion inhibitors. However, in spite of the above mentioned limitations, the green corrosion inhibitors are still the most promising alternatives because they are generally synthesized from natural products which in turn boost up their ready availability and cost effectiveness [112].

Conclusion

Metals - an essential part of our civilization - have the characteristic properties of degrading in presence of harmful atmospheric conditions created by oxygen or acidic, basic or even neutral conditions, which in turn compel us to think about preventing the phenomenon of corrosion. There are several techniques being applied to prevent corrosion. Among them use of inhibitor is the best option. Many countries have already used these green inhibitors to prevent corrosion. Due to environmental concern some bio-based inhibitors nowadays are well pronounced. These are also known as green corrosion inhibitors as they have no toxicity, are naturally available and very safe to handle. Moreover, the extraction process of the products is also generally cost-effective. As these products are easily available from economical point of view it is very feasible. From the literature survey it is inferred that the inhibition process is based on adsorption techniques which may follow Freundlich, Langmuir and Temkin isotherm processes. In a nutshell, it can be said that though green corrosion inhibitors have some limitations in terms of bioaccumulation, considering environmental protection these inhibitors are very much needed to make a cleaner, safer, sustainable surrounding and most importantly to get rid of the problems caused by corrosion.

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