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Study of Green Corrosion Inhibitors using Plant Extract

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Abstract: *Corrosion is an ubiquitous process,causing huge economic loss to industries.One of the most economical and practical methods for reducingcorrosive attack on metals and alloys is use of corrosion inhibitors. Increased environmental awareness in last few decades has motivated scientists to reorient their studies to develop green alternatives to widely used synthetic corrosion inhibitors which are not only expensive but also toxic and non biodegradable. Various plant extracts and phytoharmones are therefore being explored as green corrosion inhibitors as a substitute to their hazardous counterparts.Besides being environment friendly and ecologically acceptable, green corrosion inhibitors are inexpensive, readily available and renewable.This paper intends to highlight the research work reported in this field in last decade.This work focusses on advances made in use of plant extracts as green corrosion inhibhitors for mild steel in corrosive fluids due to their industrial importance.*

Keywords: Corrosion, Green Inhibitors, Plant Extracts, Mild Steel

I. INTRODUCTION

A comparative study of the inhibitory effect of various parts of the plant Mimusaps Elangi (ME) extract (leaves, fruits, barks, seeds) on the corrosion of mild steel in 1 N HCl medium was investigated using weight loss method, potentio dynamic polarization and electrochemical impedance spectroscopy techniques. The polarization studies revealed that the plants extract act as mixed type inhibitor. It was found from the weight loss method that the inhibition efficiency of ME extracts increase in concentration dependents manner which was also supported by the results of electrochemical techniques. On comparison, maximum inhibition efficiency was found in ME leaves extracts with 98.50% at 20 ppm concentration. The SEM morphology of the adsorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the plant extract. Surface coverage values were tested graphically for suitable adsorption. Temperature studies revealed decrease in inhibition efficiency with increase temperature which suggests physisorption mechanism.

Corrosion is the deterioration of metal by chemical attack or reaction with environment. It is a constant and continuous problem, often difficult to eliminate completely. Prevention would be more practical and achievable than complete elimination. Corrosion process develop fast after disruption of the protective barrier and are accompanied by a number of reaction that change the composition and properties of both the metal surface and the local environment, for example, formation of oxides, diffusion of metal cations into matrix, local pH change, and electrochemical potential. Mild steel suffer from severe corrosion in aggressive medium of acids and pickling process. Hydrochloric acid is widely used for pickling, descaling, and chemical cleaning of mild steel. Generally, organic compounds containing O, N, and S atoms are used as inhibitors to reduce the corrosion of mild steel in hydrochloric acid medium [1]. Environmental friendly inhibitors have attracted several researchers. Corrosion control of metals is of technical, economical, environmental and aesthetic importance. The use of inhibitor is one amongst the simplest choices of protective metals and alloys against corrosion particularly in acid solution. Corrosion inhibitor is a substance added in

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small concentration to an environment, effectively reduces the corrosion rate of a metal exposed to it. Large numbers of organic compound have been studied and are still being studied to assess their corrosion inhibition potential. However, most of these substances are not only expensive but also pose health and environment hazards prompting the search for their replacement. The plant extracts are considered as an incredibly rich source of environmentally acceptable corrosion inhibitor. A lot of natural products have been previously used as corrosion inhibitor for different metals in various environments [2–15]. Also plants have been recognized as source of naturally occurring compounds that are generally referred to as ‘‘green’’ compound, some with rather complex molecular structure and having a variety of physical, chemical and biological properties. A number of these compounds are enjoying use in traditional application such as pharmaceuticals and biofuels. Furthermore, there has been a growing trend in the use of natural and medicinal plant used as corrosion inhibitor as they are environmentally safe, readily available and renewable source of a wide range of chemical. Due to biodegradable, ecofriendly, low cost and easily availability, the extract of some common plants based chemical and their by-product have been tried inhibitor for metal under different environment and Mimusaps Elangi (ME) is one of the universal plants having medicinal activities. Recently, many medicinal plants extract have been reported as effective corrosion inhibitor (allium sativum and madhuca longifolia). Medicinal values of Mimusaps Elangi plants lie in some phytochemical substances that produce a definite physiological action on human body In this study, same medicinal plants but various parts like leaves, seeds, barks, and fruits have been selected to study the inhibition effect on the corrosion of mild steel in 1 N HCl media.

A. Corrosion inhibitors & Their Classification

Corrosion inhibitors are compounds that slow down the process of corrosion by forming a thin layer of molecules on the surface of the metal through adsorption. This layer reduces the metal’s dissolution and prevents direct contact of the corrosive medium (the atmosphere) with the metal. They achieve this by modifying the reactions at the anode or cathode or by slowing down the pace at which reactants diffuse through the metal’s surface, thereby reducing the rate of corrosion [7].

There are two types of corrosion inhibitors based on their molecular structure: inorganic and organic. Inorganic inhibitors (such as nitrites, arsenates, nitrates, phosphates, and chromate) create a passive film or coating on the metal anode, while organic inhibitors are mostly composed of heterocyclic substances (such as pyridine, amine, etc.) that either create a film to cover the metal’s surface or adsorb on the metal due to the presence of various functional groups (e.g. nitro groups, cyanides, and isocyanides).

These functional groups facilitate the transport of electrons from the inhibitor to the vacant d-orbital of the metal. Inorganic inhibitors build brittle passive layers that can make the metal surface susceptible to local corrosion attacks, such as pitting and fissures. On the other hand, organic green corrosion inhibitors can evenly passivate metal surfaces, providing superior protection against aggressive media.

B. Adsorption and mechanism

Corrosion inhibition works by forming a protective film on the metal surface, which reduces the availability of active sites. This process involves adsorption, which can occur in three ways: physisorption, chemisorption, or combination. Each mode of adsorption affects corrosion inhibition in different ways. Physisorption occurs due to ionic interactions between the charged corrosion inhibitor and the metal surface, which reduces active sites [9]. Chemisorption involves the sharing of electrons, leading to coordination bonds between the metal surface and high electron density heteroatoms such as oxygen, sulfur, phosphorus, or nitrogen in the aromatic ring. The strength of the bond, conjugation in the aromatic ring, and the length of the carbon chain (affecting solubility) play an important role in inhibition. Mixed adsorption occurs when adsorption takes place at both the anodic and cathodic sites of the corroding metal. Fig. 1 shows the schematic representation of physisorption and chemisorption taking place in the same compound. Anodic

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inhibitors are also known as passivation inhibitors, which work by slowing down the anodic reaction, preventing the anode reaction, and promoting natural passivation by creating a cohesive and insoluble film on the metal surface. On the other hand, cathodic corrosion inhibitors prevent the cathodic reaction by triggering a cathodic reaction through metal ions, leading to the formation of precipitates on cathodic sites. This results in a dense film that restricts the diffusion of reducible species. Both anodic and cathodic inhibitors need to be present in adequate concentrations to form protective films. If the amount of inhibitors is inappropriate, it may lead to incomplete coverage, resulting in localized corrosion.

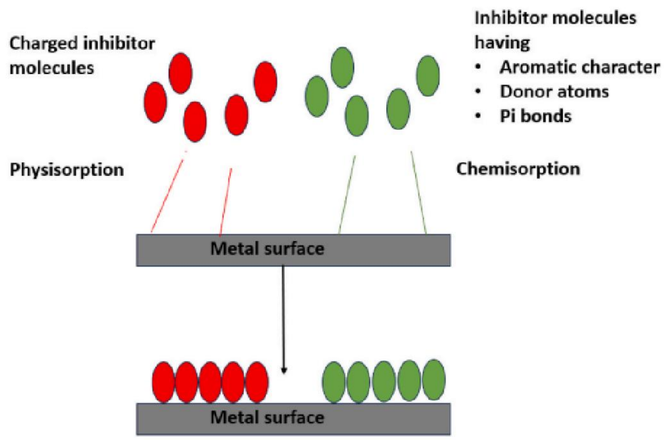

Fig1: Schematic representation of physisorption and chemisorption

The cost associated with corrosion inhibitors is quite high, which has prompted researchers to focus on green corrosion inhibitors for their biodegradable and non-toxic properties. These inhibitors are made by extracting various plant extracts and using their complex phytochemicals to prevent corrosion. Phytochemicals include alkaloids, tannins, pectin, steroids, flavonoids, and glycosides, which contain nitrogen, sulfur, oxygen, or phosphorus. Various parts of plants such as stems, leaves, fruits, flowers, seeds, and roots can be used to extract desired phytochemicals. Leaves, being the main site of photosynthesis, exhibit heightened protective qualities even at low concentrations. Literature reviews indicate the feasibility of using plant extracts as effective corrosion inhibitors. The process of extracting phytochemicals from plants involves selecting the plant portion (leaves, bark, stem, fruit, etc.) from which the phytochemicals are to be extracted. This plant component is then dried, ground, and sieved to create a powder. The desired phytochemical is then isolated and extracted using techniques such as solvent extraction, distillation, or sublimation processes. Solvent extraction is the most popular method and depends on extraction time, the ratio of solvent to solid, and a temperature that prevents active ingredients from being broken down. Ethanol is used as a solvent to extract alkaloids, flavonols, polyacetyles, tannins, sterols, and terpenoids. Methanol is used as a solvent to extract lactones, quassinoids, phenones, saponins, and total. Ether is used as a solvent to extract coumarins, fatty acids, and alkaloids, while acetone is used as a solvent to extract flavonols and tannins [11]

II. CORROSION INHIBITATION ON DIFFERENT KIND OF STEEL

In a study conducted by Thapa et al., Khasianine alkaloid was extracted from Solanum xanthocarpum stem and found to be a highly effective corrosion inhibitor for mild steel in 1 M H2SO4. The inhibitor demonstrated a 98 % efficacy rate when tested using electrochemical measurements and was shown to be a mixed type of corrosion inhibitor. It was also found that the Khasianine alkaloid could withstand temperatures of up to 55 ◦C. The molecular structure of the Khasianine alkaloid is shown in Fig. 2 [12], and the mechanism of corrosion inhibition by the alkaloid is represented in

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Fig. 3. Mwakalesi and their team have found a valuable use for waste by extracting an aqueous solution from it and using it as a corrosion inhibitor for mild steel in an acidic solution.

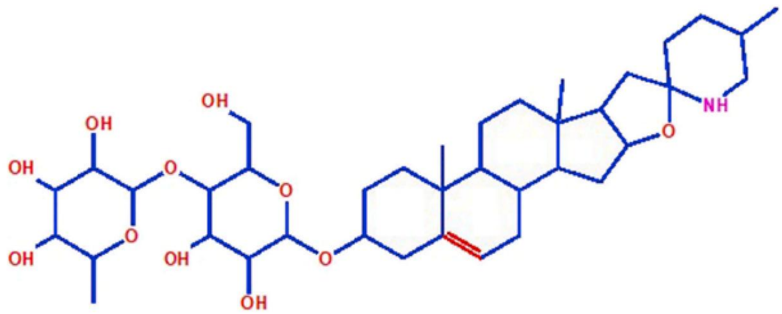

Fig2: Schematic Molecular structure of Khasainine alkaloid

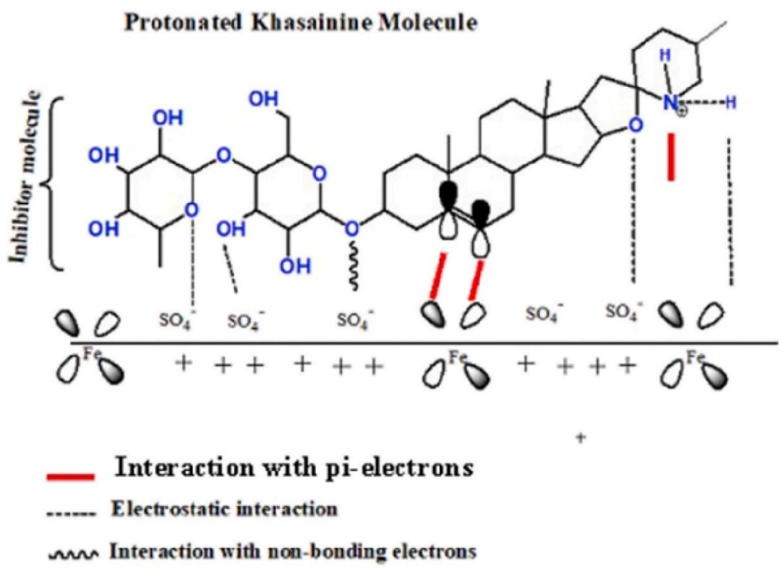

Fig3: Schematic representation of the mechanism of inhibition via interaction of alkaloid molecules with vacant d-orbitals of Fe. (MS – Mild Steel)

Their research showed that an 81 % efficiency rate was achieved when the extract was used at a concentration of 0.5 g/L. Additionally, with elevated concentration levels, efficiency saw an increase. The inhibition arose from a homogeneous distribution of molecules adsorbed via physisorption, adhering to the Langmuir adsorption isotherm [13]. Khadom and his colleagues conducted a study to investigate the potential of Cardaria darba leaves combined with potassium iodide as a corrosion inhibitor for mild steel in a 1 M HCl environment. The inhibitor was found to form a monolayer film on the metal surface through chemisorption. The Langmuir isotherm confirmed this process, and the inhibitor showed an impressive 96 % effectiveness, especially at 60 ◦C. The weight-loss method revealed an inverse relationship between temperature and the extract concentration [14]. In another study, pomegranate aril extract was used as a corrosion inhibitor for mild steel exposed to 1 M HCl. This inhibitor was identified as a mixed-type anodic-cathodic inhibitor, achieving an efficiency of 74 % at 25 ◦C with an extract concentration of 400 g/L. However, its

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efficacy declined at higher temperatures. The inhibition mechanism was attributed to physical adsorption, as validated by adherence to the Langmuir adsorption isotherm [15]. El-Etre and his colleagues investigated the use of Olea Europaea Sylvestris (Olive leaves) as a corrosion inhibitor for steel in 1 M HCl. The inhibition mechanism was determined to be physical adsorption, in line with the Langmuir adsorption isotherm, resulting in an efficiency of 66 % at an extract concentration of 0.96 g/L [16]. Betle nutshell was discovered to avoid corrosion in Q235 steel by forming a film over the Q235 and HCl interface due to the presence of several active components like chrysophanic acid and emodin-3-methyl ether. The inhibition effect was calculated to be 93.1 % based on the corrosion current produced, which was found to be minimum i.e., 0.27 mA cm^{-2} at 0.5 g/L of extract concentration when compared to 0.05, 0.1, 0.3 g/L concentrations. This shows that inhibition efficacy is directly related to the concentration [17]. R. Karki and his team reported that alkaloids extracted from Acacia catechu have inhibitory effects on mild steel exposed to 1 M H_2SO_4. The plant extract exhibited physical adsorption and was effective up to 48 ◦C, displaying an efficiency of 84.4 % and had a maximum inhibitory efficiency of 93.9 % after 3 h of immersion, at 1000 ppm concentration, 28 ◦C [18]. Sweet yellow capsicum extract (SYCE) showed inhibitory capabilities towards steel bars in cement pore solution. The maximum degree of inhibition was 97.5 % at 300 ppm concentration. The adsorption mechanism was physisorption and obeyed the Freundlich adsorption isotherm. Gallic acid, caffeic acid, p-coumaric acid, ferulic acid, luteolin, and cinnamic acid are some of the most important components in the sweet yellow capsicum extract responsible for inhibiting corrosion [19]. The leaves of Fenugreek seed and Cape gooseberry were found to demonstrate corrosion inhibition for steel immersed in the H_3PO_4 for 1 h, with the formation of a coating on the surface due to L-tryptophan and Ferulic acid. The inhibition was accomplished through the physisorption mechanism. 0.4 g/L of Cape gooseberry extract and 1.2 g/L of fenugreek extracts had an 80 % inhibitory effectiveness for steel in a 20 % aqueous H_3PO_4 solution. Up to 55 ◦C, the inhibitory effectiveness was still strong, however as the temperature rose, the corrosion rate also increased. The structure of L-tryptophan and Ferulic acid is given in fig.

III. METHODOLOGY

A. Mechanism Of Corrosion Inhibition By Plant Extracts

Adsorption of various phytochemicals contained in plant extract on metal surface and formation of protective film is the most probable mechanism involved in corrosion inhibition. The corrosion of mild steel in HCl solution has been reported to be inhibited by green corrosion inhibitors due to adsorption of organic compounds present in plant extracts electrons of multiple bonds or lone pairs on through interaction of their polar functions with N, O, S, P with metal d orbitals on mild steel surface.

B. Corrosion Inhibitors For Mild Steel In Corrosive Media\

Some essential oils present in Ginger, Henna, Jojoba, Artemisia are reported to be efficient corrosion inhibitors for steel. Tannins and their derivatives and alkaloids like paparvarine, strychinine, Quinine, nicotine etc are also novel corrosion inhibitors to protect steel. Aminoacids such as alanine, cysteine, glutamic acid, glycine, lucine, serine, threonine, tryptophan have also been studied for corrosion inhibition in mild steel.Some of the plant materials reported to be efficient corrosion inhibitors for mild steel are listed

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Table 1: Block Diagram of System

Inhibitor	Medium	Method
Aloe vera	H_2SO_4	Langmuir adsorption isotherm
Pennyroyal mint	1M HCl	Weight loss method
Justica gendarssa	1M HCl	Weight loss, AFM,electrochemical polarisation
Caeffic acid	0.1M H_2SO_4	Weight loss,potentiodynamic polarisation
Phyllanthus amarus	1M HCl	Weightloss, gasometric technique
Mangifera indica	0.2M HCl	Electrochemical impedance
Eucalyptus,Hibiscus & Agaricus	H_2SO_4	Weight loss, polarisation method
Rhizome(Curcuma longa) powder	60ppm Cl	Weight loss,FTIR,UV fluorescence
Andrographis paniculata	1M HCl	Tafel polarisation & impedance studies
Olea europaea	2M HCl	Weight loss method
Hibiscus sabdariffa	1M H_2SO_4	Weight loss method

IV. CONCLUSION

The fight against corrosion is complex, and it demands innovative preventive methods. Green corrosion inhibitors, particularly those derived from plants, are gaining significant interest due to their safety and environmental benefits. They are safer to handle, gentler on the environment, and offer a distinct advantage over traditional inhibitors. With their inherent chemical diversity, plant extracts create a synergistic effect that produces a more complete and effective corrosion inhibition mechanism. This review explores the various plant-based inhibitors and highlights the need to evaluate their efficacy. Careful selection and performance assessment are essential for maximizing the benefits of green corrosion inhibitors. By using green inhibitors, we can protect metals efficiently with minimal environmental and health impact, aligning perfectly with sustainability goals. Organic corrosion inhibitors are vital weapons in the battle against metal corrosion. Continued research is necessary to enhance their effectiveness and unlock the secrets behind their complex mechanisms. The pursuit of new and improved organic inhibitors holds the potential to reduce the toll corrosion takes on metal surfaces and extend the lifespan of countless metal structures. Therefore, the importance of organic corrosion inhibitors cannot be understated, and ongoing research is essential to unlock their full potential in preventing corrosion.

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