

## Green Inhibitors for Corrosion of Metals

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### ABSTRACT

The ability of electrochemical processes to break compounds down into elements or to create new compounds can be destructive as well as productive. Corrosion is an all-too-common result of electrochemical reactions between materials and substances in their environment. Corrosion is a dangerous and extremely costly problem. Because of it, buildings and bridges can collapse, oil pipelines break, chemical plants leak, and bathrooms flood. Corroded electrical contacts can cause fires and other problems, corroded medical implants may lead to blood poisoning, and air pollution has caused corrosion damage to works of art around the world. Corrosion threatens the safe disposal of radioactive waste that must be stored in containers for tens of thousands of years. The most common kinds of corrosion result from electrochemical reactions. General corrosion occurs when most or all of the atoms on the same metal surface are oxidized, damaging the entire surface. Most metals are easily oxidized: they tend to lose electrons to oxygen (and other substances) in the air or in water. As oxygen is reduced (gains electrons), it forms an oxide with the metal. When reduction and oxidation take place on different kinds of metal in contact with one another, the process is called galvanic corrosion. In electrolytic corrosion, which occurs most commonly in electronic equipment, water or other moisture becomes trapped between two electrical contacts that have an electrical voltage applied between them. The result is an unintended electrolytic cell. Take a metal structure such as the Statue of Liberty. It looks strong and permanent. Like nearly all metal objects, however, it can become unstable as it reacts with substances in its environment and deteriorates. Sometimes this corrosion is harmless or even beneficial: the greenish patina that covers the statue's copper skin protected the metal beneath from weather damage. Inside the statue, however, corrosion caused serious harm over the years. Its iron frame and copper skin acted like the electrodes of a huge galvanic cell, so that nearly half of the frame had rusted away by 1986, the statue's one hundredth anniversary. Plant extracts act as natural green inhibitors against corrosion of metals. They are ecofriendly and inhibit corrosion called green inhibitors.

**KEYWORDS:** corrosion, metals, oxidation, plant, extracts, green, inhibitors, ecofriendly, damage

### INTRODUCTION

Some metals acquire a natural passivity, or resistance to corrosion. This occurs when the metal reacts with, or corrodes in, the oxygen in air. The result is a thin oxide film that blocks the metal's tendency to undergo further reaction. The patina that forms on copper and the weathering of certain sculpture materials are examples of this. The protection fails if

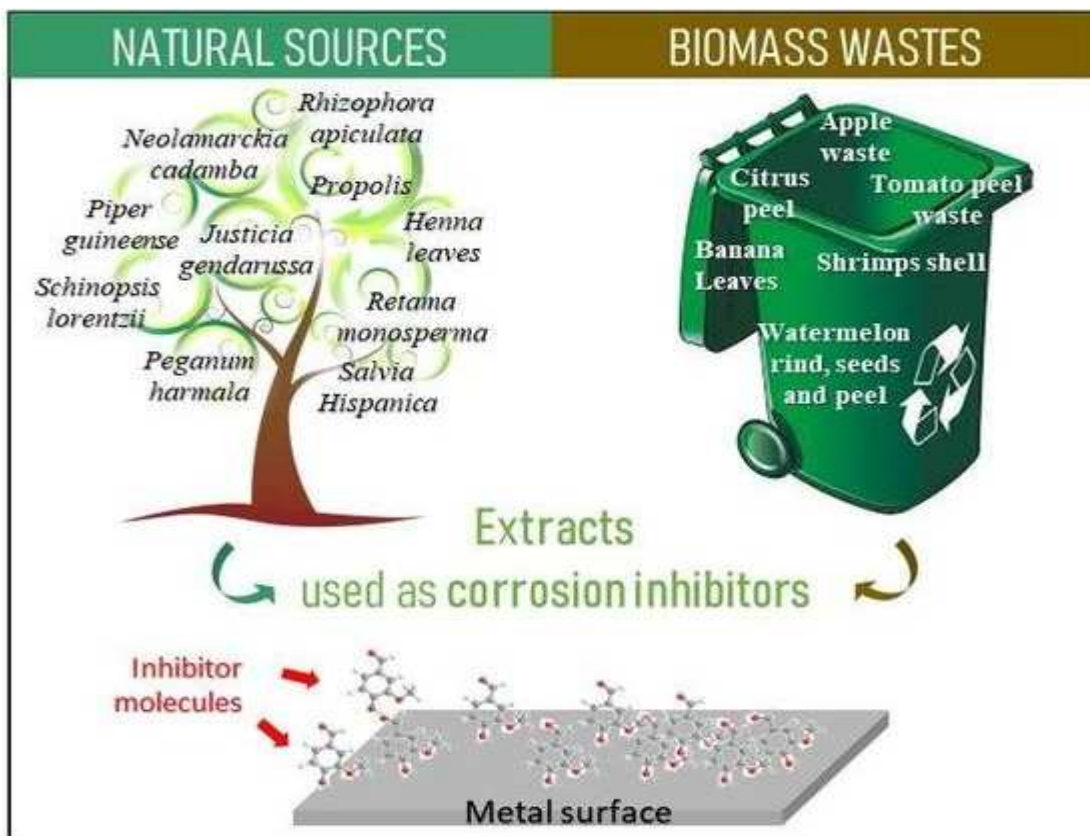
the thin film is damaged or destroyed by structural stress — on a bridge, for example — or by scraping or scratching. In such cases the material may re-passivate, but if that is not possible, only parts of the object corrode.[1,2] Then the damage is often worse because it is concentrated at these sites. Harmful corrosion can be prevented in numerous ways.

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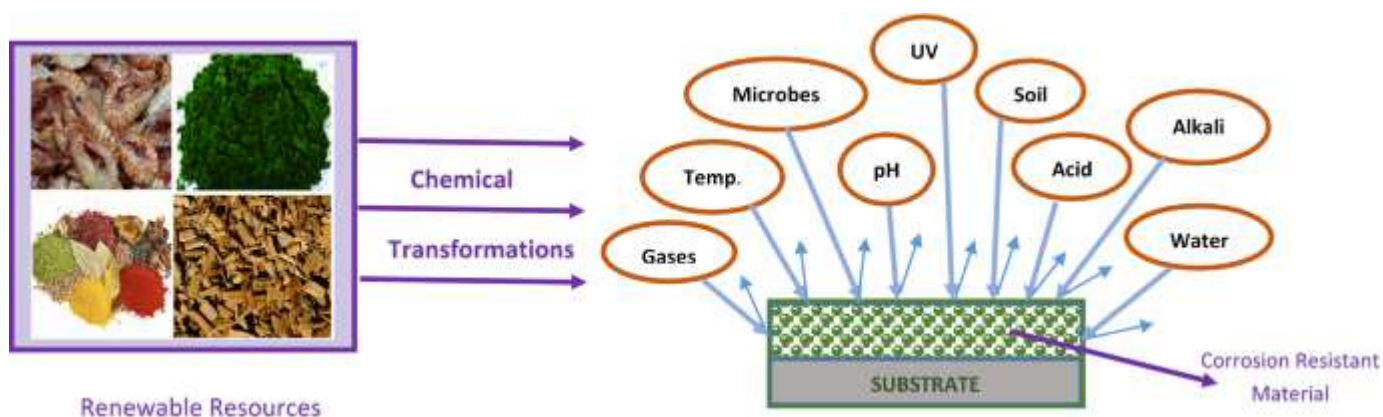
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Electrical currents can produce passive films on metals that do not normally have them. Some metals are more stable in particular environments than others, and scientists have invented alloys such as stainless steel to improve performance under particular conditions. Some metals can be treated with lasers to give them a non-crystalline structure, which resists corrosion. In galvanization, iron or steel is coated with the more active zinc; this forms a galvanic cell where the zinc corrodes rather than the iron. Other metals are protected by electroplating with an inert or passivating metal. Non-metallic coatings — plastics, paints, and oils — can also prevent corrosion. Driven by the increasingly overwhelming environmental issues caused by the widespread application of traditional toxic corrosion inhibitors, eco-friendly inhibitors have attracted strong attention over the past decades. Green inhibitors are produced from cheap and renewable sources and simultaneously offer high inhibition efficiency and low or even zero environmental impact.

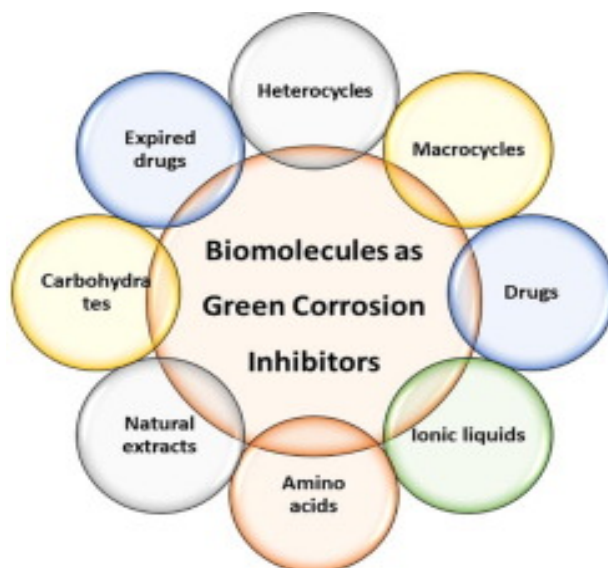
Green corrosion inhibitors as an effective environmentally friendly technique have attracted more attention in recent years. Several common sources of green inhibitors include plant extracts, pharmaceutical drugs, ionic liquids, and synthetic inhibitors are the common sources of eco-friendly corrosion inhibitors. Plants (i.e., extract and oils) are the essential source of the extensive range of green corrosion inhibitors in different acidic media due to versatile physical, chemical, and biological properties. Other advantages of plants as the sources of corrosion inhibitors include low-cost, plentiful availability and their biodegradability. Plants are well-known as a rich source of natural chemical compounds that can be readily extracted with low cost and minimum environmental pollution.[3,4]



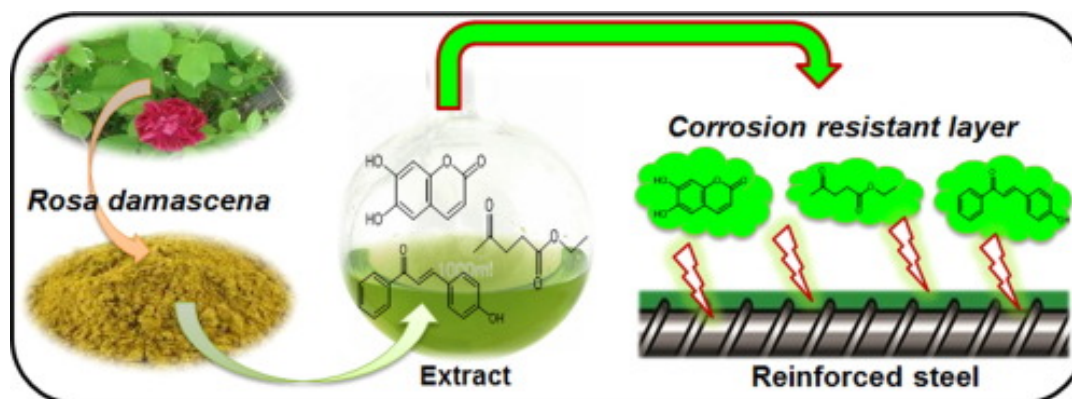
Ionic liquids are also green solvents composed of ions that can dissolve different types of inorganic and organic compounds. The ever increasing application of ionic liquids in almost all fields of chemical engineering results

from their attractive properties which have nominated them as eco-friendly chemicals. Concerning the use of drugs as a source of green corrosion inhibitors, they are substances with relatively complex structures composed of natural or synthesized constituents. Drugs derived from natural sources have attracted more attention in recent years to be used as corrosion inhibitors. In addition, the tendency to use expired drugs as corrosion inhibitors is increasing because it can diminish their disposal cost and environmental pollution

## Discussion



The working principle of corrosion inhibitors is based on the direct or in-direct adsorption of inhibitor molecules on the metal surface thereby decreasing the metal surface contact with the aggressive media. The majority of metallic materials are naturally unstable such that they tend to chemically/electrochemically react with aggressive agents of the environment (e.g.  $H^+$ ,  $Cl^-$ , and so on) to form more stable substances as corrosion product. Green inhibitors are extensively used to control the corrosion of different types of steels in acidic environments, especially in the oil and gas industry. Based on their chemical nature, green inhibitors can be classified into two groups namely organic and inorganic. Several types of organic green inhibitors include plants (extracts, oil), ionic liquids, amino acids, drugs, and natural polymers. All these compounds have heteroatoms containing elements with high electron density. [5,6]

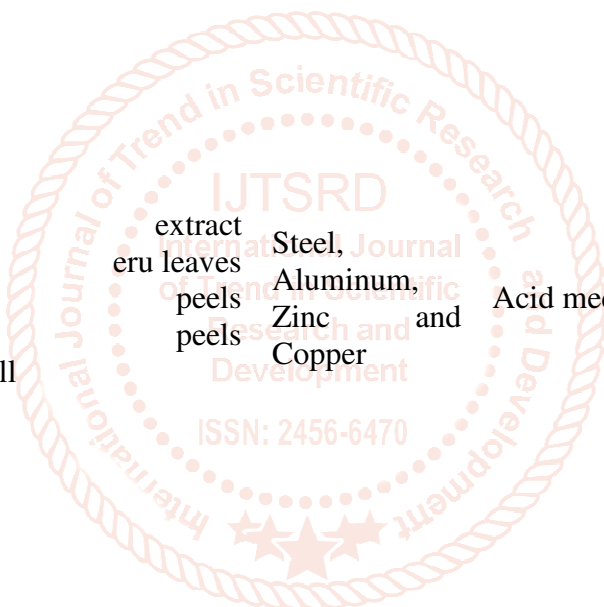


Steels are widely used in engineering materials. These are prone to experience corrosion damage during interaction with acidic solutions in many engineering processes such as pickling, descaling, and oil-well acidification. The application of inhibitors can control this damage by retarding the corrosion process. Nowadays, green inhibitors are gaining substantial attention. Besides being eco-friendly, they are generally inexpensive, readily accessible, and renewable.

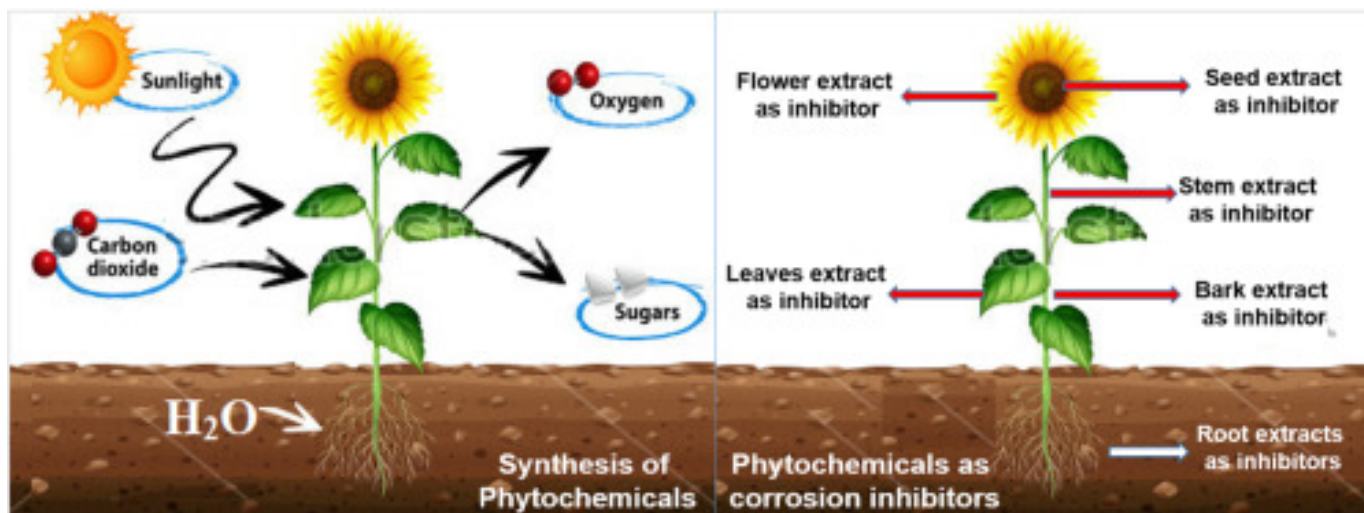


**Table 1 The interest in green inhibitors versus corrosion is indicated below:**

Source of natural products	Metal/alloy studied	Agg. media studied	Efficiency (%)
Flour and yeast	Iron	Acid media	65–82
Furit—peels of pomegranate	Aluminum	Acid media	83
<i>Hibiscus sabdariffa</i> extract	Al and Zn	HCl	85
			87.5 (steel),
			77.5 (Al)
			71.0 (steel),
			45.9 (Al)
Tobacco leaves			87.5 (steel),
Castor seeds			65.8 (Al)
Black pepper			65.5 (steel),
Soya bean	Mild steel and Aluminum	Neutral then acidic media	27.1 (Al)
Gum (acacia)			NA (steel),
Catechu			21.8 (Al)
Opium (0.1%)			50.0 (steel),
			6.3 (Al)
			NA (steel),
			42.7 (Al)
			75 (steel), 70
			(Al), 55 (Zn),
			56 (Cu)
			80 (steel), 64
			(Al), 43 (Zn),
			43 (Cu)
<i>Opuntia</i> extract	Steel,		80 (steel), 59
<i>Aloe</i> eru leaves	Aluminum,		(Al), 59 (Zn),
Orange peels	Zinc and	Acid media	NA (Cu)
Mango peels	Copper		82 (steel), 82
Pomegranate fruit shell			(Al), 80 (Zn),
			30 (Cu)
			65 (steel), 81
			(Al), 71 (Zn),
			73 (Cu)
Papaia			94
<i>Poinciana pulcherrima</i>	<i>Cassia</i>		96
<i>occidentalis</i>			94
<i>Datura stramonium</i> seeds	<i>Calotropis</i>	Mild steel	Acid media
<i>procera</i>			93
<i>Azadirachta</i>	<i>indica</i>		98
<i>Auforpio turkiale</i> sap			84
<i>Swertia angustifolia</i>			69
<i>A. indica</i>		Mild steel	Acid media
<i>A.</i>	<i>indica</i>	Mild steel	Acid media
<i>Punica</i>	<i>granatum</i>	Mild steel	NaCl
<i>Momordica charantia</i>			79.2
<i>Pongamia glabra, Annona squamosa</i>		Mild steel	Acid media
<i>Acacia arabica</i>		Mild steel	Acid media
Natural honey		Carbon steel	NaCl
<i>Rosmarinus officinalis</i>		Al–Mg alloy	NaCl
Mimosa tannin		Carbon steel	Acid media
Vanillin		Carbon steel	Acid media
Dodecanohydrazide, octadecanohydrazide	cis-9- and 10-	Mild steel	Acid media
			85



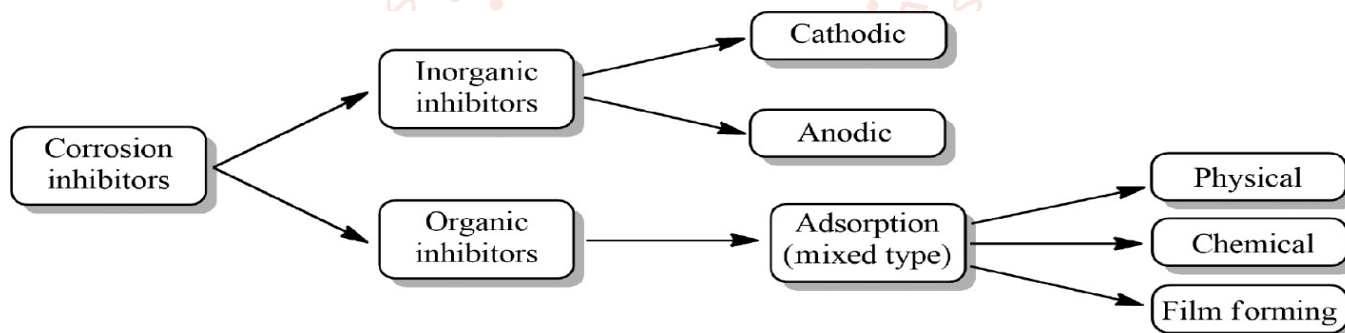
Source of natural products	Metal/alloy studied	Agg. media studied	Efficiency (%)
undecanohydrazide derived from fatty acids			
Herbs (thyme, coriander, hibiscus, anis, black cumin, and garden cress)	Steel	Acid media	37–92
Reducing saccharides fructose and mannose	Aluminum and Zinc	Alkaline media	92
<i>Opuntia extract</i>	Aluminum	Acid media	76–96
<i>Vernonia amygdalina</i>	Al alloys	Acid media	49.5–72.5
<i>Allium cepa</i> , <i>Allium sativum</i> , <i>M. charantia</i>	Mild steel	Acid media	86–94
Guar gum	Carbon steel	Acid media	75–93.88
<i>Zanthoxylum alatum</i>	Mild steel	Acid media	76–95
<i>Nypa fructicans</i>	Mild steel	Acid media	75.11
Caffeine–Mn <sup>2+</sup>	Carbon steel	Chloride ions	50
Caffeine and nicotine			80–90
Eugenol from cloves	Steel	Acid media	80
acetyluogeno			91
<i>Ricinus communis</i> leaves	Mild steel	NaCl	43–84
Berberine extracted from <i>Coptis chinensis</i>	Mild steel	Acid media	79.7
Halfabar			90.50
Chamomile			92.97
Black cumin	Steel	Acid media	88.43
Kidney bean			88.43
<i>Sansevieria trifasciata</i>	Aluminum	Acid and alkaline media + halides	94.3 (HCl) 95.3 (KOH)
Exudate gum from <i>Dacryodes edulis</i>	Aluminum	Acid media	42
Gum arabic			80
Exudate gum from <i>Raphia hookeri</i>	Aluminum	Acid media + halide	56.3
Exudate gum from <i>Pachylobus edulis</i>	Mild steel	Acid media	56
<i>Bambusa arundinacea</i>	Steel rebar	Chloride and nitrite	85
Parts of the kola tree (leaves, nuts, and bark) and tobacco	Steel rebar	NaCl	70–91
<i>Artemisia pallens</i>	Mild steel	Acid media	93–98
<i>V. amygdalina</i>	Steel rebar	NaCl	90.8
<i>Chamaerops humilis</i> L.	Steel rebar	Alkaline media	42.2
<i>Mangrove tannin</i>	Copper	Acid media	82.4
<i>Chitosan</i>	Copper	Acid media	93
<i>Myrtus communis</i>	Copper	Acid media	>85
<i>Tagetes erecta</i>	Copper	Acid media	98.07
<i>Morinda lucida</i>	Steel rebar	NaCl	92.8
<i>Opuntia ficus indica</i>	Carbon steel	Acid media	70–91
<i>Alhagi maurorum</i> plant extract	Copper	Acid media	33–83
<i>Egyptian licorice</i> extract	Copper	Acid media	89.55
<i>Tridax procumbens</i> <i>Chromolaena odorata</i>	Stainless steel	Oilfield environment	82.03 95.6
<i>Corchorus olitorius</i>	Mild steel	Acid media	93



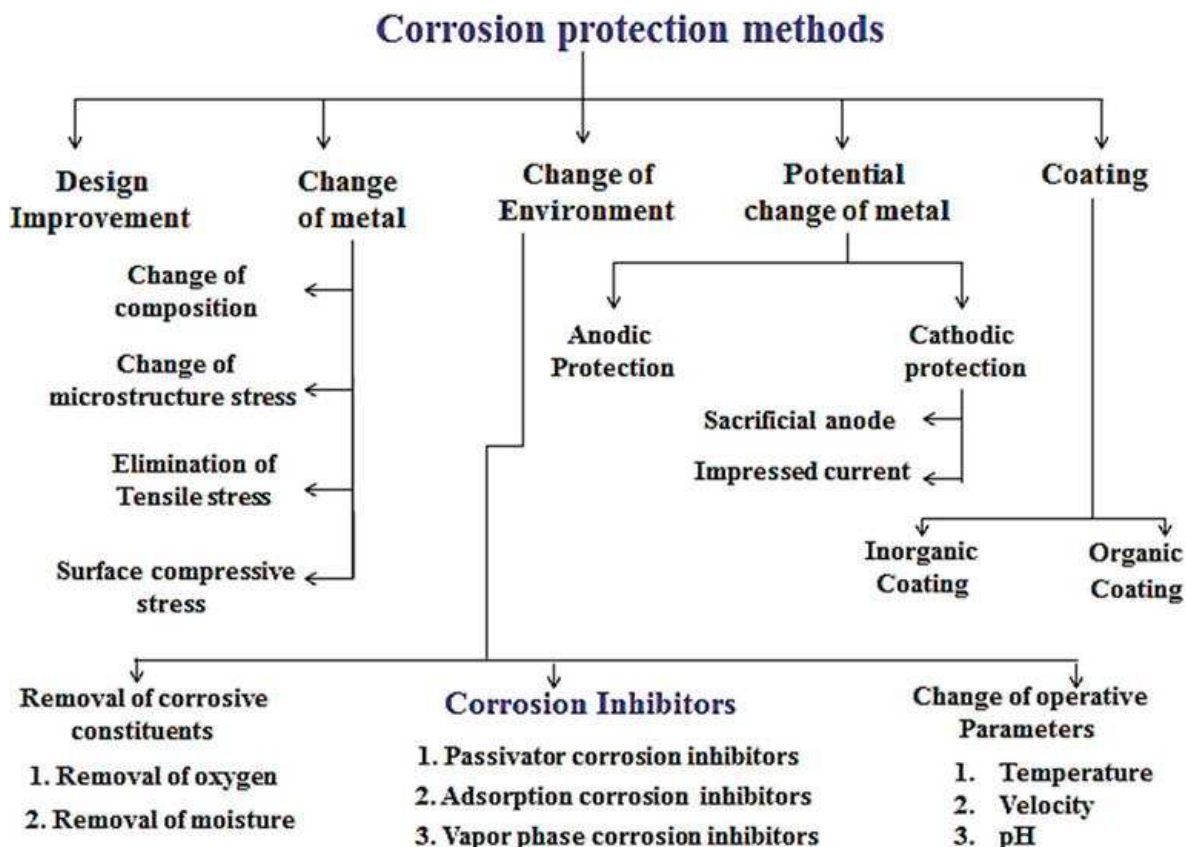
**Mechanism in Detail**

Corrosion is a spontaneous process; the relative rate of corrosion is related to the change in standard Gibbs free energy ( $\Delta G^\circ$ ). A more negative value of  $\Delta G^\circ$  is related to higher spontaneous reaction, i.e. higher corrosion rate. Metals and alloys when exposed to the environment corrode to form stable corrosion products. Utilization of additive corrosion inhibitors is necessary to mitigate corrosion rate. Corrosion products such as rust and scale can also act as corrosion inhibitors because they can accumulate on the surface and act as physical protective barriers; however, the relative rate of corrosion of any particular metal depends on the Pilling–Bedworth ratio, which is used at high-temperature oxidation (corrosion).

The magnitude of the Pilling–Bed worth ratio can be used to explain the status of surface film, i.e. whether it will be protective or not. When the volume of corrosion product is smaller than the volume of metal from which it is formed, then  $Md/nmD < 1$  and in this situation it is expected that the surface film of the corrosion product contains pores and cracks that would be relatively nonprotective. When the volume of the corrosion product is larger than the volume of metal for  $Md/nmD > 1$ , it is expected that the surface film of the corrosion product is relatively more compressed and compact than would result in a more protective film.[7,8]



Adsorption is the first step in forming a corrosion protective film or coat in the presence of aggressive media that occurs on metallic surfaces on the active sites. Several factors affect the adsorption of inhibitor on the metallic surface and isolate it including adsorption mode, chemical and electronic characteristics of the inhibitor, temperature, type of electrolyte employed, steric effects, and the nature and surface charge of metals. The Langmuir adsorption isotherm is the most favorable to clarify interaction between the inhibitor and metal surface. Adsorption on the corroded surfaces approximates to a steady-state adsorption that may be physical adsorption (physisorption) or chemical adsorption (chemisorption), or a mixed adsorption mechanism that is considered ideal for effective corrosion inhibition.



Physical adsorption is related to the standard free energy of adsorption  $\Delta G^{\circ}_{ads}$  in aqueous solution. If its value is  $-20 \text{ kJ.mol}^{-1}$  or less negative it is associated with an electrostatic interaction between charged centers of molecules and the charged metal surface, which results in a dipole interaction of the molecules and metal surface. However, chemical adsorption is a process that involves the transfer or sharing of electrons from the inhibitor to the metallic surface and results in the formation of a coordinate covalent bond. The bonding strength is much larger than physical adsorption where the value of  $\Delta G^{\circ}_{ads}$  is around  $-40 \text{ kJ.mol}^{-1}$  or more negative. Adsorption of green corrosion inhibitor retards corrosion by detraction of the active metallic surface area, leaving inactive sites on the surface exposed to corrosive media. Green inhibitors are more efficient at room temperature or low temperatures, while inhibition efficiency is decreased with an increase in temperature in most cases.



The action of green inhibitors depends on the structure of the active ingredient; many researchers have postulated numerous theories to explain the mechanism of their effect. The active ingredient derived from natural inhibitors changes from one plant species to another but their structures are closely related to their



organic coordinate. As an example, garlic contains allyl propyl disulfide, mustard seeds contain an alkaloid berberine that has a long chain of aromatic rings and an N atom in the ring, carrot contains pyrrolidine, and castor seed contains the alkaloid ricinine. Eucalyptus oil contains monomtrene-1,8-cineole. Lawsonia extract contains 2-hydroxy-1,4-naphthoquinone resin and tannin, coumarin, gallic acid, and sterols. Gum exudate contains hexuronic acid, neutral sugar residues, volatile monoterpenes, canaric and related triterpene acids, and reducing and nonreducing sugars. Garcinia kola seed contains primary and secondary amines, unsaturated fatty acids, and bioflavonoids. Calyx extract contains ascorbic acid, amino acids, flavonoids, pigments, and carotene. The corrosion inhibition activity of these plant extracts could be due to the presence of heterocyclic constituents like alkaloids, flavonoids, etc.

## Results and Conclusion

Natural plant extracts are effective green corrosion inhibitors against various metals and alloys. In addition, the efficiency of green and sustainable inhibitors of ionic liquids for the corrosion of metals and alloys is preferred compared to traditional corrosion inhibitors because of their advantageous physiochemical properties. Finally, adsorption behavior following the Langmuir isotherm, the Temkin adsorption isotherm, and in particular the adsorption behavior of ionic liquids on metallic surfaces using DFT-based quantum chemical calculations. Quantum chemical calculations (DFT) provide a good insight into the inhibition mechanism and experimental order of inhibition efficiency. The tendency to explore vapor-phase corrosion inhibitors and green nanoinhibitors is a new area for future research.

A lot of potential is still untapped, especially computational modeling of the major extract components of various metals and alloys. Further research should also be focused on plant extraction methods and their active constituents as well as scale-up experiments for industrial applications that are needed to commercialize these natural extracts to effectively replace conventional chemicals.[9]

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