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Okra Leaf Extract as a Friendly Corrosion Inhibitor for Mild Steel in Acidic Solution

A Thesis Submitted to the Council of College of Engineering, University of Diyala in Partial Fulfillment of the Requirements the Degree of Master of Science in Chemical Engineering.

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Abstract

Corrosion is the detrimental effect of various corrosive environments on metals and alloys. Sulfuric acid is one of the most common types of these environments due to its widespread use in the chemical industry. Several strategies are used to prevent and control corrosion. Plant extract inhibitors are the most common and widely used of these strategies because they are inexpensive, readily available, sustainable and environmentally friendly.

In this investigation, Okra Leaf Extract (OLE) was used as an inhibitor for corrosion of mild steel (N80) in acidic solution (1M H_2SO_4), the solvent extraction method which is the most widely used to separate plant components, where by the Soxhlet device, solid organic compounds were extracted from okra leaves using distilled water as a solvent. Optimizing the effect of extraction time, solvent volume, and dried okra leaf powder mass on the yield percentage. Two mathematical models were proposed, the polynomial and the power model. It was found that the highest correlation coefficient (0.9707) was obtained from the polynomial model and the highest extraction yield was obtained at the ideal values of time 200.0 min and 29.07 g for the powder mass and 290 mL for solvent volume.

The metal corrosion rate in the absence and presence of the inhibitor at concentrations (0, 25, 50, 75, 100 mL\L) and temperatures (30, 40, 50, 60 °C) was evaluated using mass loss technique and electrochemical polarization technique with the highest efficiency of 96%, 95% respectively. The electrochemical measurements showed that the inhibitor is of a mixed type, providing both cathodic and anodic protection. The corrosion inhibition process was modeled mathematically and statistically by proposing two models, the first is polynomial and the second is power model. Levenberg-Marquardt estimation and nonlinear estimation using least squares were used. The correlation coefficient for the first polynomial model was 0.9421 and the second is power model 0.9487. The force model had the highest correlation coefficient and was more accurate.

Measurements of FTIR, HPLC and UV were used to confirm and support the results of the weight loss technique and electrochemical polarization technique. To study the surface morphology, Optical Microscopy (OM), Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) were used, all of which showed the formation of a protective layer on the metal surface. The thermal stability of the inhibitor molecules was studied using Thermogravimetric Analysis (TGA), which showed that the OLE molecules are thermally stable up to a temperature of 85 °C.

Chapter One

Introduction

Introduction

1.1 Definition of Corrosion

Corrosion can be defined as a destructive attack by chemical or electrochemical interactions between metals and the environments to which they are exposed. Rust is a term that indicates the corrosion of iron and the formation of corrosion products consisting largely of hydrated ferric oxides. The corrosion processes are mostly electrochemical and the structure of the metal and its components determine the corrosion behavior (Lin et al, 2023).

In general, the corrosion process is an oxidation and reduction reaction that occurs between metals and their surrounding environments, which contain oxidizing agents. Electrons are exchanged between metals and those environments during the oxidation and reduction processes.

The corrosion process is considered an electrochemical cell, where the metal is oxidized or corroded at the anodic electrode while reduction of hydrogen in acidic media at the cathode electrode (Xia., et al. 2022) In general corrosion reactions occur as follows:

$Fe \rightarrow Fe^{+2} + 2e^-$ Anodic oxidation reaction (1-1)

Where (1.1-1) is the oxidation reaction at the anodic electrode and the transformation of the metal from the metallic state to the ionic state which means corrosion of the metal (each metal atom releases two electrons, changing its valence state from 0 to 2). Through this reaction, electrons are transferred to the cathode through the metal surface until they interact with oxygen in the presence of water.

$2H^+ + 2e^- \rightarrow H_2 \uparrow$ Cathodic Reduction Reaction at acidic PH (1-2)

$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$ Cathodic reduction reaction at neutral or alkaline PH (1-3)

$Fe^{+2} + 2OH^- \rightarrow Fe(OH)_2$ Cathodic reduction reaction (1-4)

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ Oxygen depolarization reaction (1-5)

Where equation (1.1-2) represents the reduction reaction and the release of hydrogen gas at the cathodic electrode and equation (1.1-3) which O_2 is absorbed to give OH^- ions, equation (1.1-4) represents the metal ions Fe^{+2} resulting from the anode reaction react with hydroxide ions OH^- (Popov, et al. 2015). Equation (1.1-5) in acidic solution, oxygen depolarization reaction (Zarasvand, et al. 2014). The above equations can be reduced to one equation as below:

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2 \qquad (1\text{-}6)$$

The resulting $Fe(OH)_2$ is oxidized in the presence of oxygen and moisture to $Fe(OH)_3$ as below:

$$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O \rightarrow 2Fe(OH)_3 \qquad (1\text{-}7)$$

At the product is in equilibrium (it is expressed by Rust $Fe_2O_3 . H_2O$) as below:

$$2Fe(OH)_3 \rightarrow Fe_2O_3 . H_2O$$

Figure (1-1) (Prabhu, 2021) shows the electrochemical reaction that occurs when the iron is exposed to moisture air, where the iron reacts with oxygen in air oxygen to form (Fe_2O_3) in a moisture medium.

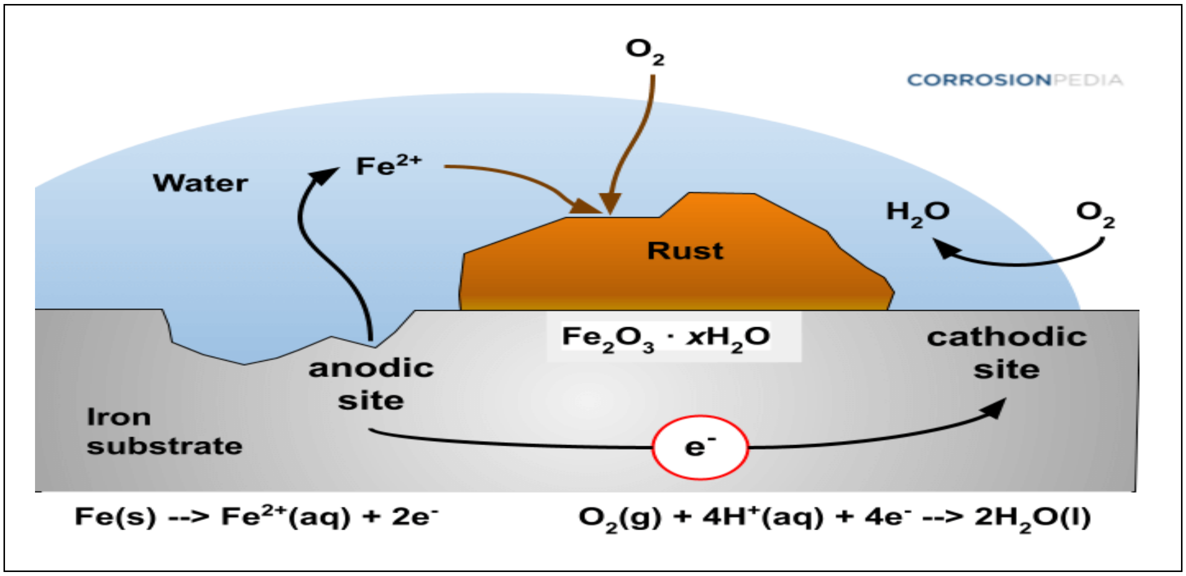

Figure 1.1: Electrochemical reaction of iron in humid air (Prabhu, 2021).

Corrosion of metals is an important problem that causes significant economic, human and environmental losses (Mourya, et al. 2014, De Lima, et al. 2020). Environmental deterioration of metals and their alloys is considered a serious problem all over the world because of its impact on infrastructure, industrial and architecture through the exposure of metal alloys to corrosive environments (oxidizing environments), such as in cleaning with industrial acids or acidifying oil wells or during competitive treatment processes such as acid pickling, etching and descaling (Khadiri, et al. 2016). To prevent the detrimental effect of the corrosion problem, various corrosion protection methods are used (Ahamd, 2006, Okafor and Zheng, 2009).

1.2 The Detrimental Effect of Corrosion

There are various detrimental effects of corrosion, including:

1. Time loss and decreased worth of goods and financial losses brought on by industrial plant shutdown.

2. Decrease in metal thickness, which causes metallic components to break down or lose their mechanical integrity.
3. Fluid contamination and holes in pipelines and containers
4. People's risks or injuries as a result of structural deterioration
5. loss of a metallic element's technically necessary surface characteristics, mechanical damage to pumps and valves,
6. Additional money spent on repairing corroded parts and creating equipment that is resistant to corrosion (Calle, 2009, Groysman, 2017).

Low-carbon steel is considered one of the most widely used and common types of metals in many industrial fields such as chemical, petroleum, power plants, heat exchangers, cooling towers, etc., because it is characterized by its high mechanical strength, ease of manufacturing, and low cost (Verma, et al. 2016, Sasikumar, et al. 2015). Because of the wide applications of low-carbon steel, it brings it into contact with corrosive environments such as Salty, Alkaline and Acidic solutions.

1.3 Corrosion Categorization

Wet (electrochemical) and dry (chemical) corrosion are the two categories into which the corrosion falls. In the presence of fluids, wet corrosion takes place. When there is no moisture to facilitate the corrosion and the metal oxidizes using only the environment, the process is known as dry corrosion. Wet corrosion differs from dry corrosion in that it necessitates the presence of an aqueous medium, which is typically in the form of an electrolyte or aqueous solution. It is the cause of the majority of corrosion forms that harm metal components. Steel corrodes in the presence of oxygen and water, as an illustration of this. Regarding dry corrosion, it typically happens at a temperature greater than the medium's condensation point and doesn't require the presence of any liquid or aqueous solution. It happens whenever there isn't a liquid condition or when the outside temperature rises above the dew point. Gases and vapors are the medium responsible for this kind of corrosion. The most frequent reason for dry corrosion is an increase in temperature. For instance, furnace gasses can corrode steel. Small amounts of moisture can significantly change how corrosion appears. For example, chlorine wet, or water with dissolved chlorine, is extremely corrosive and degrades most alloys and metals, yet dry chlorine is essentially non-corrosive to steel. There are several categories for corrosion, including high-temperature and low-temperature. Additionally, dry or chemical corrosion appears regularly and spreads over the entire metal surface, either wet or electrochemical corrosion is caused by electrical currents resulting from the presence of metallic impurities in the original metal, the metal being subjected to mechanical stress or the contact of two different metals (Garverick, 1994) There are other ways to categorize corrosion, including high-temperature and low-temperature corrosion. Here, localized and uniform corrosion are the recommended classifications. One prevalent kind of corrosion that spreads uniformly across the metal substrate's surface is called uniform corrosion. Specific locations on the metal substrate experience localized corrosion (Groysman, 2017).

1.4 Corrosion Control (Corrosion Prevention and Protection Methods)

Corrosion causes significant damage to properties such as industrial machinery, houses, structures, vehicles, and railroad bridges (Yang, et al. 2016). Every year, 3% - 4% of the world's steel supply is lost to corrosion (Pikaar, et al. 2014). Industries have created a variety of corrosion prevention techniques to prevent this loss (Liu, et al. 2018). There are primarily four methods to corrosion control. In different ways, every method seeks to lessen or resist the corrosive impacts on metal surfaces.

- Electrochemical protection (cathodic and anodic protection)
- Appropriate design and materials selection
- Coating resistant to corrosion
- Corrosion inhibitors

Between these, applying corrosion inhibitors is considered to be the simplest and cheapest method to reduce corrosion (Rani, et al. 2021, Umoren, et al. 2019).

1.4.1 Electrochemical Protection

Cathodic electrochemical protection is a technique used to manage corrosion in which the surface of the metal to be protected is made the cathode of an electrochemical cell, bonding it to another metal that is more prone to corrosion. This technique is used to safeguard metal structures that come into touch with a loose electrolyte, such as tanks, ships, boats, offshore oil platforms, water and fuel pipelines, and oil wells. Steel structures that are submerged in soil or water are also protected (Belgiu, and Dragut, 2016, Mobin, and Zehra, 2023, Evitts, and Kennell, 2018)

By providing a current from an external source to the metal that has to be protected, cathodic protection lowers the corrosive effect by minimizing the difference in capacitance between the anode and the cathode. The two primary cathodic protection systems are applied current and galvanic current. Cathodic protection extends the life of industrial equipment structures in general. By connecting the metal to be protected to another highly active, passive metal, which will corrode and discharge current into it, the galvanic cathodic protection mechanism works. Using a ground bed and a power source, current is applied from an external source to the metal that has to be protected in the applied current method. The electrical source lowers the rate of corrosion by converting alternating electrical energy into low-voltage direct current energy (Emelu, et al. 2023, Yao, et al. 2023, Xu, et al. 2021, Khudhair, and Hussein, 2024).

1.4.2 Appropriate Design and Materials Selection

The equipment consists of a substance that is intended to minimize corroding. When there is a corrosive environment present, it should be designed to prevent contact between two different metals. If direct contact between the two different metals is required, either an insulating substance must be provided between them to prevent direct electrical contact, or the metals must be as close to one another as possible in the electrochemical series. Additionally, since sharp corners increase the accumulation and rapid corrosion of solid materials, it is best to avoid designing with them.

The construction properties of suitable corrosion-resistant materials are high corrosion resistance, tensile strength and low cost. The material is selected according to previous experience and safety aspects, as well as the diagnosis of the suitable material under specific laboratory conditions to evaluate important laboratory results such as the effect of impurities, high temperature and pressure on it (Lyon, et al. 2017, Harsimran, et al. 2021)

The selection of materials is a crucial step in the design of industrial equipment, as the selection of the material, in addition to the physical and chemical properties, is affected by the environmental conditions of the operating or manufacturing process, such as temperature, acidity, humidity, stray currents, oxygen concentration, and chloride content, as these conditions are the cause of the deterioration and corrosion of materials (Bahadori, 2014, Hakimian, 2023, Diao, et al. 2021)

1.4.3 Coating Resistant to Corrosion

The most significant, practical, and inexpensive manner to slow down the rate of corrosion on metals is to coat them with a protective coating (Askari, et al. 2021). Well-known anti-corrosion coatings that are used to improve the Anti-Corrosion Protection Performance (APP) of the metallic substrates include Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD), electrochemical deposition, and organic/inorganic hybrid coatings (Hayatdavoudi, and Rahsepar, 2017a)

Coatings can therefore be utilized to functionalize a variety of material surfaces. Functional coatings are a type of materials that have a specific purpose and can be utilized in many different applications. They can be inorganic, organic, hybrid, nano, or green. In addition to being highly hydrophobic, a dependable coating should also be cheap to produce, stick effectively to materials, be sustainable, flexible, and simple to apply in corrosive environments (Hayatdavoudi, and Rahsepar, 2017b)

The common consensus is that coatings work by acting as a barrier, ideally with a high resistance to ionic mobility, between the substrate and the surrounding environment. In addition to these characteristics, it is assumed that suitable adherence to the metal substrate either directly or by the use of a primer or undercoat is necessary for good performance (Ralkhal, et al. 2019).

1.4.4 Corrosion Inhibitors

Corrosion inhibitors are the most practical and cost-effective way for reducing corrosion. Corrosion inhibitors prevent corrosion by adsorbing on low carbon steel surfaces and inhibiting electrochemical processes at the solution/metal contact (Farh, et al. 2023). Inhibitors adsorbed on the surface of metals change the structure of the electrical double layer between them by changing the rate of consumption of metals in acids, which affects the kinetics of electrochemical reactions that regulate the reaction process (Alhaffar, et al. 2018). Inhibitors are of two types: inorganic and organic. Inorganic inhibitors act as anodic inhibitors, while organic inhibitors form a protective layer on the metal surface to protect it from the corrosive environment (Khadom, et al. 2018). Organic inhibitors are organic molecules with structures that contain oxygen, nitrogen, sulfur, phosphorus, and heterogeneous atoms with a greater electron density, which operate as reaction centers. These chemicals are absorbed by the metal surface and work to inhibit active sites. The majority of them are toxic and damaging to the environment, thus their use is limited. As a result, the demand for effective and environmentally friendly organic inhibitors has increased, with a focus on plant-derived inhibitors that are known for their low cost, ease of extraction, non-toxicity, environmentally friendly properties, and availability on demand (Patel, et al. 2014a, Abakedi, and Asuquo, 2016).

1.5 Problem statement

This study deals with the problem of corrosion that threatens devices and equipment in various chemical, petroleum and other industries, which causes great material damage in addition to the risks that effect peoples as a result of their dealing with this equipment.

1.6 Objectives

The aim of this study is to focus attention on extracting non-toxicity, environmentally friendly, low cost, sustainable and availability on demand and ease to extract materials then studying the inhibition potential and the efficiency of the organic inhibition.

The organic materials in okra leaves were extracted, characterized and tested as a green corrosion inhibitor for carbon steel in sulfuric acid.

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مستخلص أوراق البامية كمثبط صديق للبيئة لتأكل الحديد المطاوع في الوسط الحامضي

رسالة مقدمة الى مجلس كلية الهندسة / جامعة ديالى
وهي جزء من متطلبات نيل درجة الماجستير في علوم الهندسة الكيمياوية

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