Chapter 7

Green Corrosion Inhibitors for Coatings

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Abstract

Corrosion is emerging as a potential hazard which abolishes metals and their structures and hence become an imperative menace. It is an omnipotent and omnipresent process which is present in every environment, *i.e.*, air, soil, water. Green chemistry is one of the notable branches of chemistry that focuses on the protection of environment and human well-being in an economically viable approach allowing dodging of toxins and reducing hazards due to corrosion. Green chemistry exploited well-known strategy namely green inhibitors to prevent, control or impede the growth of corrosion. Green inhibitors are eco-friendly, cost-effective, renewable natural products which are favourable over toxic synthetic corrosion inhibitors. Extracts of natural products contain natural products containing alkaloids, carboxylic acids, nicotine, polyphenols, quinine, terpenes, and other functional groups possessing elements like C, N, O, S, *etc.*, prompting adsorption *via* forming a thin layer (coating) on the metallic surface to shield the surface and encumber corrosion. In the field of economical loop, this approach develops various potential applications in manufacturing areas other than 'Trash to treasure'. Even though a bunch of experiments have been performed and several research articles have been in print, however, the area of green inhibitors is still demanding more investigation on this open issue. More and more interest in the area extended the research, consequentially to a large variety of tried molecules. Nevertheless, the most accepted protocols are classical and, therefore, are incompetent to completely portray the probable worth of inhibitors. Hence all above stated features should be the objective of the contemporary research so that productive analysis to emphasize the weak areas of the green inhibitors field and tackle the prospect research in the field that still requires validation.

Keywords

Anodic Inhibitor, Cathodic Inhibitor, Green Corrosion Inhibitors, Coatings, Ionic Liquids, Vapor-Phase Inhibitor, Sustainable

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1. Introduction

Corrosion is derived from Latin word *corrōdere* which means “to gnaw”. Corrosion is a universal phenomenon where living tissues, metals, alloys, ceramic, polymer or materials are consumed by virtue of chemical or electrochemical reaction. In this process materials attempt to return to their most stable thermodynamics state as a result of their reaction with the environment medium [1]. The more corrosive environment comprises of air, carbon dioxide, gaseous sulphur, molten salts, organic liquids, water, whereas, innocuous environments include gamma radiation, nuclear fission fragments, neutron beams, and ultraviolet light. Materials such as alloys, ionic and covalent solids, rubber, plastics, metals, composite materials concrete and wood are highly subjected to corrosion [2]. Corrosion is an exorbitant growth as a consequence of damaging resources or their

properties (estimated economy expenditure of various countries due to corrosion is mentioned in Table 1), which in turn, causes shut down or severe debacle of systems, excessive time loss throughout maintenance. In some cases, injuries and several hazardous effects on living systems have been reported [3-7].

Table 1. Corrosion cost in different countries.

Country	Cost (in \$)	Reference
Australia	470 million	[8]
Finland	47–62 million	[9]
India	320 million	[10]
Japan	9.2 billion	[11]
Russia	6.7 billion	[12]
Sweden	58–77 million	[13]
United Kingdom	3.2 billion	[14]
Unites state of America	276 billion	[15]
West Germany	1.5 billion	[16]

Different kind of corrosion, their carriers and various synthetic organic and inorganic corrosion inhibitors are mentioned in literature (Fig. 1, Table 2) [17–20], however, hazardous effects triggered by these toxic regular inhibitors paved way for green corrosion inhibitors derived from eco-friendly and biodegradable natural products. Plant extracts are widely used as green corrosion inhibitors as they reckoned to be bounteous in producing chemical compounds [21–23]. Generally, small amount of corrosion inhibitors are added to the corrosive surface of alloys or metals to decrease the rate of corrosion *via* accumulation of operative species onto affected metal surfaces by: 1) altering the anodic or cathodic cell reactions, 2) trifling the interaction between violent ions and metal surfaces, 3) enhancing metallic surface's electrical resistance by means of creating a protective layer (coating) onto the surface [2].

In this chapter different categories of corrosion, and various sources of green corrosion inhibitors has been discussed. Different natural products which are utilized for preparation of corrosion inhibitors are mentioned. Here, we will be focussing on the coating of metallic surface to prevent them from erosion. The mechanism outline has also included.

Figure 1. Corrosion under different environment conditions [24].

2. Classifications of inhibitors

Corrosion inhibitors are chemical reagents that reduce the rate of metal depletion on adding to a corrosive aqueous environment in smaller quantity. The inhibitors are classified into different categories depending on their mode of action:

2.1 Anodic inhibitor

Anodic inhibitors are liable to hinder the anodic reaction by forming either a deposit layer or a passive layer on the anode by the deposition of sparingly soluble species, like oxides, hydroxides, or salts. These are operative in the pH range of ~6.5–10.5. Examples of anodic inhibitors include NO_2^- , MoO_4^{2-} , CrO_4^{2-} , borates, molybdates, phosphates, tungstates, etc. however, they suffer a serious drawback in terms of accelerating corrosion due to poor management and hence, not fit for oil and gas industry. Inorganic anodic inhibitors offer approximately 80–95% prevention.

2.2 Cathodic inhibitor

Cathodic corrosion inhibitors inhibit cathodic reaction either by selective precipitation on the cathodic side to decrease the dispersion of deoxidized species or by decelerating their reactions by creating a shielding on cathodic zones for counterattack on hydrogen and oxygen in acidic–and alkaline conditions, respectively. Examples of Cathodic inhibitors

are oxygen scavengers, cathodic poisons, cathodic precipitates, borates or silicates in alkaline solutions,

Table 2. Different Types of Corrosion [25-29]

Corrosion	Type	Description
Localized	Crevice	Concentration cell corrosion owing to the trapping of corrosive liquid within the voids of the metal.
	Pitting	Voids are formed due to attacks on the selective portions of metal surface. The voids and unharmed fragment of the metal worked as anode and cathode, respectively.
	Filiform	Cell corrosion on surface of metal covered with a thin layer of organic film.
General	Galvanic	Result from interaction of electrolytes with different metals that varies in electrical potentials.
	Uniform	Deteriorates the whole surface or large fraction of the metal and makes the surface thin.
Microbiological	–	Loss of metal surface initiated by biological organisms and can ensue in any aqueous environments owing to omnipresence of microbes and adequate nutrients in fluids.
Metallurgical influenced	Dealloying	Capable of corroding various components of an alloy.
	Exfoliation	Occurs when corrosion propagates along intergranular paths parallel to the material surface.
	Intergranular	Corrosion ensues on the edges or the grain boundaries of the surface of metal.
Q1	Erosion	Movement supported corrosion owing to flow of corrosive liquids on the surface of metal.
	Corrosion fatigue	A combination of cyclic stress and corrosion.
	Wear	Wear Corrosion is defined as the damage caused by synergistic attack of surface failure resulting from dynamic reaction between surface and corrosion in a corrosive environment.

Environmental induced	Stress corrosion cracking	A complex type of corrosion as a result of corrosive environment and pressure.
	Hydrogen Embrittlement	Heat treatment to remove absorbed hydrogen.
	Hot cracking	Formation of shrinkage cracks during the solidification of weld metal.
	Liquid metal Embrittlement	Cracking caused by contact with a liquid metal.

inorganic phosphates, polyphosphates ($\text{Na}_4(\text{P}_2\text{O}_7)_n$), *etc.* Cathodic inhibitors function by obstructing hydrogen growth in acidic medium or by reducing the oxygen concentration in alkaline or neutral solutions. Rare earth salts also find mention as cathodic inhibitor which forms a thin film of its metal oxide at cathodic sites as a result of enflamed alkalinity at these sites due to oxygen diminished reaction and increased solubility product of these metal oxide [2].

2.3 Adsorptive corrosion inhibitors or mixed inhibitors

Additives that cause stimulation of both anodic and cathodic reactions are known as mixed inhibitors. These inhibitors adsorb on anode and cathode (metal surface) by chemisorption or physisorption and block the contact with the metal. The organic molecules having functional groups such as phosphates ($-\text{PO}_3^{2-}$), carboxylic acids ($-\text{COOH}$), amino ($-\text{NH}_2$) as well as multiple bonds in their structure form chemisorbed bonds with metal surfaces [30].

2.4 Barrier layer forming inhibitors

Corrosion inhibitors are further categorized into oxidizers, conversion layer formers and adsorbed layer former. These inhibitors form a molecular barrier on the surface of metal and are efficient in decreasing both cathodic and anodic reaction rates except the oxidizers, which transfer the corrosion tendency of the metal to specified site at which a steady oxide or hydroxide is formed and save the metal surface [31]. Santos and coworkers described displacing adsorbed water molecules from the metallic surface with soluble organic compounds inhibitors [32].

2.5 Neutralizing inhibitors

These types of inhibitors take out the hydrogen ions (H^+) from the corrosive atmosphere and hence decreasing the tendency of corrosion. These inhibitors are generally employed for the treatment of boiler waters and in oil field work.

2.6 Scavengers

These are used to eliminate corrosive species other than hydrogen ions (H^+). General example is hydrazine (NH_2NH_2) in boiler systems, which eliminates traces of cathodic reactant *viz.*, oxygen.

Other than these classifications, corrosion inhibitors can also be categorized as inorganic and organic inhibitors attributed to hard and soft acid and base theory (HSAB), and are labelled as hard, soft, and borderline inhibitors. Approximately 80% of organic inhibitors come under this category.

3. Selection of corrosion inhibitors

The phenomenon of adsorption forms the basis of the corrosion inhibition in which inhibitor gets accumulated onto the metal surface, thus, shielding the surface from encountering corrosion or by retarding electrochemical processes [33]. The corrosion inhibitors can be chosen on the basis on 1) structural features, and 2) theoretical considerations.

3.1 Structural features

In 1954 Hackerman proposed the idea of a 2-D virtual complex based on strength and stability of metal-inhibitor adsorbate complex [34]. The surface coating hinders either the anodic reaction (known as anodic inhibitors) or the cathodic reaction (alias cathodic inhibitors), or both. The coating on the surface also blocks the transference of reactant onto the product or stimulates the rate constant, which results into corrosion inhibition. One of the publications established *ortho*-substituted organic compounds, *for example*, *ortho*-toluidine as more effective corrosion inhibitor comparative to *meta*- and *para*-substituted toluidines in oil reservoirs [35]. The outcomes of structural variation and the impact of C-N-C bond angles on the backbone of organic compounds on corrosion inhibition was evaluated by altering the methylene rings of polyethylene imines. These factors strike the accessibility of the electron pairs and therefore, change the magnitude of corrosion inhibition efficacy.

Sastri [2] also revealed that a mixture of cerium chloride in 0.1M sodium chloride solution diminish rate of deterioration of Al-Zn-Mg-Cu composite by ~2 times. Popova

et al. [36] examined some benzimidazoles as corrosion inhibitor for mild steel in deaerated 1 mol L⁻¹ HCl solution. They testified that these benzimidazoles have noticeable corrosion inhibition properties. Subsequently, Popova and teammates [37] also showed 8-benzimidazole derivatives as pronounced mixed corrosion inhibitor for mild steel in acidic medium at 20°C. Their effectiveness increases with increased concentration of the additive. Furthermore, Popova *et al.* [38] also recognized azoles as mixed corrosion inhibitor for mild steel. Samardzija and associates [39] investigated four alcohols as corrosion inhibitors for iron in 1 mol L⁻¹ HCl at ambient temperatures and found that these reagents worked as mixed inhibitors and their efficiency differs on the chain length as well as location of the triple bond. Finšgar *et al.* [40] discovered a corrosion inhibitor formulation, a blended mixture of solvent, surfactant, and an intensifier with the aim of increasing the effectiveness of a corrosion inhibitor in protecting steel. The residuary charge around the metal as well as inhibitor's chemical structure facilitates the surface assimilation of inhibitors on the surface of metal.

In major applications, environment friendly, inhibitors, such as tungstates, and molybdates are widely used which have replaced governmental agencies banned organic inhibitors like chromates. Some common inhibitors such as silicates, carbonates, and borates, are still in use. Inorganic inhibitor borates provide corrosion defence by enhancing the pH of the system [2]. Therefore, it can be established that geometry, steric effects, stoichiometry and backbone of a cluster played a crucial role in designing the efficacy of anti-corrosion compounds.

3.2 Theoretical considerations

Computational tools (Quantum chemical and Molecular dynamics calculations) have been developed to study the adsorption mechanism on metallic surfaces to forecast corrosion inhibition efficacy which is otherwise quite challenging to determine experimentally. Academicians and scholars are constantly working in the theoretical field to identify the most active adsorption site present within the molecule.

Soltani and co-workers [41] performed quantum chemical calculations to illuminate the adsorption progression of extracts of two gum resins namely, *Ferula asafoetida* and *Dorema ammoniacum* in acidic media on mild steel corrosion. Molecular orbitals: highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were generated to recognize the active adsorption sites of gums on steel. The energies of HOMO, LUMO, their energy gap ($\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$), and dipole moment (μ) were calculated to relate their inhibition effect. They found that *Ferula asafoetida* is more effective corrosion inhibitor than *Dorema ammoniacum* due to its high E_{HOMO} , lower E_{LUMO} and lower ΔE .

Hasanov *et al.* [42] considered theoretical calculations to study the effects of poly(N-ethylaniline) as monolayer coating or bilayer coatings on the low carbon steel 1 M H₂SO₄ using AM1 semiempirical method. The theoretical data was well versed with experimental results. It was found that bilayer conducting polymers coatings on the steel surface in 1 M H₂SO₄ are proficient than monolayer coating conditions as interaction of additive with the steel surface was dependent on electron donor tendency of oxidized forms of dimers. Peter *et al.* [43] used quantitative structure activity relationship method on natural gums to study their efficiency as green corrosion inhibitors.

Egbedi *et al.* [44] implemented theoretical studies on red apple fruit extract to utilize them as green corrosion inhibitors. They observed a dipole interaction between the chemical additive and metal surface and concluded that physical adsorption occurred from electrostatic contact amid charged metal surface and charged centres of additive. Oguzie [45] performed Molecular dynamics simulations to theoretically elucidate the electronic structure as well as adsorption behaviour of alkaloid constituent of Capsicum frutescens extract and to study their corrosion obstructing action on carbon steel.

Umoreon and colleagues [46] investigated DFT-based quantum chemical computations on red apple fruit extract as corrosion inhibition for mild steel in hydrochloric acid (HCl). Inhibition proficiency was found to intensify with the escalation in temperature and concentration. Polarization curves specified red apple extract behaved as mixed-type inhibitor. Low energy band gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) indicated a stable complex formation with the metal surface, consequently enhanced adsorption of additive on the metal surface. Also, high dipole moment (μ) value recommend adsorption occurred by physical mechanism.

Mehmeti and Podvorica [47] performed Molecular Dynamic and Monte Carlo calculations to study the adsorption behaviour of carboxylated graphene oxide with reference to Nb, Ta, their oxides (NbO, TaO) surfaces. Shen and coworkers [48], Hajjahmadi and Tavangar [49] also performed theoretical studies on gum Arabic as corrosion inhibitor in oil industry and pyrimidine derivatives corrosion inhibition on iron, respectively.

4. Sustainable green corrosion inhibitors

Environmental distresses need corrosion inhibitors that are conventional, eco-friendly and non-toxic. Green chemistry provides a reservoir of sustainable green corrosion inhibitors (Fig. 2, Table 3). Plant products are rich sources of globally acceptable environment-friendly green corrosion inhibitors such as alkaloids, phthalocyanines, terpenes, *etc.*

4.1 Natural sources of green corrosion inhibitors

First report on inhibition of corrosion of iron in acids using extracts of gelatin, glue, and bran was given by Marangoni and Stefanelli in 1908. The first patent in the field of corrosion inhibition was given to Baldwin (British Patent 2327), which stated the utilization of naturally obtained molasses with vegetable oils for preserving sheet steel in acids. Recently, gums obtained from plants also finds mentioned as an important class of green corrosion inhibitors. These are mixtures of polysaccharides which either possess hydrophilicity or absorb water and gets swell up on captivating water to form a jelly like structure [43].

Figure 2. Some widely used natural products exploited as green corrosion inhibitors.

Eddy *et al.* [50] researched on gums and recognized them to be harmless, eco-friendly and virtuous green corrosion inhibitors for mild steel in 0.1 M HCl due to various reasons. They can form adsorbate complexes with the metal or their surfaces *via* their functional group and the surface gets blanketed from corrosive agents. The presence of carbohydrates like arbinogalactan, glucoprotein, oligosaccharides, polysaccharides, and

sucrose provide ample of oxygen and nitrogen atoms to the gums and hence, possess multiple sites for adsorption. Most of the gums possess carboxylic group, which has property to intensify electronic or charge transfer, hence, enable inhibition *via* adsorption.

Gudić and co-workers [51] implemented Quantum chemical and molecular dynamics studies to evaluate adsorption of one caffeine molecule and polymeric structure of caffeine on copper surface and was well versed with the experimental results. Also, increase in number of caffeine molecules on the adsorptive site increases the binding energy. Caffeine was established as a cathodic inhibitor as a result of adsorption on the copper surface agreeing Langmuir adsorption isotherm. A negative free energy of ~ -37 kJ mol⁻¹ specifies robust adsorption of the caffeine on copper surface.

The corrosion inhibition efficiency of lemongrass extract was assessed for carbon steel in oilfield water by means of electrochemical impedance spectroscopy as well as weight loss method. Quantum chemical calculations in addition to molecular dynamics simulations were also performed on two abundant species, *namely* geranial and neral present in lemongrass extract to gain knowledge about probable active sites apt for adsorption. The corrosion rate was found to decrease with both geranial and neral, however, former has slightly better tendency to get adsorbed on iron surface than later [52].

The corrosion inhibitory efficacy of Senecio anteuphorbium (SA) extract on S300 steel in 1 M HCl was estimated by using electrochemical impedance spectroscopy and potentiodynamic polarization. SA extract worked as mixed-type inhibitor for steel corrosion in acidic media as established from their polarization curve. The adsorption inhibition was found to enhance with increasing extract concentration and attained a maximum of 91% and followed Langmuir isotherm. Activation energy values proposed it as a physical-chemical adsorption [53].

Sharma *et. al.* [54] investigated anti-corrosion action of Azadirachta indica (neem) for mild steel, aluminium, and tin using computational approach. The reports on NaOH extracts of Ziziphus jujuba leaves [55], stem bark of Mangifera indica [56], Moringa oleifera [56], terminalia arjuna [56], as mixed-type inhibitors for aluminium were also recognized. Hibiscus petal extract in H₂SO₄ was also testified as a mixed-type inhibitor against pure aluminium [57]. Aspilia africana leaf extract in HCl was cited as a cathodic inhibitor for aluminium [58].

To make environment clean, scientists are constantly exploring natural new products as green corrosion inhibitors. Research work done on this topic includes utilization of barley remains [59], opuntia [60], vernonia [61], hibiscus [62], mangrove [63], tree roots [64], and overabundance of others are explained in Table 3.

Table 3. Sustainable green corrosion inhibitors

Source of natural products	Metal/Alloy	Reference
Leaves and roots of medicinal plants	Mild steel	[64]
Sodium molybdate and calcium gluconate synergism	Carbon steel	[65]
Zinc phosphate base, molybdate base inhibitors	Carbon steel	[66]
Hibiscus sabdariffa	Steel	[62]
Mixture of Garcinia kola + KI	Mild steel in H ₂ SO ₄	[67]
Acid extracts of Calotropis gigantea	Mild steel in acid medium	[68]
Carica papaya extracts	Mild steel in acid medium	[69]
Bacillus mycoides	mild steel, aluminium, zinc	[70]
Structure composed of Zn ²⁺ , ascorbate, and –N, N-bis-(phosphonomethyl) glycine	Carbon steel	[71]
Phosphonated glycine	Carbon steel	[72]
Rosemary oil	Steel in phosphoric acid	[73]
Powdered seeds of Eugenia jambolans	Mild steel in HCl	[74]
Nicotinic acid	Zn, Zn–Al steels	[75]
Mangrove tannins	Steel	[63]
Carboxymethylchitosan	Mild steel in 1M HCl	[76]
Datura stramonium extract	Mild steel	[77]
Surfactants	Stainless steel	[78]
Black pepper extract	Mild steel in H ₂ SO ₄	[79]
Cerium	Tin plate	[80]
Azadirachta indica	Mild steel, tin, aluminium	[81]
Xanthates	Steel	[82]
Pomegranate fruit shells	Steel	[83]
Eucalyptus extract	Steel	[84]
Jasminum auriculatum	Steel in NaCl	[85]
Barbiturates	Mild steel in 1M HCl	[86]

Table 3. Sustainable green corrosion inhibitors contd.....

Source of natural products	Metal/Alloy	Reference
Tobacco leaves	Mild steel and aluminium	[87]
Natural honey	Carbon steel	[88]
Vanillin	Carbon steel	[89]
Vernonia amygdalina	Aluminium alloy	[61]
Allium cepa	Mild steel	[90]
Guar gum	Carbon steel in acid	[91]
Caffeine	Copper	[51]
Halfabar	Steel	[92]
gum from Dacryodes edulis	Aluminium	[93]
Chitosan	Copper	[94]
Flour and yeast	Iron in acid	[95]
Opuntia extract	Aluminium	[60]
Reducing saccharides fructose and mannose	Aluminium and zinc	[96]
Mangifera indica	Aluminium	[56]
Aspilia	Aluminium	[58]
Ziziphus jujuba leaves	Aluminium in NaOH	[55]
Xylopi aethiopica seeds in KOH	Aluminium	[97]
Moringa oleifera	Aluminium alloy in 1M NaOH	[56]
Eugenol from cloves	Steel	[98]
Polyphosphate–silicate–zinc	Steel	[99]
Recent Patents		
Polybenzoxazine–Chitosan	Steel	[100]
Polyaspartic acid–phosphinocarboxylic acid–hydroxyphosphonoacetic acid	Carbon steel	[101]
Polyaspartic acid–Sn (II) or Sn (IV)	Carbon steel	[102]
Corn stillage product	Steel	[103]

4.2 Ionic liquids (ILs) as green corrosion inhibitors

Scientists are also searching a feasible alternative in ILs as a green option to use them as green corrosion inhibitor apart from inhibitors attained from plants as decontamination of plant extracts is tiresome, strenuous, and tremendously costly as well as more time consuming, and needs comparatively huge quantity of organic solvents which can unfavourably influence the atmosphere and living beings moreover elevated temperature can also degrade the active components and thus reduce comparative inhibition competence. Progress of green chemistry and new greener chemical knowledge presents new synthetic routes for ILs, which is now a day's explored as innovative green corrosion inhibitors. Consequently, there is an urgent need of the hour to expand green inhibitors (due to various applications, Fig. 3) by suitable mean of the amalgamation, which could be accomplished by employing inexpensive and environmentally benign goods. This is the commencement of green chemistry as ILs is sustainable and eco-friendly solvents containing ions that have an ability to relocate a broad variety of organic and inorganic compounds.

ILs pursues the green chemistry principles which are projected by Anastas and his colleague Warner [104]. ILs present enlightening workspace in the era of benign chemistry, thereby gaining immense popularity as they are broadly employed in a range of applications. It is found that chitosan which is a straight chain copolymer type having formula (1-4)-2- acetamido-deoxy-d-glucan (N-acetylglucosamine) and (1-4)-2- amido-2-deoxy-d-glucan (glucosamine), are main basis of ILs. Chitosan is dug out from shell of the crab based on amino polysaccharides and have been utilized to create quite a lot of new-fangled materials [105,106]. Their elevated aptitude for functionalization builds them valid to use in numerous manufacturing applications since they display improved solubility in aqueous and organic solvents as compared to chitosan. Chitosan has a potential to prevent the corrosion of copper in acidic solution since hydrogen chloride is employed as a mixed-type inhibitor (work together with the help of other), pursuing a Langmuir isotherm [107].

Protection of metallic corrosion in the occurrence of ILs engages inhibition of oxidative metallic dissolution at anode along with hydrogen evolution reactions at cathode [108] as shown:

Where

M = dissolution of metals at anode in corrosive solution made in aqueous medium

ILsC^+ = ionic liquid cationic equivalent

X^- = ionic liquid anionic equivalent

Mechanistically, anionic counterpart (X^-) draw charge from cationic counterpart of the ILs (ILsC^+) *via* Coulombic forces of attraction (known as physio-sorption) and outline a unimolecular layer as hydrophobic composite on the surface of the metal. The accumulation of ILsC^+ on the surface of the metal results in the modification of the polarity of the surface, that persuades readsorption of X^- and ILsC^+ ions on the surface forming multi-molecular deposits [108]. These deposits then become stable by van der Waal's force of attraction among organic entities of the ILs, consequently forming a more intimately adsorbed layer at the interfaces of metal–electrolyte. In general, ILsC^+ network with the surface of the metal and outline the multi-molecular layers, whereas the remaining ILs form hydrophobic surface agglomeration [108,109]. multi-molecular deposits on the ILs separates the metal from its corrosive atmosphere and guards it from degradation.

4.3 Vapor–phase inhibitors (VPI)

VPI are a class of corrosion inhibitors having high atmospheric pressure and are volatile in nature. Now a days they are widely emerging as potent green inhibitors and also requisite in numerous grounds including packaging, electronics, manufacturing processing, resistant solid, finishing, and metal working solutions owing to their harmless characteristics. As they are free from nitrites, phosphates, and halogens hence considered to be completely safe to handle. Moreover, VPI are proficient in preventing the deterioration of iron and non–iron metals.

As literature shows, Bastidas *et al.* [110] considered a range of aspects impacting VPI act and mechanisms. It is also explored that nano–vapor–phase inhibitors derived from renewable agricultural waste stabilize the natural balance of the environment (Trash to Treasure approach). Their properties are dependent on their dispersal, seizing all empty space as well as active sites through defensive vapor molecules which are fascinated to surface of the metal and adsorbed physically or chemically onto the resultant formed nano–protective barrier film [111,112].

5. How do green inhibitors act as corrosion inhibitors?

Corrosion, an unprompted progression is measured via kinetics studies and is linked to the variation in standard Gibbs free energy (ΔG°). Large $-\Delta G^\circ$ value indicates elevated unprompted progression, *i.e.*, elevated corrosion kinetics [113]. Metals and their alloys tend to form stable corrosion products when exposed to any atmospheric medium [114]. To reduce the corrosion rate, corrosion inhibitors are required. Corrosion products like

scale and rust can itself work as corrosion preventers since they are having a tendency to assemble on the metallic surface and serve as outer defensive barriers; though, the corrosion kinetics of the metal is dependent upon the Pilling–Bedworth ratio [115,116]. The ratio could be employed to check the potency of the surface film and is described as follow:

$$\frac{M * d}{n * m * D}$$

where, M, D, n depicts molecular weight, density and amount of the atoms of deposited deterioration product on the surface of metal; d, m represents density and atomic weight of metal, respectively.

If the degree of deterioration of product is reasonably lesser comparative to its precursor metal, then Md/nmD is less than 1 and these circumstances institute that the outer surface layer of the deterioration product includes holes and splits that are comparatively non-shielding. However, Md/nmD greater than 1 specifies that the deterioration of product is higher than that of precursor metal, affirming outer surface layer of the deterioration product as comparatively compact, dense and packed tightly and consequently recognised as a palisade layer.

Generally, these inhibitors include some functionality sometimes along with π -electrons which are in resonance with double or triple bonds, influencing organic compounds through particular binding among required elements *e.g.* nitrogen, oxygen and sulphur *via* freely available lone pairs of electrons, and then get accumulated on the surface of the metal or by providing electrons (e^-) from π -orbitals [117]. Through a mechanistic point of view, process of corrosion can be seen *via* following way: During deterioration, metal ions (M^+) flow towards active sites of fluid (anode) and transfer e^- towards less active site *i.e.* cathodic acceptor. This cathodic route needs the availability of an e^- acceptor like hydrogen ions (H^+), oxygen or other oxidizing agents, or. Deterioration could be reduced by delaying or entirely ending the cathodic and/or anodic reactions. A protective barrier is formed when an inhibitor is adsorbed on the metallic surface. This barrier interacts with cathodic and/or anodic reaction areas to reduce the oxidation reactions or other corrosive reactions [22].

Common cathodic reactions occurring in corrosive environment are as follow:

Reduction reaction comprises evolution of hydrogen gas as shown:

Eq. 5 shows accumulation of hydrogen ions (H^+) on the surface of metal and lead to evolution of hydrogen gas (H_2) on cathodic surface due to the amalgamation with other hydrogen ions (H^+). Quantity of hydrogen gas evolved refers to capacity of inhibitor to stop this process and saving metal from deterioration [23]. Here adsorption of inhibitor on the exposed surface of metal occurred as neutral molecules.

This process can easily be explained by following reaction:

or *via* replacement of molecules of water on the surface of metal, as explained using Eq. 4.

These green corrosion inhibitors possess wide variety of applications in various fields and are displayed in Fig. 3.

Figure 3. Applications of green corrosion inhibitors in various industries.

Conclusion

The goal of this chapter is to reassess biogenic compounds as valuable green and natural corrosion inhibitors due to various characteristics such as their biodegradability, effortless accessibility, economical and safe nature. Literature surveys mentioned biogenic plant extracts as efficient green deteriorators for different metals and their

alloys. Moreover, the article also centred on “the competence of green and sustainable inhibitors for the corrosion of metals and alloys is favoured as compare to conventional corrosion inhibitors”. At last, interest was shown to the adsorption behaviour of green inhibitors usually, following the Langmuir isotherm and by means of DFT-based quantum chemical simulations. Quantum chemical computations offer a superior approach interested in the inhibition pathway. The affinity to investigate VPI and green nano inhibitors is a fresh quarter for upcoming investigations.

Voluminous research in this field is yet to be explored, particularly virtual computational modelling of the chief extract entities of diverse metals and their alloys. additional investigation should be determined too on various plant extraction protocols and their dynamic components along with scale-up procedures for business relevance that are required to market these biogenic extracts to successfully reinstate traditional chemicals.

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