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Green Inhibitors for Corrosion Inhibition of Metals

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Synonyms

Adsorption; Corrosion; Electrochemical techniques; Green inhibitors; Metals; Plant extracts; Surface morphology; Weight loss method

Definition

The term corrosion is defined as destruction or deterioration of metals when they are in contact with an aggressive medium.

Introduction

Rusting of metals not only disturbs the profit of industries but also affects the national economy. Corrosion is mainly induced by chemical and electrochemical processes. The problems related to corrosion are present in all domains of the national economy. The fiscal consequences of corrosion affect technology development, as the materials are required to withstand highly corrosive environments. Millions of dollars are lost each year because of metal corrosion. Besides enormous work on corrosion control, there is a need to put forth some qualitative or quantitative proceedings, appropriate for laboratory as well as for industrial conditions. Numerous types of corrosion are possible based on the material and the environment they are surrounded by, such as, uniform corrosion, pitting corrosion, crevice corrosion, intergranular corrosion, stress corrosion, cracking, galvanic corrosion, erosion corrosion, fretting, fatigue corrosion, cavitation, and so on. Apart from metal corrosion, there is nonmetal corrosion which includes the corrosion of ceramic materials, glasses, and even rubbers. It is difficult and impossible to stop corrosion completely. However, it can be reduced to the minimum level by adopting some special techniques and methods. Corrosion can be controlled by changing the metal shape and design, modifying the metal composition and contact medium. Also, it can be prevented by electroplating, protective coating, sacrificial coating, and by the use of inhibitors. Among the various types of prevention methods, using inhibitors is the best technique. A corrosion inhibitor is a substance added in a small quantity to the contact medium to decrease the corrosion rate. This may be a green or synthetic compound (Raja et al. 2013).

© Springer Nature Singapore Pte Ltd. 2022
C. Baskar et al. (eds.), *Encyclopedia of Green Materials*,
https://doi.org/10.1007/978-981-16-4921-9_176-1

Although variety of chemical inhibitors are available, they are highly expensive, require more time for preparation, and they cause a huge damage to the environment. Therefore, to overcome these problems, research on plant extracts as corrosion inhibitors is being concentrated on, due to their renewability, cost-effectiveness, eco-friendliness, biodegradability, and easy availability.

Intensive work has been dedicated to use plant materials as corrosion inhibitors for mild steel, aluminum, aluminum alloy, and copper since they have wide industrial and domestic applications. Many authors investigated the corrosion behavior of mild steel, aluminum, and copper in the presence of plant extracts as corrosion inhibitors that showed good results. Some authors have proposed the molecular modeling that shows the possibility of electron transfer from the inhibitor to the metal. As the proposed study focuses on two important criteria, viz. stability and durability of the plant extract and how it can be used in industries, transfer of technology is essential. Based on the above criteria, all the parts of the plant have been utilized and showed good results. Most of the research work is being concentrated using leaves for investigation. Sometimes, the seed extract has also been reported to show good efficiency. In order to determine the structural and electronic parameters of the molecules responsible for inhibition, DFT calculations are very useful and such works have been reported in some of the reputed journals. Several authors have investigated the corrosion behavior of mild steel and aluminum using plant extracts as inhibitors and reported that they exhibit good inhibition efficiency (Umoren et al. 2012).

Need for Eco-Friendly Green Corrosion Inhibitors

Plant materials find enormous applications for human beings in fulfilling the basic needs such as production of food stuff, shelters, clothing, and many more. Most of the reported chemical inhibitors are found to be costly and few are harmful to the environment. Generally, acids are widely used in most of the metal industries for different purposes like pickling and cleaning, and so there is a chance for metals to undergo corrosion, when it is exposed to acid environment. Hence, there is a need to study about the corrosion of metals in various media. Usually, HCl is used for pickling of mild steel and aluminum in the industries. Various methods like protective coatings, polarizing or shifting the potential of the metal, cathodic protection, and application of inhibitors are used to prevent corrosion. Among the various methods, inhibitor method is commonly employed. The inhibition process is due to the formation of a protective film formed on the metal surface by a heteroatom/multiple bonds present in the inhibitors. Various parts of plants have been tested for their performance in protecting metals against corrosion under aqueous conditions. Recent investigations showed that natural products of plant origin possess good corrosion inhibition properties. The use of natural products as eco-friendly corrosion inhibitors for metals in acid medium started very early (Zhang et al. 2022). Researchers around the world reported several plant extracts as promising green anticorrosive agents. Natural products have been extensively studied as green corrosion inhibitors both as product mixtures extracted from plants or essentially pure products derived from animals or plants. From the economic and environmental point of view, plant extracts are excellent alternative eco-friendly corrosion inhibitors. These extracts contain a variety of natural products such as essential oils, tannins, pigments, steroids, terpenes, flavones, and flavonoids, among other well-known active substances used as corrosion inhibitors. In general, these compounds are present as conjugated aromatic structures with heteroatoms like nitrogen, sulfur, and oxygen with lone pair of electrons that are available to form bonds with the metal surface; in most cases, they act synergistically to exhibit good efficiency in corrosion protection.

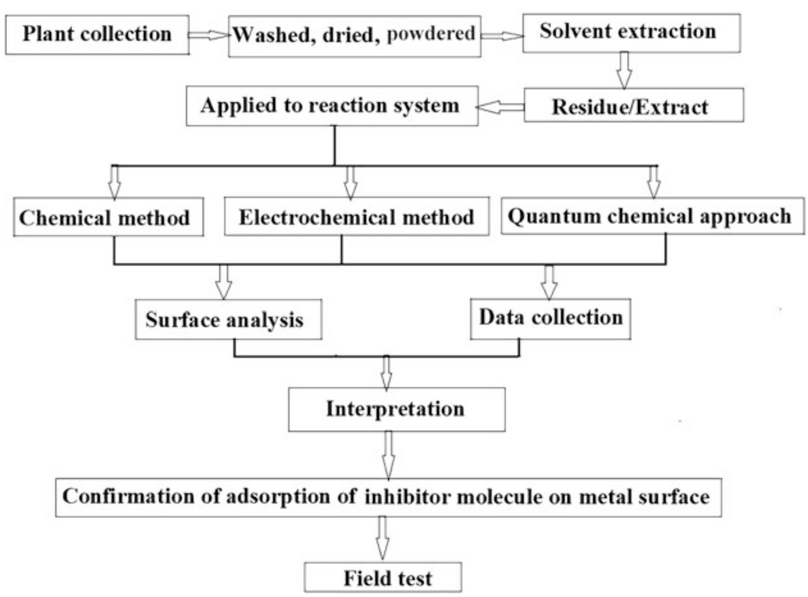
Although a number of plants as well as their phytochemical constituents have been reported as effective corrosion inhibitors, majority of plants have not yet been properly investigated for their anticorrosive activity. Thus, an enormous opportunity prevails to find out novel, economical, and eco-friendly corrosion inhibitors from natural sources (Salleh et al. 2021).

Green Materials Synthesis and Characterization

Research on using plant extracts as corrosion inhibitors is on the rise. Green synthesis does not require lot of chemicals, high temperature, and pressure. The methods are relatively simple and reproducible. Waste production is minimum during the process. Plant materials are rich sources of mixture of organic compounds containing heteroatoms like nitrogen, sulfur, oxygen, etc., and have the ability to function as effective inhibitors for metals in acid, alkaline, and neutral media. These extracts can be obtained in a simple way and purification methods are not required. The extracts are generally obtained from cheap solvents that are widely available; the aqueous extract is more common, but due to the low solubility of many natural products in water, ethanol extracts are also obtained.

The leaves of *Ailanthus excelsa Roxb., Bauhinia racemosa Lam, and Hardwickia binata Roxb* have been used as inhibitors on mild steel corrosion in acidic medium (Vasanthajothi et al. 2021). Similarly, the leaf extract of *Morinda tinctoria* has been used as a green corrosion inhibitor on mild steel (Krishnaveni et al. 2014) and copper (Krishnaveni and Ravichandran 2014) in acidic medium, and aluminium (Krishnaveni and Ravichandran 2015; Krishnaveni and Vasanthajothi 2021) both in acidic and alkaline media.

The phytoconstituents present in the leaves of *Ailanthus excelsa Roxb*. (Simaroubaceae family) were found to contain flavonoids, phenolic compounds, lignin, saponins, and sterols. The antiproliferative activity, nutritional and therapeutic potential, and antifungal activity of the plant extracts have also been studied. Flavonoids and coumarins have been reported in the leaves of *Bauhinia racemosa Lam*, which belongs to the Caesalpiniaceae family. The plant extracts are also studied for their antihistaminic effect, antimicrobial activity, and therapeutic potential. The preliminary phytochemical screening showed the presence of saponins, tannins, terpenoids, phenolic groups, flavonoids, and carbohydrates in the leaves of *Hardwickia binata Roxb* (Fabaceae family). In vitro propagation, and antibacterial and antifungal activities have also been carried out by various authors. The leaves of *Morinda tinctoria* (Rubiaceae family) have been found to contain phytoconstituents like alkaloids, flavonoids, terpenoids, steroids, and amino acids. They show active therapeutic functions. Figure 1 shows the stepwise process involved in the



Green Inhibitors for Corrosion Inhibition of Metals, Fig. 1 The schematic diagram for the green materials: synthesis, characterization, and applications synthesis, characterization, and applications of green inhibitors.

The plant extracts are prepared as per the standard procedures and applied to the reaction systems. The corrosion inhibition efficiency is ascertained by weight loss, electrochemical, gasometric, and thermometric methods. The shelf-life of the green extracts can be studied by stability and durability test. These extracts can be tested on the metal surface under acidic or alkaline conditions. They can also be tested from low to high temperature for the efficiency. These results can be further confirmed by surface morphological analyses like scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDAX), Fourier transform infrared spectroscopy (FTIR), density functional theory (DFT), and molecular docking approach (MD).

These analytical techniques are employed to investigate the adsorption of the phytocompounds present in the extract onto the metal surface (Obot et al. 2014; Wang et al. 2022). Since plant extracts contain phytoconstituents in the form of organic compounds, they are adsorbed onto the metal surface providing protection against corrosion.

Surface profiles of metal specimens are analyzed using zeta 3D optical profiler. The metal specimens after the corrosion experiments are placed on the sample holder provided with an operating program on computer and 3D photos are taken. It is a powerful technique to investigate the surface morphology at nano- to microscale that is being used currently to study the influence of corrosion inhibitors on metal/solution interface. From the analysis, useful information can be gained regarding the roughness and uniformity of the metal surface.

The corrosion inhibition process is due to the formation of a protective film on the metal surface by heteroatoms/multiple bonds present in the inhibitors which can be concluded by the surface analysis process.

SEM images are taken in order to study the changes that occur on metal surface during the corrosion process in the absence and presence of selected plant extracts.

Field test ensures the stability activity and metal protection ability of the plant extracts. The result obtained from microscale laboratory experiments is directly applied to the industrial process by field test (David et al. 2022).

In general, numerous phytoconstituents are present in different plant parts. Based on the efficacy, the fresh plant parts are collected and washed under tap water to remove dust particles present on the surface. The washed parts are then dried in shade for 3–7 days. The dried parts are finely powered and taken for solvent extraction. Different solvents may be used depending on the inhibition performance. The solvent range may vary from polar to nonpolar. The extraction may be carried out in the temperature range 40–60 °C for 3 h so that no phytoconstituent evaporates. After 3 h, the extract is left for cooling overnight without any disturbance. The cooled extract is filtered and the filtered extract is taken for further processes. The prepared extracts may be tested for antioxidant, anticancer, pharmacological, and antimicrobial properties and as food preservatives, pesticides, and as inhibitors for metal corrosion. The trial-and-error method starts from the beginning. Depending on the inhibition percentage, the extract concentration may vary for the reaction system. In some cases, instead of using extract, the direct powered material can also be used to achieve the inhibition.

The extract prepared from particular solvent is tested for corrosion prevention of metals in various aggressive media. To compare the protection ability of the extract toward metal inhibition, many trials are carried out with different systems. The pre-weighed metal coupons/metal specimens with specific dimensions are taken and placed in the reaction system (only acid or alkaline content) without the addition of extract (namely inhibitor) for an hour. Similar procedure is followed in the reaction system with the addition of particular concentration of inhibitor. After an hour, the metal coupons/metal specimens kept in the reaction system with and without inhibitor are taken out, washed under tap water, and hung in the air for draining. The drained specimens are kept in a desiccator for further moisture removal. The weights of the specimens are taken for both the reaction systems. From the weight loss, the amount of inhibitor molecules adsorbed on the metal surface can be calculated. By this way, the metal gets protected from the aggressive medium with the support of green materials. Numerous methods can be applied for corrosion inhibition of metals by the application of green materials (Long et al. 2022).

The inhibitor is added to the medium (acid or alkaline) with which the metal is in contact. Established mechanisms show that when an inhibitor is added to the reaction medium, the phytocompounds present in the plant extracts get attached itself on the metal surface through adsorption process. The adsorption may be physical or chemical based on the nature of the phytocompounds.

There are numerous methods available for the metal protection, such as weight loss method, stability and durability test, electrochemical studies, gasometric method, and thermometric method.

In weight loss method, previously cleaned metal specimens are weighed and suspended with the help of a glass rod and hook in an open beaker containing required volume of acid solution. The procedure is conducted with and without the inhibitor (green plant extract). After a specified time interval, the metal specimens are withdrawn, washed, dried, and re-weighed. The difference in the weight of the specimen before and after immersion is taken as the weight loss. The inhibition efficiency (%IE) is calculated from the following equation:

$$\%\mathrm{IE} = [\mathrm{W_{blank}} - \mathrm{W_{inh}}]/\mathrm{W_{blank}} \times 100,$$

where W_{blank} and W_{inh} are weight loss of the metal in blank acid and in the inhibitor system.

The development of any product depends on various factors like storage condition of the product (whether it is kept under refrigerated condition or at room temperature). The weight loss measurements are carried out to evaluate the durability of the extracts under room and refrigerated condition.

Adsorption of inhibitor molecule onto the metal surface can also be studied through electrochemical studies. Experiments like electrochemical impedance and potentiodynamic polarization studies provide the data such as charge transfer resistance, double-layer capacitance, open-circuit potential, corrosion current density, corrosion potential, as well as anodic and cathodic slope. Percentage inhibition efficiency of the inhibitor can also be calculated from Nyquist plot as given below:

$$\%\mathrm{IE} = \left[\left(\mathrm{R_{ct\ (i)}} - \mathrm{R_{ct\ (b)}}\right)/\mathrm{R_{ct\ (i)}}\right] \times 100,$$

where $R_{ct\ (b)}$ and $R_{ct\ (i)}$ are the charge transfer resistance values in the absence and presence of inhibitor, respectively.

Similarly, for Tafel extrapolation method, the efficiency can be calculated as follows:

$$\%\mathrm{IE} = \left[\left(\mathrm{I_{corr\ (b)}} - \mathrm{I_{corr\ (i)}}\right)/\mathrm{I_{corr\ (b)}}\right] \times 100,$$

where $I_{corr\ (b)}$ and $I_{corr\ (i)}$ are corrosion current densities without and with inhibitor, respectively.

In gasometric method, the metal specimen is inserted into the round bottomed flask (containing test solution) of the gasometric setup. The volumes of hydrogen evolved are measured after every minute until steady values are obtained. Inhibition efficiency is calculated using the following equation:

$$\%\mathrm{IE} = \left[1 - \mathrm{V_{Ht}}^1/\mathrm{V_{Ht}}^0\right] \times 100,$$

where $V_{Ht}{}^1$ and $V_{Ht}{}^0$ are the values of H_2 gas evolved at time "t" for inhibited and uninhibited solutions, respectively.

In thermometric method, a piece of metal of a specified area is dropped into a definite volume of acid solution and the variation of the temperature of the thermally isolated system is followed as a function of time. The temperature rises during the course of the reaction to attain a maximum value. The reaction number (RN) is defined as

$$\mathrm{RN} = [\mathrm{T_m} - \mathrm{T_i}]/\mathrm{t} = \Delta\mathrm{T}/\mathrm{t}\ \ ^\circ\mathrm{C/min},$$

where T_m and T_i are the maximum and initial temperatures, respectively, and "t" is the time in minutes taken to attain T_m. The inhibition efficiency is calculated using the following equation:

$$\%IE = \left[RN_{aq} - RN_{wi}\right]/RN_{aq} \times 100,$$

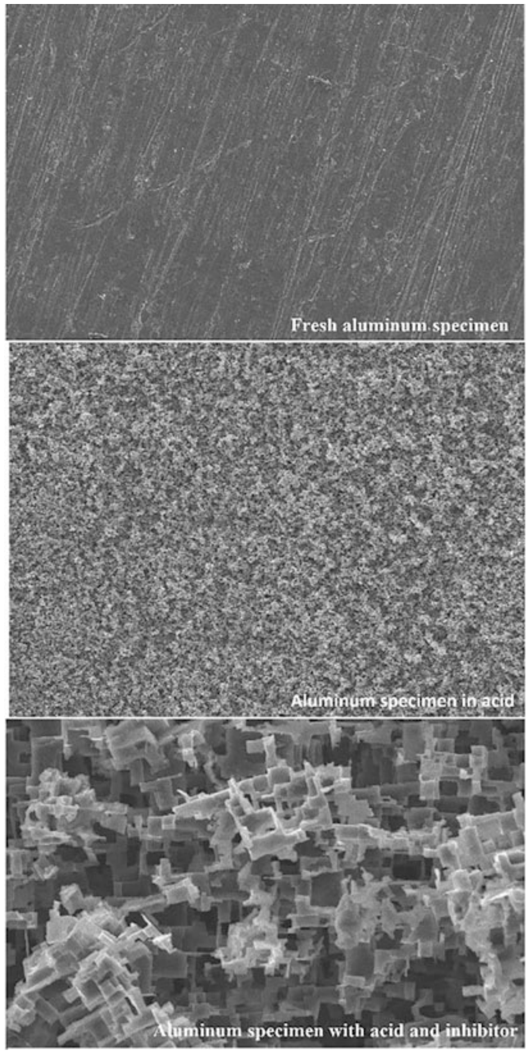
where RN_{aq} = reaction number in the absence of inhibitor and RN_{wi} = reaction number with inhibitor.

Surface analysis techniques are performed after all the laboratory trial and error methods. The simplest techniques like SEM, EDAX, and FTIR are adopted for surface analysis and through these techniques the surface morphology of metal before and after interaction with the inhibitor, types of heteroatoms, functional groups, and multiple bonds present in the green inhibitor molecules could be found out. It is well established that FT-IR spectroscopy is a powerful tool that can be used to identify the type of bonding, particularly the functional groups present in organic compounds. The corrosion product (powered material) scratched from the metal sample immersed in the corrosive medium is then analyzed using an FTIR spectrometer. The metal specimen immersed in the acid with and without inhibitor after a particular time were taken for surface morphology study.

The following surface morphology (SEM) images (Fig. 2) show the coating or coverage of the green inhibitor molecules on the metal surface. The percentage composition of elements on the metal can be obtained from energy-dispersive X-ray analysis.

After the trail and confirmation report from the laboratory, the inhibitor is taken from micro- to major scale for the industrial application. The inhibitor is directly tested with the metals used in the industries. Based on the result obtained from the microlevel, the amount of inhibitor is changed accordingly.

Based on the above discussion, it is learnt that most of the plant species exhibit best protection toward the corrosion inhibition of metals in aggressive media. The plants, namely *Ailanthus excelsa Roxb., Bauhinia racemose Lam., Hardwickia binata Roxb.* and *Morinda tinctoria* proved to be leading green inhibitors for metals and meet the criteria of acting as an effective eco-friendly corrosion inhibitor for various metals in different media.



Green Inhibitors for Corrosion Inhibition of Metals, Fig. 2 SEM images of aluminum specimen without and with inhibitor

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