

Review Article

Recent Natural Corrosion Inhibitors for Mild Steel: An Overview

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Traditionally, reduction of corrosion has been managed by various methods including cathodic protection, process control, reduction of the metal impurity content, and application of surface treatment techniques, as well as incorporation of suitable alloys. However, the use of corrosion inhibitors has proven to be the easiest and cheapest method for corrosion protection and prevention in acidic media. These inhibitors slow down the corrosion rate and thus prevent monetary losses due to metallic corrosion on industrial vessels, equipment, or surfaces. Inorganic and organic inhibitors are toxic and costly and thus recent focus has been turned to develop environmentally benign methods for corrosion retardation. Many researchers have recently focused on corrosion prevention methods using green inhibitors for mild steel in acidic solutions to mimic industrial processes. This paper provides an overview of types of corrosion, corrosion process, and mainly recent work done on the application of natural plant extracts as corrosion inhibitors for mild steel.

1. Introduction

Mild steel, also known as plain-carbon steel, is now the most common form of steel because its price is relatively low, while it provides material properties that are acceptable for many applications [1]. However, the challenge is that it has low corrosion resistance especially in acidic environments [2]. Industrial processes such as acid cleaning, pickling, descaling, and drilling operations in oil and gas exploration use acidic solutions extensively and as such iron and steel vessels or surfaces used in these environments are prone to corrosion [3]. The use of many inorganic inhibitors, particularly those containing phosphate, chromate, and other heavy metals, is now being gradually restricted or banned by various environmental regulations because of their toxicity and difficulties faced in their disposal especially in the marine industry, where aquatic life is at threat [4]. Synthetic organic inhibitors have also been extensively applied but their use is now being marred by their toxicity and high cost of manufacturing. This has prompted researchers to explore other areas to produce eco-friendly, cheap, and biodegradable green corrosion inhibitors to replace inorganic and synthetic

organic inhibitors. Natural products such as plant extract, amino acids, proteins, and biopolymers have been reported to be efficient corrosion inhibitors [5]. Plant extracts are viewed as rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost [6]. These natural extracts are analogous to the synthetic organic inhibitors and are being proven to work as much as their synthetic counterparts. This review gives an overview of recent work on the inhibitive effect of various plant extracts particularly for mild steel in acidic medium so as to provide industrialists with vital comparative literature for possible large scale use of natural inhibitors in their operations. This will contribute to sustainable and green manufacturing. The effects of temperature, concentration, and reaction medium on the inhibition efficiency were compared. Methods used for studying corrosion and the adsorption isotherms deduced are also highlighted.

2. Types of Corrosion

Corrosion is defined as the deterioration of a substance or its properties due to interactions between the substance and its

TABLE 1: Types of corrosion.

Type of corrosion	Description
Uniform corrosion	Deteriorates the whole surface of the metal and makes the surface thin.
Galvanic corrosion	Occurs with an electrolyte with metals having different values of electrical potentials.
Pitting corrosion	Occurs because of random attacks on particular parts of the metal's surface to form pits. The pit acts as the anode, while the undamaged part of the metal is the cathode.
Stress corrosion cracking	A complex form of corrosion which arises due to stress and corrosive environment.
Corrosion fatigue	A combination of cyclic stress and corrosion.
Intergranular corrosion	Corrosion occurs on or near the grain boundaries of a metal.
Crevice corrosion	Concentration cell corrosion due to the trapping of corrosive liquid between the gaps of the metal.
Filiform corrosion	Concentration cell corrosion on metallic surfaces coated with a thin organic film.
Erosion corrosion	Flow-assisted corrosion which is due to the movement of corrosive liquids on metal surface.
Fretting corrosion	A form of erosion-corrosion which shows the combined effect of corrosion and fretting of metal.

environment [7]. The tendency of a metal to corrode depends on the grain structure of the metal, its composition as formed during alloying, or the temperature for deformation of a single metal surface developed during fabrication. Corrosion prevention would be more practical than trying to eliminate it completely. Given that the environment plays an important part in corrosion, corrosion mechanisms can be as varied as the environments to which a substance is exposed and thus may be complex to understand. Factors that cause corrosion include reactivity of metal, presence of impurities, presence of air, moisture, gases like sulphur dioxide and carbon dioxide, and presence of electrolytes. Corrosion prevention and retardation are aimed at addressing these factors [8].

The different types of corrosion which depend on the environment surrounding the material, type of material, or chemical reaction are briefly described in Table 1 [9].

3. Corrosion Prevention Processes

The protection of materials especially steel structures from corrosion is achieved by basically two methods, namely, cathodic protection and the use of corrosion inhibitors. Cathodic protection to a metal structure can be done by either the technique of impressed current or using a sacrificial anode. Cathodic protection is achieved by making a metal to work as a cathode in an electrochemical cell. Sacrificial anodes are highly active metals with more negative electrochemical potential than the other metal which they are used to protect. Thus sacrificial anodes are consumed in place of the metal they protect. Impressed cathodic protection is obtained during the stage, where open circuit potential of cathodic sites gets polarized into the same circuits' potential of anodic sites and thus makes the whole circuit cathodic in nature to prevent corrosion [8].

Among these methods, corrosion inhibition is the most economical, practical, and convenient technique to control corrosion on metals in aqueous environment [10]. Corrosion inhibitors control the metal dissolution as well as the acid consumption. Inhibitors are adsorbed on the metal surface,

forming a protective barrier, and interact with anodic or/and cathodic reaction sites to decrease the oxidation or/and reduction of corrosion reactions [11]. Most of the well-known inhibitors are organic compounds containing electronegative functional groups and π -electrons in conjugated double or triple bonds and hence exhibit good inhibitive properties by supplying electrons through π -orbitals [12]. There is also a specific interaction between functional groups containing heteroatoms like nitrogen, sulfur, oxygen having free lone pair of electrons, and the metal surface, which play an important role in inhibition. When both of these features combine, increased inhibition can be observed [13].

4. Synthetic Organic Corrosion Inhibitors

Synthetic compounds containing multiple bonds and heteroatoms are effective inhibitors, but at the same time the processing time, cost, and their toxic nature have compelled researchers to look for alternatives [6]. The inhibiting effect of some of these synthetic organic compounds on the corrosion of mild steel has been recently reported by several authors [1, 5, 10, 12–20]. However, most of the compounds that constitute these inhibitors are expensive and toxic to human and the environment. The toxicity of these organic inhibitors has paved way to explore the use of nontoxic natural products inhibitors that are environmentally friendly and biodegradable.

5. Some Active Ingredients in Green Corrosion Inhibitors for Mild Steel

Plant extracts have potential to replace synthetic organic and inorganic inhibitors given their success story in literature. The mechanism of action of green inhibitors depends on the structure of the active ingredient and thus many researchers have to date postulated many theories to explain this phenomenon [12]. One suggestion is that the active compounds form onium ions in acidic solutions and are

TABLE 2: Plants extracts as corrosion inhibitors for mild steel.

Plant extracted	Material solution	Effect of temperature on % inhibition efficiency	Effect of concentration on % inhibition efficiency	Methods	Adsorption isotherm	Reference
Molasses	HCl	Done at constant temperature	Increase	Potentiodynamic polarization, dynamic electrochemical impedance spectroscopy, and gasometry	—	[29]
<i>Pterolobium hexapetalum</i> and <i>Celosia argentea</i>	Industrial water	Decrease	Increase	Weight loss and electrochemical impedance spectroscopy	Langmuir	[25]
<i>Pentaclethra macrophylla</i> Bentham	HCl	Decrease	Increase	Weight loss and electrochemical impedance spectroscopy	Langmuir and Temkin	[30]
<i>Phyllanthus fraternus</i>	H ₂ SO ₄	Decrease	Increase	Weight loss, gasometric techniques, and electrochemical impedance spectroscopy	—	[31]
<i>Antigonon leptopus</i>	H ₂ SO ₄	Increase then decrease	Increase	Weight loss	—	[32]
<i>Nypa fruticans</i> Wümb	H ₂ SO ₄	Increase	Increase	Weight loss	—	[33]
<i>Aniba roseaodora</i>	HCl	Done at constant temperature	Increase	Potentiodynamic polarization and electrochemical impedance spectroscopy	Langmuir	[34]
<i>Caesalpinia pulcherrima</i>	H ₂ SO ₄	Increase then decrease	Decrease	Weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy	—	[26]
<i>Adenopus breviflorus</i>	HCl	Decrease	Increase	Weight loss	Langmuir	[35]
<i>Anacardium occidentale</i>	H ₂ SO ₄	Done at constant temperature	Increase	Gravimetric analysis	Langmuir	[36]
<i>Amaranthus cordatus</i>	H ₂ SO ₄	Done at constant temperature	Increase	Weight loss	—	[37]
<i>Rotula aquatica</i>	H ₂ SO ₄	Decrease	Increase	Weight loss, gasometric techniques, and electrochemical impedance spectroscopy	—	[38]
<i>Polyalthia longifolia</i>	H ₂ SO ₄	Increase	Increase	Weight loss	Langmuir, Temkin, and Freundlich	[27]
Coconut coir	H ₂ SO ₄	Decrease	Increase	Weight loss, gasometric techniques, electrochemical impedance spectroscopy, and potentiodynamic polarization	Temkin and Freundlich	[39]
<i>Juniperus</i>	H ₂ SO ₄	Decrease	Increase	Weight loss, gasometric techniques, electrochemical impedance spectroscopy, and potentiodynamic polarization	Temkin	[40]
<i>Cucurbita maxima</i>	HCl	Increase	Increase	Weight loss	Langmuir and Temkin	[28]
<i>Hyptis suaveolens</i>	H ₂ SO ₄	Decrease	Increase	Weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy	Langmuir	[41]
<i>Aloe barbadensis</i>	HNO ₃	Increase	Increase	Gravimetric analysis	—	[23]
<i>C. Papaya</i>	HCl	Done at constant temperature	Decrease	Weight loss	—	[42]

TABLE 2: Continued.

Plant extracted	Material solution	Effect of temperature on % inhibition efficiency	Effect of concentration on % inhibition efficiency	Methods	Adsorption isotherm	Reference
<i>Citrus aurantifolia</i>	H ₂ SO ₄	Decrease	Increase	Weight loss	Langmuir and Freundlich	[43]
<i>Terminalia chebula</i>	HCl	Done at constant temperature	Increase	Gravimetric analysis, potentiodynamic polarization, and electrochemical impedance spectroscopy	Langmuir	[44]
<i>Hibiscus sabdariffa</i>	H ₂ SO ₄ and HCl	Done at constant temperature	Increase	Weight loss	Langmuir	[45]
Turmeric and ginger rhizomes	HCl	No trend	Increase	Weight loss and potentiodynamic polarization	Langmuir	[46]
Watermelon rind	H ₂ SO ₄ and HCl	Done at constant temperature	Increase	potentiodynamic polarization and electrochemical impedance spectroscopy	Temkin	[47]
<i>Piper nigrum</i>	H ₂ SO ₄	Decrease	Increase	Weight loss and gravimetric and thermometric analysis	—	[48]
<i>African Perquetina</i>	H ₂ SO ₄	Decrease	Increase	Weight loss and gravimetric, gasometric, and thermometric analysis	Langmuir	[49]
<i>Musa paradisiaca</i>	HCl	Done at constant temperature	Increase	Weight loss, electrochemical impedance spectroscopy, and Tafel polarization	Langmuir	[50]
<i>Nicotiana tabacum</i>	H ₂ SO ₄	Decrease	Increase	Weight loss	Langmuir	[51]
Pectin	HCl	Increase	Increase	Weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy	Langmuir	[3]
<i>Hunteria umbellata</i>	H ₂ SO ₄ and HCl	Decrease	Increase	Weight loss	Langmuir	[2]
<i>Vernonia amygdalina</i>	H ₂ SO ₄	Decrease	Increase	Weight loss, gasometry, and thermometric measurements	Langmuir	[52]
Neem	Salt water	Done at constant temperature	Increase	Weight loss	—	[24]
African breadfruit	H ₂ SO ₄	Increase	Increase	Weight loss	Freundlich	[53]
<i>Ligularia fischeri</i>	HCl	Decrease	Increase	Weight loss, potentiodynamic polarization, Tafel polarization, and electrochemical impedance spectroscopy	Langmuir	[54]
<i>Phyllanthus amarus</i>	HCl	Decrease	Increase	Weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy	Langmuir	[55]
<i>Elaeis guineensis</i>	HCl	Decrease	Increase	Weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy	Langmuir	[56]
<i>Aloe vera</i>	HCl	Decrease	Increase	Weight loss and electrochemical impedance	Langmuir	[57]

adsorbed on the cathodic sites of the metal surface and interfere with the cathodic reaction [21]. The active constituents of natural inhibitors vary from one plant species to another but their structures are closely related to their organic counterparts. For example, garlic contains allyl propyl disulphide, mustard seeds contain an alkaloid berberine which has a long chain of aromatic rings and an N atom in the ring, and, at several places, 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 [21].

6. Plant Extracts as Corrosion Inhibitors for Mild Steel

The adsorption of natural corrosion inhibitors on metal surfaces is influenced by a number of factors including nature of metal, testing media, chemical structure of inhibitor, nature of substituents present in the inhibitor, presence of additives, solution temperature, and solution concentration [22]. Recent studies by various authors on the inhibition of mild steel by plant extracts are shown in Table 2.

It can be observed from the reviewed summarized literature in the table that there has been active research on the application of plant extracts as green corrosion inhibitors for mild steel for the period of about two years reviewed. The analysis of the review summary above in Table 2 is thus presented below.

6.1. Corrosion Media. The research was mainly conducted in sulphuric acid and hydrochloric acid and in some cases in both media and thus covered fair representation of real industrial scenarios, where steel exposed to these acids is used. It is interesting to note that nitric acid [23] and salt [24] media were also explored although in isolated cases. The research conducted in the industrial effluent [25] medium shows that the application of green corrosion inhibitors in real effluent is beginning to show up and this may lead to large scale implementation.

6.2. Effect of Increasing Inhibitor Concentration and Temperature of Inhibition Efficiency. The effect of increasing concentration of inhibitor resulted in increase in inhibition efficiency for all studies except an extract from *Caesalpinia pulcherrima* [26], where inhibition efficient increases with decrease in inhibitor concentration. This is encouraging because it means green inhibitors can be used in low concentration, thus making them cheaper and eco-friendly. The inhibition efficiency decreased with an increase in temperature in most cases, thus proving that the process is efficient at room temperature or low temperatures. In some

few cases [3, 23, 27, 28], inhibition efficiency was high at high temperature and this can be an advantage, where mild steel is used in high temperature applications.

6.3. Methods Used for Studying Inhibition Efficiency, Inhibitor Type, and Adsorption Process. In all cases, the weight loss method was employed in measuring inhibition efficiency. The other popular method was gravimetric analysis. Potentiodynamic polarization and electrochemical impedance spectroscopy were mostly used in deducing inhibitor type and adsorption process. Tafel polarization and gasometric, thermometric methods were also used in addition to the above in some few cases. The adsorption of plant extracts and acid ions on the surface of mild steel in the majority of the studies followed the Langmuir isotherm model.

7. Conclusion

From the above discussion, it is quite obvious that natural plant extracts are effective green corrosion inhibitors against mild steel. Weight loss, electrochemical impedance, and potentiodynamic polarization techniques were mainly used to confirm corrosion inhibition mainly in sulphuric acid or hydrochloric acid media. A lot of potential is still untapped especially computational modelling of the major extract components on mild steel. This will help in establishing detailed mechanisms for corrosion inhibition. Work on the studies of real industrial effluent or real life situations is limited. There is need for further work on the exploration of these plant materials in other corrosive environments such as carbon dioxide, sulphur dioxide, and hydrogen sulfide. Further research should also be focused on the extraction and structural elucidation of active plants extracts to ascertain the structure of these compounds so as to help understand the process of corrosion inhibition. Scale-up experiments for industrial applications also need to be done so as to commercialize these natural extracts to effectively replace the conventional chemicals currently used to control corrosion.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

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