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Chapter

Green Corrosion Inhibitors

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Abstract

Corrosion is an unavoidable fact in everyday life but always receive attention to control due to its technical, economical, and esthetical importance. Corrosion inhibitors are one of the most widely used and economically viable methods protecting metals and alloys against corrosion. Typical corrosion inhibitors are bio-toxic organic compounds, which have serious issue on toxicity. Considering the toxicity of the inhibitors, there is a tremendous interest in searching for an eco-friendly, and non-toxic green corrosion inhibitor. This chapter briefly discusses the importance and different methods of corrosion inhibitors with a particular emphasis given to the discussion on the different characteristic feature of the green corrosion inhibitors reported in the literature as a comparative view of organic inhibitors.

Keywords: corrosion inhibitors, mild steel, green corrosion, organic, adsorption

1. Introduction

Generally, corrosion is regarded as the loss of a metal by the influence of corrosive agents [1]. However, in a broad sense, corrosion is the devastative consequence of chemical reaction between a metal or metal alloy and its environment [2]. General corrosion or uniform corrosion is the most prevalent form of corrosion that takes place on an entirely exposed metal surface *via* the electrochemical reactions in atmospheric or aqueous media and continues uniformly to cause the greatest destruction of that metal [3]. Even though only metals come to mind when describing corrosion, non-metallic materials, such as plastics, concrete, ceramics, rubber, etc. are prone to corrosion as well when exposed to different corrosive environments [4].

The difference in the potential energies of the corroding metal and the corrosion product is the fundamental force that drives the corrosion reaction. A certain amount of energy is required to be provided to naturally occurring minerals and ores to extract metals from them. Therefore, it is natural that these metals tend to revert back to their original state from which they were obtained when they are exposed to their environments. It is noteworthy that each metal is different in terms of the amount of energy required and stored in it or that is released during its corrosion. The greater the amount of energy needed during metal extraction, the more thermodynamically unstable is the metal and the shorter is its temporary existence in metallic form. Hence, corrosion has also been defined as the reverse of extractive metallurgy [1, 5].The electrochemical dissolution of a metal is the most important mechanism involved in its corrosion and makes the basis of all uniform and localized corrosion types. However, there are some corrosion types, such as oxidation, fretting corrosion, molten salt corrosion, etc. that can be described without reference to electrochemistry [1]. The mechanism of corrosion attack in an atmospheric environment and in an aqueous environment will be always governed by some

aspect of electrochemistry. Electrons will be flowing from certain areas of a metal surface to other areas through an electrolyte that is capable of conducting ions. This stems from the incredible tendency of metals to react electrochemically with water, oxygen, and other substances in the aqueous environment. In an electrochemical corrosion process, the anode is that area of the metal surface that is corroding due to the loss of electrons while the cathode is the area that consumes the electrons generated by the corrosion reaction [6].

Almost all of us are familiar with corrosion happening to metal structures, boats, steel pilings, household utensils, etc. Unfortunately, many of us are not aware of corrosion that is deteriorating the properties of underground water, oil, and gas pipelines crisscrossing our land or water pipes in the home where corrosion occurs mostly from the inside. Successful enterprises put in considerable efforts in controlling corrosion at the design stage and in the operational phase to avoid major corrosion failures, such as unscheduled shutdowns, fatalities, personal injuries, and environmental contamination in a modern business environment. However, even the best design is unable to foresee all conditions that can allow corrosion intruding into the life of a system [5]. Steel reinforced bar (rebar) can corrode in concrete without being noticed at all and can cause damage to buildings, bridges, parking structures, the collapse of electrical towers, failure of a section of highway, etc., resulting in a huge amount of repairing cost and threatening public safety [7]. This is why regular maintenance of the metallic components that are susceptible to corrosion is of paramount importance.

2. Impact of corrosion

Even though the main reasons for considering corrosion are economic and ecological, losses due to corrosion or costs of corrosion can be actually divided into three main categories as shown in **Figure 1** [8].

2.1 Material and energy

The impact of corrosion on the equipment and its surrounding deserves a huge attention when it comes to designing an industry. Corrosion is considered to be one of the most challenging issues for most of the industrialized countries. Corrosion of tanks, piping, metal components of machines, bridges, ships, etc. can incur a massive material and economic losses upon a nation. Additionally, the safety of operating equipment, such as boilers, pressure vessels, metallic containers for toxic chemicals, bridges, turbine blades and rotors, automotive steering mechanisms, and airplane components can be threatened by corrosion failure [8]. Furthermore, the
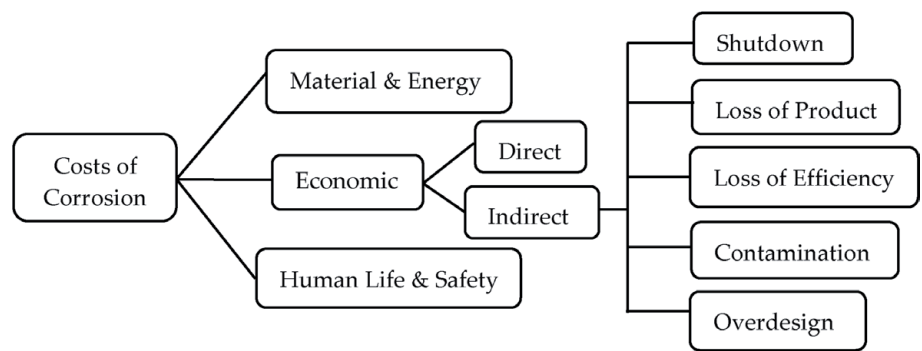

Figure 1.
Breakdown of corrosion costs.

devastative impact of corrosion goes beyond the metals and extends to energy, water, and the manufacturing phase of the metal frames [9]. It has been reported that one ton of steel turns into rust every 90 seconds, and, on the contrary, the energy needed to manufacture one ton of steel is approximately equal to the energy an average family consumes over 3 months. Approximately 50% of every ton of steel produced by the world is used to replace rusted steel [10].

2.2 Economic

Economic losses are classified into two types: (i) direct losses and (ii) indirect losses. Replacing the corroded structures and machinery of their components, for instance, mufflers, condenser tubes, pipelines, metal roofing, including necessary labor, repainting structures to prevent rusting, maintenance cost of cathodic protection system for underground pipelines, replacement cost of millions of domestic hot-water tanks and automobile mufflers, extra cost of using corrosion-resistant metals and alloys, galvanizing or nickel plating of steel, addition of corrosion inhibitors to water, and dehumidifying cost of the metal equipment storage rooms contribute to the direct losses. While it is quite difficult to assess the indirect losses, they have still been reported to add several billion dollars to the direct losses. Indirect losses include sudden shutdown of plants, loss of water, gas, or oil through a corroded pipeline, loss of efficiency in the energy conversion systems imposed by corrosion processes, contamination of water and food products in metal piping and containers, and overdesign requiring equipment to be designed many times heavier than normal operating pressure or applied stress to extend their lifetime [8]. Uhlig made the first ever systematic study on the cost of corrosion in 1949 [11]. Uhlig's report estimated the annual cost of corrosion in the United States to be US$ 5.5 billion or 2.1% of the 1949 gross national product (GNP). This study measured the total costs by summing the costs related to anti-corrosion materials and corrosion-induced maintenance and replacement handled by owners and operators (direct) as well as those related to users (indirect) [5, 12].

Corrosion cost studies using different methods, such as Uhlig method invented by Uhlig in 1949 [11], Hoar method invented by Hoar in 1971 [13], and economic input/output model devised by National Bureau of Standards (NBS) collaborating with Battelle Memorial Institute in 1978 [14] have been undertaken by several major economies, including Australia, China, Finland, Germany, India, Japan, Kuwait, the United Kingdom, and the United States [15]. A common observation of these studies was that the costs of corrosion ranged from approximately 1–5% of the GNP of each nation. The variation in the corrosion cost with respect to GNP was ascribed to the methodology used by each study and the specifics of each country [12].

A study done by National Association of Corrosion Engineers (NACE) as part of its International Measures of Prevention, Application, and Economics of Corrosion Technologies Study (IMPACT) revealed that the global cost of corrosion in 2013 was estimated to be US$ 2.5 trillion which was equivalent to 3.4% of the global GDP in that year [15]. This study utilized the World Bank economic sector and GDP data to relate the cost of corrosion studies to a global cost of corrosion. In order to address the economic sectors across the world, the global economy was divided into economic regions with similar economies (according to World Bank). These were: United States, European Region, India, Arab World (defined by the World Bank), Russia, China, Japan, Four Asian Tigers plus Macau, and Rest of the World. However, the costs estimated typically do not include environmental consequences or individual safety. It is noteworthy that receiving additional funds for corrosion studies, or updated information on these studies, more detailed and accurate global costs can be assessed.

2.3 Human life and safety

Corrosion can take a toll more than imaginable in human life and safety. This destructive phenomenon has been overlooked as the main reason of many fatal accidents for reasons of liability or simply because the evidence disappeared in the catastrophic event. The Silver Bridge collapse is one of the most dangerous and discussed corrosion accidents [16]. On December 15, 1967, this bridge connecting Point Pleasant, West Virginia and Kanauga, Ohio suddenly collapsed into the Ohio River to claim 46 lives. Stress corrosion cracking (SCC) and corrosion fatigue were determined to be responsible for this disaster. The Bhopal accident that took place in Bhopal, India on the night of the December 2–3, 1984 is one of the worst industrial accidents in terms of the lives lost and injuries. An unfortunate seepage of water (500 liters) caused by the corrosion of pipelines, valves, and other safety equipment into a methylisocyanate (MIC) storage tank at Union Carbide India Limited caused the release of MIC and other toxic reaction products into the surrounding areas that killed 3000 people and injured an estimated 500,000 people [17]. Swimming Pool Roof Collapse is another infamous corrosion accident that took place in Uster, Switzerland in 1985. The roof of this swimming pool was supported by stainless steel rods that failed due to SCC and killed 12 people [18].

3. Techniques for corrosion measurement

3.1 Weight loss measurement

Weight loss analysis is known to the simplest, most reliable, and long-established method of assessing corrosion losses in plant and equipment. A sample of metal or alloy under experiment is weighed and then immersed into a corrosive solution, and later removed from the corrosive medium after a predetermined time interval. The metal specimen is then weighed again after cleaning all corrosion products. The corrosion rate, surface coverage (θ), and corrosion inhibition efficiency ($\eta\%$) can be calculated using (Eqs. (1)–(3)):

$$\text{Corrosion rate} \left(\frac{mm}{year}\right) = 8.76 \times 10^3 \frac{m_i - m_f}{S\rho t} \tag{1}$$

$$\theta = \frac{CR_o - CR}{CR_o} \tag{2}$$

$$\eta\% = \frac{CR_o - CR}{CR_o} \times 100\% \tag{3}$$

where m_i is the weight of the metal sample in grams before immersion, m_f is the weight of the metal sample in grams after immersion, S is the total area of metal in cm^2 that has been exposed to corrosive solution, ρ is the density of metal sample in g/cm^2, t is the time in hours during which the sample was immersed, $CR_\circ$ and CR represent the corrosion rates (in mmpy) without and with the inhibitor, respectively [19, 20].

3.2 Polarization measurements

Since corrosion is a phenomenon that involves electrochemistry, electrochemical-based corrosion measuring experiments provide valuable information about the

rate of corrosion and mechanism of corrosion protection [20]. Polarization methods are based on changing the current or potential on a sample under investigation and recording the corresponding potential or current change. This can be facilitated with the help of either a direct current (DC) or an alternating current (AC) source [5]. Some important and widely used techniques have been discussed briefly below.

3.2.1 Tafel extrapolation

Tafel curve is a current-potential plot that shows the anodic and cathodic reactions in the electrochemical cell. In this method, the potential of the working electrode (metal sample) varied over a range at a specific rate and the resulting response in current is recorded. The anodic and cathodic reactions that are taking place simultaneously produce a total current that is represented by a curved line. The linear portions of logarithmic Tafel plot are extrapolated to produce an intersection that generates a point that signifies an approximation of the corrosion current (i_{corr}) and the corrosion potential (E_{corr}). This i_{corr} facilitates the calculation of the corrosion rate based on (Eq. (4)) and the corrosion inhibition efficiency ($\eta\%$) based on (Eq. (5)):

$$\text{Corrosion rate} \quad = \quad \frac{i_{corr} \times K \times EW}{\rho \times A} \tag{4}$$

$$\eta\% = \frac{i^o_{corr} - i_{corr}}{i^o_{corr}} \times 100\% \tag{5}$$

where K is a constant that represents the units for the corrosion rate, EW is the equivalent weight in gram/equivalent, ρ is density in g/cm^3, A is the area in cm^2 exposed to corrosive solution, i^o_{corr} and i_{corr} are the corrosion currents in amperes without and with the inhibitor, respectively.

3.2.2 Linear polarization resistance (LPR)

Because the linear polarization resistance (LPR) method is non-destructive [21], it has quick application and can be used in the field test through portable instrumentation [22], it is the most popular of the electrochemical techniques [23]. The principal of LPR is based upon introducing a small perturbative DC electrical signal to disturb the corrosion equilibrium on the surface of metal specimen. The response of the equilibrium to this perturbation is measured with respect to a reference half-cell [24]. The polarization resistance (R_p) of a material is known to be the $\Delta E/\Delta i$ slope of a potential-current density curve at the free-corroding potential. The polarization resistance can be related to the corrosion current (i_{corr}) using the Stern-Geary approximation in which the anodic (b_a) and cathodic (b_c) Tafel slopes can be experimentally obtained from real polarization plots.

3.2.3 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a very powerful electrochemical technique that has wide applications in the evaluation of coatings in corrosion research. This technique provides valuable information about the corrosion protection imparted by an inhibitor. In this technique, an AC voltage (in the case of potentiostatic EIS) or current (in the case of galvanostatic EIS) is applied to the system under investigation to receive response in the form of AC current (voltage) or voltage (current) as a function of the frequency. This technique can be

performed in a 2- or 3-electrodes system with the help of a potentiostat-galvanostat and a frequency response analyzer (FRA) [25]. Usually, an AC voltage having small perturbations ranging from 5 to 10 mV is applied in the system over a range of frequencies typically starting from 100 kHz to 10 mHz. Based on the shape of the Nyquist plot produced by the experiment, the electrochemical cell containing the metal sample, adsorbed inhibitors, and the electrolyte medium is represented by an equivalent circuit that includes information about the solution resistance R_s, charge transfer resistance R_{ct}, and the double layer capacitance C_{dl}. A large R_{ct} value and decreasing C_{dl} values with increasing inhibitor concentrations indicate better corrosion protection [26].

4. Corrosion inhibitors

A corrosion inhibitor is known as a chemical constituent that can diminish or prevent and control corrosion when added in small amount to the metal environment. Corrosion inhibitors are considered as the first line of defense against oil and chemical industry corrosion [27]. Corrosion inhibitors are sought after giving metals temporary protection during transportation and storage as well as localized protection to prevent corrosion that may have resulted from accumulation of small amounts of an aggressive phase. An effective corrosion inhibitor should be cost-effective, compatible with the corrosive medium, and produce desired effect when present in small concentrations [28]. Corrosion inhibitors act by (i) forming a film that is adsorbed on the metal surface, (ii) producing corrosion products, for example, iron sulfide (FeS) that acts as a passivator, and (iii) yielding precipitates that can eliminate or inactivate an aggressive constituent [29].

Depending on which electrochemical reactions are being blocked, these film-forming or interface inhibitors can be classified into anodic, cathodic, or mixed-type [28, 30]. Anodic inhibitors, alternately known as passivation inhibitors, suppress the rate of anodic reactions by producing sparingly soluble deposits, such as hydroxides, oxides, or salts in close to neutral conditions. On the other hand, cathodic inhibitors function by reducing the rate of cathodic or reduction reactions by producing a protective layer on cathodic areas against hydrogen in acidic conditions and oxygen in alkaline conditions. Mixed inhibitors influence both the anodic and cathodic reaction sites by forming an adsorptive film on the metal surface. About 80% of organic inhibitors fall into this category. Based on the chemical nature of the inhibitors, they can be divided into organic and inorganic [31]. Organic and inorganic inhibitors, based on their compositions and mechanism of actions, can be further classified into neutralizing, scavenging, barrier or film-forming, and other miscellaneous inhibitors [32].

4.1 Organic inhibitors

Organic inhibitors act through forming a film on the surface of the metals and they can act as anodic, cathodic, or mixed inhibitors. The formation of this protective film happens with the help of strong interactions, such as π-orbital adsorption, chemisorption, and electrostatic adsorption that prevent the corrosive species from attacking the metal surface [33]. This adsorption is usually one molecular layer thick and does not penetrate into the bulk of the metal itself [34]. Physicochemical properties, such as functional groups, steric factors, aromaticity, π-orbital character of donating electrons, electron density at the donor atoms, and the electronic structure of the molecules govern the adsorption process [35, 36]. The corrosion inhibition efficiency of an organic inhibitor relies on its adsorption

ability and mechanical, structural, and chemical characteristics of the adsorption layers formed under a specific environment [37]. An efficient organic inhibitor will usually contain polar functional groups with S, O, or N atoms in the molecule and a hydrophobic moiety that will repel the aqueous corrosive species away from the metal surface. However, the polar head is considered to be responsible for establishing the adsorption layer [38]. Some chemical families of organic inhibitors are pyridines, fatty amides, imidazolines, and 1,3-azoles [39].

4.2 Inorganic inhibitors

Inorganic inhibitors are those inhibitors in which the active substance is an inorganic compound. The addition of electropositive metal salts to a corrosive medium is one of the simplest ways to improve the passivity of a metal. However, the protective metal ion must have a redox potential more positive than the one to be protected and potentially more positive than that required for discharging protons so that the protective metal ion can be discharged on the surface of the metal in need of protection. Cathodic depolarization by overvoltage reduction and subsequent formation of an adherent deposit take place through the deposition of the protective metal on the surface of the metal susceptible to corrosion. Some of the metals that serve this purpose are palladium (Pd), platinum (Pt), iridium (Ir), rhodium (Rh), mercury (Hg), and rhenium (Re). Many inorganic anions, such as chromates (CrO_4^{2-}), molybdate (MoO_3^-), silicates (SiO_4^{4-}), phosphate ($H_2PO_3^-$), and nitrate (NO_2^-) as well provide passivation protection to the metal surfaces through their incorporation into the oxide layer [39].

Environmental friendliness, cost, availability, and toxicity are some factors that should play an extremely important role when it comes to choosing an inhibitor for a particular condition [40]. The toxicity, biodegradability, and bioaccumulation of conventional corrosion inhibitors discharged into the environment are matter of huge concern. Even though the environmental implications of commercial corrosion inhibitors are not fully understood, it is not unknown that their chemical components have hazardous impact [41]. Inorganic inhibitors, for example, arsenates, phosphates, chromates, and dichromates not only have shown promising inhibition efficiency but also have been proved intolerant as well due to the threat they pose to our social health in the long run [42]. Likewise, the ecological and health risks associated with the organic inhibitors have pushed us towards finding or using non-toxic or green corrosion inhibitors that would impart maximum protection to the metallic structures but have least impact on mankind and nature [36].

4.3 Green corrosion inhibitors

Corrosion inhibitors are extensively used for the protection of metals and equipment and they are required to be acceptable, non-toxic, and eco-friendly due to environmental concerns. The cost and harmful effect associated with the commercial organic and inorganic inhibitors have raised considerable awareness in the field of corrosion mitigation. Thus, corrosion scientists and engineers are more inclined towards the implication of green corrosion inhibitors that are inexpensive, readily available, environmentally friendly and ecologically acceptable, and renewable. Several classes of such inhibitors have been discussed briefly below.

4.3.1 Plant extracts

Umoren et al. investigated the inhibition efficiency (IE) of gum arabic (GA) in absence and presence of halide ions on mild steel in 0.1 M H_2SO_4 at different

temperatures. In weight loss analysis, 0.05 M KCl, 0.05 M KBr, 0.05 M KI, and GA (0.5 g/l) alone imparted IE of 27.7, 32.2, 53.6, and 37.9%, respectively, at a maximum temperature of 60°C. At the same temperature and under similar technique, GA mixed with all of these halide solutions individually showed increased efficiency of 38.7, 47.1, and 59.1%, respectively. The ion-pair interactions between the organic cations and the halide anions have contributed to increased surface coverage that eventually led to better synergistic protection [43]. The IE of GA on AA1060 type aluminum sheets with 98.5% purity was examined at 40°C. It was found that GA (0.5 g/l) showed IE of 74.2 and 75.9% measured by hydrogen evolution and thermo-metric methods, respectively [44]. Buchweishaija and Mhinzi [45] investigated the IE of gum exudates from *Acacia seyal* var. *seyal* and Acacia gum from *seyal* var. *seyal* on mild steel in chlorinated drinking water using potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS) techniques. Gum exudates showed maximum IE of 98.5% at a concentration of 1000 ppm at 30°C. On the other hand, Acacia gum showed an IE of 96.8% at an elevated temperature of 80°C at a concentration of 600 ppm.

The anticorrosive effect of a composite coating containing chitosan (CS; green matrix), oleic acid (OA), and graphene oxide (GO; nanofiller) on mild steel in 3.5 wt.% NaCl solution has been studied by Fayyad et al. [46]. The IE of the nano-composite coating was measured by PP and EIS techniques. It was observed that oleic acid-modified chitosan/graphene oxide (CS/GO-OA) film showed corrosion resistance 100 times better than pure chitosan (CS) coating. Additionally, oxygen transmission rate (OTR) measured for the CS/GO-OA was found to decrease by 35 folds in comparison to the pure chitosan film. This decreased OTR for the CS/GO-OA coating demonstrates that an effective barrier between the metal surface and the corrosive electrolyte species was developed. Alaneme et al. [47] experimented the IE and adsorption characteristics of elephant grass (*Pennisetum purpureum*) extract on mild steel in 1 M HCl solution. At room temperature (RT), the inhibitor showed efficiency greater than 95% and increasing with increasing concentration of the extract but decreasing with increasing temperature. The presence of hydroxyl (O-H) and unsaturated (C=C) groups that have inhibitory properties were confirmed in the extract by FT-IR investigation. The scanning electronic micrographs showed significant pitting on the metal substrate that was immersed in 1 M HCl solution without the inhibitor and pitting was rarely present in the solution that contained inhibitor. The lower rate of iron dissolution in the corrosive solution that contained inhibitor was further confirmed by a higher Fe peak by energy dispersive spectroscopy (EDS) spectrum.

The inhibitory effect of hydroxyethyl cellulose (HEC) on 1018 c-steel corrosion in 3.5% NaCl solution was studied by El-Haddad using PP, EIS, and electrochemical frequency modulation (EFM) techniques [48]. The PP study revealed that HEC acted as a mixed inhibitor and the adsorption study showed that it followed Langmuir adsorption isotherm. The fact that oxygen atoms donate unshared pair of electrons to the vacant d-orbital of iron was established by the optimized geometry of HEC obtained by *DMol^3* quantum chemical calculations that showed that oxygen atoms of HEC have Muliken atomic charges with higher electron densities. The IEs measured by PP, EIS, and EFM techniques were 96.7, 95.5, and 94.8%, respectively, for the inhibitor concentration of 0.5 mM at 25°C. Mobin and Rizvi [49] explored the anticorrosion behavior of xanthan gum (XG) as an eco-friendly corrosion inhibitor for mild steel in 1 M HCl at 30, 40, 50, and 60°C, respectively. At a concentration of 1000 ppm at 30°C, XG showed the maximum IE of 74.2%. The addition of very small amounts of surfactants cetylpyridinium chloride (CPC), sodium dodecyl sulfate (SDS), and Triton X-100 (TX) improved the IE. Quantum chemical calculations found the energy differences between the highest occupied molecular

orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) to be 0.05 and 0.02 eV in XG alone and XG plus SDS, respectively. The smaller energy gap between HOMO and LUMO indicated better inhibition efficiency for XG plus SDS system. The formation of complex between XG and Fe^{2+} was further confirmed by UV-Visible spectroscopic measurements. Scanning electronic microscopy (SEM) study revealed an improved surface morphology of inhibited mild steel compared to uninhibited mild steel. The plant extracts form a major class of green corrosion inhibitors. Some recently reported plant extracts as green corrosion inhibitors and their IEs have been summarized in **Table 1**.

4.3.2 Amino acids

Amino acids are molecules that contain at least one carboxyl (-COOH) group and one amino (-NH$_2$) group bonded to the same carbon atom (α- or 2-carbon). Amino acids are considered as green corrosion inhibitors because they are non-toxic, biodegradable, inexpensive, soluble in aqueous media, and easy to produce at high purity. The presence of heteroatoms, such as N, O, and S and conjugated π-electrons system have made amino acids a significant class of green corrosion inhibitors thanks to their environmental aspect [60, 61]. El-Sayed investigated the anti-corrosive effect of some amino acids, such as glycine, valine, leucine, cysteine, methionine, histidine, threonine, phenylalanine, lysine, proline, aspartic acid, arginine, and glutamic acid on carbon steel in stagnant naturally aerated chloride solutions using PP and EIS techniques. All of the amino acids acted as mixed-type inhibitor while cysteine, phenylalanine, arginine, and histidine showed remarkably high corrosion inhibition efficiency at a concentration of 10 mM/dm^3. The presence

Inhibitor (concentration)	Metal/alloy	Test condition	Maximum efficiency (η%)	Test technique	References
Saraca asoca (100 mg/L)	Mild steel	0.5 M H$_2$SO$_4$, 25°C	95.5	Tafel	[50]
Sida cordifolia (500 mg/L)	Mild steel	0.5 M H$_2$SO$_4$, 25°C	99.0	Tafel	[51]
Myristica fragrans (500 mg/L)	Mild steel	0.5 M H$_2$SO$_4$, 25°C	87.8	EIS	[52]
Ginkgo (200 mg/L)	X70 steel	1 M HCl, 45°C	92.5	EIS	[53]
Eriobotrya japonica (100% v/v)	Mild steel	0.5 M H$_2$SO$_4$, 25°C	96.2	Weight loss	[54]
Turbinaria ornata (25 g/L)	Mild steel	1 M HCl, 25°C	94.5	EIS	[55]
Pongamia pinnata (100 ppm)	Mild steel	1 N H$_2$SO$_4$, 30°C	94.6	Weight loss	[56]
Prosopis juliflora (300 ppm)	Low-carbon steel	1 M HCl, 25°C	91.5	EIS	[57]
Rollinia occidentalis (1.0 g/L)	Carbon steel	1.0 M HCl, 25°C	85.7	Tafel	[58]
Xanthium strumarium (10 mL/L)	Low-carbon steel	1 M HCl, 60°C	94.8	Weight loss	[59]

Table 1.
Some recent plant extracts as green corrosion inhibitors of different metals and alloys.

of functional groups such as OH, SH, or phenyl in the backbone of the amino acid molecules help them undergo better adsorption [62]. Mobin et al. studied the inhibitory behavior of mercapto group containing amino acid L-cysteine (CYS) on mild steel in aerated and unstirred 1 M HCl solution using weight loss (WL), PP, and EIS techniques. The maximum IE of 85.6% at 30°C was achieved with an inhibitor concentration 500 ppm. The authors investigated the effect of surfactants CPC, SDS, and TX by adding them to CYS and found that the surfactants increased the IE. CYS separately and in combination with surfactants acted as mixed-type inhibitor and obeyed Langmuir's adsorption isotherm [63].

In their attempt to solve the "bronze disease", Wang et al. studied the corrosion behavior of bronze covered with CuCl patina in the presence of CYS using EIS and X-ray photoelectron spectroscopy (XPS) techniques. EIS results revealed that CYS can both inhibit the bronze substrate and stabilize the CuCl patina effectively. The IE reached the highest value of 95.3% at a CYS concentration of 5 mmol/L. The XPS investigation showed that the chemisorption of CYS on CuCl surface happened through sulfur atom in thiol and nitrogen atom in amino group [64]. Zeino et al. investigated the mechanistic study of polyaspartic acid (PASP) on mild steel in 3% NaCl solution. PASP alone showed a moderate IE of 61% at 2.0 g/L and zinc ion added PASP showed a superb IE of 97% at a reduced PASP concentration of 0.5 g/L. The authors studied the surface morphology of mild steel utilizing SEM and atomic force microscopy (AFM) techniques. Quantum calculation and Monte Carlo simulation helped them achieve molecular level insights into the complex adsorption mechanism [65]. Ituen et al. investigated the IE of N-acetyl cysteine (NAC)-based formulation on J55, mild steel, and X80 steel at different temperatures (30–90°C). NAC-based formulations showed IEs up to 91% at 90°C [66].

4.3.3 Drugs

The use of drugs as green corrosion inhibitors has been inspired by the fact that they are non-toxic, cheap, eco-friendly, and green enough to compete with other green corrosion inhibitors because most of these drugs can be synthesized from natural products [67]. The presence of heteroatoms, benzene ring, and heterocycles, such as thiophenes, pyridine, isoxazoles, etc. have made drug molecules as a promising source of green corrosion inhibitors. Recently, Ali investigated the inhibitory behavior of Candesartan drug on carbons steel (CS) in 1 M HCl acidic medium using WL, PP, EIS, and EFM techniques. The surface morphology of the inhibited CS was investigated by EDX, AMF, and SEM techniques. The inhibitor showed an IE of 79.8% at a concentration of 300 ppm [68]. Matad et al. investigated the inhibitive properties of an anti-inflammatory drug ketosulfone as green corrosion inhibitor of mild steel in 1 M HCl acidic medium using chemical and electrochemical methods. Ketosulfone imparted a maximum IE of 96.6% at 30°C for a concentration of 200 ppm. The inhibitor was found to be of mixed-type and follow Langmuir adsorption isotherm determined by polarization measurements and thermodynamic calculations, respectively [69]. Singh et al. investigated the corrosion behavior of mild steel in 1 M HCl acidic medium in presence of an expired atorvastatin drug using WL, PP, and EIS techniques [70]. The expired drug showed an amazing IE of 99.1% at a concentration of 150 ppm. The inhibitor acted as mixed-type inhibitor with predominant cathodic behavior. Dahiya et al. studied the anti-corrosive behavior of an expired drug ethambutol on mild steel in 0.5 M HCl using WL, PP, EIS, SEM, and molecular dynamics (MD) techniques. The inhibitor showed an IE more than 95% at a concentration of 100 ppm and it acted as a mixed-type inhibitor and followed Langmuir adsorption isotherm [71].

4.3.4 Rare earth (RE) metal compounds

Chromates have applications in deoxidizers, anodizing, conversion coatings, chromate-inhibited primers, wash primers, and repair processes. Environmental protection legislation was realized to prevent the use of unacceptable materials such as chromium salts. Chromium (Cr^{6+}) is highly toxic and carcinogenic [41, 72]. The health problems associated with the use of chromates and the cost associated with their safe use and disposal have led to efforts finding good alternatives such as rare earth metal compounds. After the first paper was published by Hinton et al. [73] in 1984 on the use of cerium chloride salts as corrosion inhibitor, a lot of research papers have been published by the researcher working in this area. In 1992, Hinton et al. [74] published a review paper highlighting the use of some RE compounds as green corrosion inhibitors of a wide range of metals. In this chapter, the authors pointed that these RE salts work by producing an oxide film at the cathodic sites of the metal substrate which prevent the supply of oxygen or electrons to the reduction reaction thus reducing the corrosion rate. A comprehensive review of the recent developments in corrosion inhibitors based on RE metal compounds can be gained from the two works published by Forsyth et al. [75, 76] and the book edited by Forsyth and Hinton [77].

4.3.5 Others

Surfactant corrosion inhibitors are also known as green corrosion inhibitors because they are highly efficient, cheap, and less/non-toxic. Surfactant molecules consist of a polar hydrophilic group or "head" and a non-polar hydrophobic group or "tail". In aqueous solutions, the adsorption of surfactant occurs through either chemisorption or physisorption. Critical micelle concentration (CMC) is the most important parameter when it comes to studying the corrosion inhibition by surfactants [78]. Recently, ionic liquids have gained widespread popularity as green corrosion inhibitors. By definition, ionic liquids are referred to as materials consisting of ions having melting point below 100°C. Ionic liquids due to their some fascinating properties, such as high polarity, lower melting point, low toxicity, lower vapor pressure, very high thermal, and chemical stability have applications in some other fields of chemical and chemical engineering researches as well [79].

5. Recent patents on green corrosion inhibitors

Corrosion inhibitors are an important and cost-effective way of dealing with corrosion. A huge effort to produce green inhibitors and evaluate them successfully is underway. Some recently patented green corrosion inhibitors that could indicate the importance of this class of inhibitors are included in **Table 2**.

Inhibitor system	Reference
Main chain type polybenzoxazine (MCTPB)-Chitosan (CHI) blend	[80]
Polyaspartic acid-hydroxyphosphonoacetic acid-phosphinocarboxylic acid composition	[81]
Polyaspartic acid-soluble Sn (II) or Sn (IV) compound blend	[82]
At least (one fatty acid-one alkanolamine-one alkylamine-one organic sulfonic acid composition)	[83]
A corn stillage product	[84]

Table 2.
Some recent patents on green corrosion inhibitors.

6. Conclusion

Corrosion is a destructive phenomenon that could strike badly at the heart of an economy as it did on many occasions. The direct and indirect global costs associated with corrosion are no longer ignorable. Corrosion is not a necessary curse because it might be almost impossible to stop it but preventable. The use of inhibitors to mitigate corrosion is an economically viable option given the maintenance costs associated with the metals and equipment is already very high. However, recent trends in the field of corrosion inhibition are more inclined towards finding not only an effective inhibitor but also an eco-friendly one. This is because an effective inhibitor may serve the purpose of mitigating corrosion well but could leave hazardous impact on the health and ecology due to the harmful aspect associated with its chemical formula. Green corrosion inhibitors in the form of plant extracts, drugs, amino acids, rare earth metal compounds, ionic liquids, surfactants, etc. are not only eco-friendly but also provide excellent corrosion prevention. The replacement of the existing harmful organic and inorganic inhibitors that are used for different industrial applications by the green ones is not merely a matter of concern anymore but an agenda that has been in implementation and will continue to be realized.

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Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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