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1.1 Introduction

Corrosion specifically refers to any process involving the deterioration or degradation of metal components, it is the primary means by which metals deteriorate. Most metals corrode on contact with water (and moisture in the air), acids, bases, salts, oils, aggressive metal polishes and other solid and liquid chemicals. Metals will also corrode when exposed to gaseous materials like acid vapours, formaldehyde gas, ammonia gas and sulfur containing gases [1]. In other words corrosion is the destructive attack on a metal by chemical or electrochemical reaction with its environment, or it is the extractive metallurgy in reverse.

All metals have a characteristic, inherent tendency to corrode and react in aqueous environments to produce metal ions and release electrons. This inherent reactivity can be shown in terms of either free-energy, ΔG. The inherent reactivity of a metal can be expressed by the magnitude of the free energy change on the metal suffering a corrosion process. The corrosion process of the metal dissolving as ions generates some electrons that are consumed by a secondary reaction; the two processes must balance their charges. The sites hosting these two processes may be located close to each other on the metals surface, or far apart depending on local circumstances. When a metal (Fe) is placed in pure water, some ions will immediately pass into solution:

$$Fe \rightarrow Fe^{+2} + 2e^{-} \quad E^{o} = 0.44v \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.1)$$

Build-up of negative charge on the metal and the existence of metal ions in solution makes it possible for a back-reaction to proceed:

$$Fe^{+2} + 2e^{-} \rightarrow Fe \quad E^{o} = -\ 0.44v \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.2)$$

and ultimately the equilibrium is established:

$$Fe \Leftrightarrow Fe^{+2} + 2e^{-} \quad (1.3)$$

Now, a steady potential difference exists between the metal and the solution. The magnitude of this potential difference depends on the metal type and composition of the solution [1]. The three main reasons for the importance of corrosion prevention are economics, safety and environmental damage. To reduce the economic impact of corrosion, corrosion engineers, with the support of corrosion scientists, aim to reduce material losses, as well as the accompanying economic losses, that result from the corrosion of piping, tanks, metal components of machines, ships, bridges, marine structures, and so on.

Loss of metal by corrosion is a waste not only of the metal, but also of the energy, and the human effort that was used to produce and fabricate the metal structures in the first place.

The economic factor is a very important motivation for much of the current research in corrosion. Losses sustained by industry and by governments amount to many billions of dollars annually.

However, corrosion has a tremendous effect on the environment in the sense corrosion-related failure of oil pipelines or gas pipelines or oil tankers can have very detrimental effect on the environment in the form of water and air pollution, leading to the demise of aquatic life . Industries depend heavily on the use of metals and alloys. One of the most challenging and difficult tasks for industries are the protection of metals from corrosion. Corrosion is a ubiquitous problem that continues to be of great relevance in a wide range of industrial applications and product [2].

Carbon steel alloys are widely used in most industries for the fabrication of various reaction vessels, such as heat exchangers, cooling towers, and

pipes, for its low cost and availability. However, carbon steel is highly susceptible to corrosion and the corrosion of carbon steel has been a matter of great concern to various industries [1].

Particularly sulfuric acid is frequently used in industrial processes such as acid cleaning, acid pickling, acid descaling, and oil well acidizing [3]. The acid constitutes strong corrosive environments for carbon steel and as a result, the study of the prevention of steel corrosion is always a subject of high theoretical and practical interest [1]. Dilute sulfuric acid reacts with metals via a single displacement reaction as with other typical acids, producing hydrogen gas and salts (the metal sulfate). It attacks reactive metals (metals at positions above copper in the reactivity series) such as iron, aluminum, zinc, manganese, magnesium and nickel.

$$Fe_{(s)} + H_2SO_{4\,(aq)} \rightarrow H_{2\,(g)} + FeSO_{4\,(aq)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.4)$$

1.2 Importance of Corrosion Studies

The importance of corrosion studies is two folds. The first is economic, including the reduction of material losses resulting from wasting away or sudden failure of piping, tanks, metal components of machines, ships, hulls, marine, structures…etc. The second is conservation, applied primarily to metal resources, the world's supply of which is limited, and the wastage of which includes corresponding losses of energy and water resources accompanying the production and fabrication of metal structures. Losses sustained by industry, by the military, by municipalities amount to many billions of dollars annually [4].

1.3 Classification of Corrosion

Corrosion can be classified in many ways as:

1.3.1. Temperature of corrosion

1.3.1.1 Low temperature corrosion

In the low - temperature region, the oxidation rate of iron is sensitive to crystal face, decreasing in the order (100) > (111) > (110). The oxide nuclei, apparently consisting of Fe_3O_4 , grow to form a uniform film of oxide. Oxidation of iron in the parabolic range is complicated by the formation of as many as three distinct layers of iron oxide, and the proportions of these layers change as the temperature or oxygen partial pressure changes. Data reported by various investigators are not in good agreement, probably because of variations in the purity of iron used for oxidation tests — particularly its carbon content [5].

1.3.1.2 High temperature corrosion

High-temperature corrosion is considered to be electrochemical in nature, with the high-temperature scale formed acting as an electrolyte. Corrosion is usually uniform in nature. The predominant effects are oxidation and carburization /decarburization. Changes in mechanical properties, specifically a loss of ductility due to phase changes, also take place. Most high-temperature reactions involve oxidation because oxides are common products in the many applications where air or oxygen-rich environments are present. In clean atmospheres, a thick oxide film forms that develops into a thicker scale. Oxidation phenomena are controlled by thermodynamic and kinetic factors, notably gas composition and temperature [5].

1.3.2. Reaction of corrosion:

1.3.2.1 Electrochemical corrosion

Corrosion can be separated into two or more partial reactions. These partial reactions are divided into two classes: oxidation and reduction [6]. These two separated reactions are taking place at different areas on the metal surface. One of the reactions (oxidation and reduction) being the anodic reaction consists of an oxidation type chemical change in which the metal changes from the metallic state to an ionic state, i.e. the valance of metal is increased by giving off electrons.

$$M \rightarrow M^{++} + 2e^{-} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.5)$$

At different sites from the anodic one will occur the cathodic reaction. There are different cathodic reactions which are frequently encountered in metallic corrosion. The most widespread cathodic reactions are:

1. Hydrogen formation:

   $$2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2\,(g)\uparrow} \quad E^{o} = 0.0\ v \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.6)$$

2. Oxygen reduction (acid solution):

   $$O_{2\,(g)\uparrow} + 4H^{+}_{(aq)} + 4e^{-} \rightarrow 2H_2O_{(L)} \quad E^{o} = 1.23\ v \ \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.7)$$

3. Oxygen reduction (neutral or basic solutions):

   $$O_{2\,(g)\uparrow} + 2H_2O_{(L)} + 4e^{-} \rightarrow 4OH^{-}_{(aq)} \quad E^{o} = 0.40\ v \ldots\ldots\ldots\ldots\ldots \quad (1.8)$$

4. Metal ion reduction:

   $$M^{+3} + e^{-} \rightarrow M^{+2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.9)$$

5. Metal deposition:

   $$M^{+} + e^{-} \rightarrow M \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.10)$$

1.3.2.2 Chemical corrosion

Direct chemical attack, or pure chemical corrosion, is an attack resulting from a direct exposure of a bare metal surface to caustic liquid or gaseous agents. Unlike electrochemical attack where the anodic and cathodic changes may be taking place a measurable distance apart, the changes in direct chemical attack are occurring simultaneously at the same point. The most common agents causing direct chemical attack on aircraft are: (1) spilled battery acid or fumes from batteries; (2) residual flux deposits resulting from inadequately cleaned, welded, brazed, or soldered joints; and (3) entrapped caustic cleaning solutions.

1.3.3 Medium of corrosion:

1.3.3.1 Dry corrosion:

It's occurs with gases as the corrosive agent and in the absence of aqueous phases on the metal surface such as Cl_2 ; HF ; fumes H_2SO_4.

1.3.3.2 Wet corrosion:

It's occurs when aqueous phases are present on the surface of the metal [7]. The wet corrosion proceeds faster than dry corrosion since the dipolar water molecule stabilizes the free metal ions in solution, in addition, the metallic structure and water in contact with it are both electric current conducting. Various forms of wet corrosion have therefore been identified and classified such as uniform, pitting, crevice, erosion, intergranular, selective leaching and stress corrosion cracking, as shown below [8]:

a. General (uniform) corrosion

It's an even rate of metal loss over the exposed surface, which is characterized by corrosive attack proceeding evenly over the entire surface area, or a large fraction of the total area.

Uniform corrosion is the simplest form of corrosion, it is one of the most easily measured and predictable forms of corrosion, making disastrous failures relatively rare therefore it is not always the most important in terms of cost or safety. But if surface corrosion is permitted to continue, the surface may become rough and surface corrosion can lead to more serious types of corrosion [8, 7].

b. Pitting corrosion

Pitting corrosion is characterized by a highly localized loss of metal. It appears as a deep, tiny hole on the metal. The width of the pit may increase with time but not to the extent to which the depth increases. Most often, the pit opening remains covered with the corrosion product, making it difficult to detect during inspection [8, 7].

Pitting may occur in most metal with protective film. Therefore initiation of a pit is associated with the breakdown of the protective film on the metal surface. Many metals and their alloys are subject to pitting in different environments such as alloys of carbon steels, stainless steels, titanium, nickel, copper, and aluminum [7].

c. Crevice corrosion (CC)

This is localized corrosion concentrated in crevices in which the gap is sufficiently wide for liquid to penetrate into the crevice and sufficiently narrow for the liquid in the crevice to be stagnant.

Various metals, e.g. Al, Fe, Cr and Ni, may suffer from crevice corrosion. CC which is affected by several factors; of a metallurgical, environmental, electrochemical, surface physical and last but not least, a geometrical nature. CC occurs beneath flange gaskets nail and screw heads and paint coating edges in overlap joints between tubes and tube plates in heat exchangers etc. The same form of corrosion develops beneath deposits of,

e.g. corrosion products, dirt, sand, leaves and marine organisms, hence it is called deposit corrosion in such cases. It comprises mechanisms, modelling, test methods and results, practical experience, protective measures and monitoring. A review of the mechanisms of CC has recently been published [7].

d. Intergranular corrosion

Intergranular corrosion is a localized attack on or at grain boundaries with insignificant corrosion on other parts of the surface. The attacks propagate into the material. This is a dangerous form of corrosion because the cohesive forces between the grains may be too small to withstand tensile stresses; the toughness of the material is seriously reduced at a relatively early stage, and fracture can occur without warning [8].

e. Selective corrosion (Selective leaching)

This form of corrosion is observed in alloys in which one element is clearly less noble than the other (s). The corrosion mechanism implies that the less noble element is removed from the material. The most common example of selective corrosion is dezincification of brass, in which is the term used to describe the leaching of zinc from brass [8].

f. Erosion corrosion

The term "erosion" applies to deterioration due to mechanical force. Erosion corrosion is usually caused by a gaseous or corrosive liquid flowing over the metal. It is affected by velocity, turbulence, impingement, the presence of suspended solids and temperature.

Turbulence phenomena can destroy protective films and cause very high corrosion rates in materials, therefore all equipment exposed to flowing fluid is subject to erosion corrosion [8].

g. Cavitation corrosion

This corrosion form is closely related to erosion corrosion, but the appearance of the attack differs from the erosion corrosion attacks described in the last section. While the latter has a pattern reflecting the flow direction, cavitation attacks are deep pits grown perpendicularly to the surface. Both high corrosion resistance and high hardness improve the resistance to cavitation attacks. Relative resistance of various steels, stainless steels, irons, copper alloys and nickel alloys are reported in references [7].

h. Stress corrosion cracking

Stress corrosion cracking (SCC) is a process involving the initiation of cracks and their propagation, possibly up to complete failure of a component, due to the combined action of tensile mechanical loading and a corrosive medium. This stress can either be applied (external load), or can be residual stress in the metal (e.g., due to production process or heat treatment) [7].

1.4 Thermodynamics of The Corrosion

Thermodynamics could suggest which reactions are possible and whether a particular reaction is likely will occur. This helps in the understanding of corrosion phenomena and is essential to the study of corrosion cells. Chemical thermodynamics studies investigate the role of entropy in chemical reactions [1]. Thermodynamics defines equilibrium as a function of the elements and compounds present and the environmental conditions, such as pressure, temperature, and chemical composition. Thermodynamics is used to determine whether corrosion can occur and to predict which stable corrosion products will be formed. A law of nature postulates that the most stable state for a set of reactants is that state which has the lowest free energy. Consequently, metal surfaces in contact with a

solution tend toward the lowest free-energy state possible. When the system reaches at this state, there is no further change. Ultimately this final, unique, lowest-energy state is the equilibrium state. At equilibrium, the system is stable, no driving forces are available for any change from that state.

1.5 Corrosion Control

Corrosion control is a process focuses mainly on (i) materials and (ii) environments. Corrosion management focuses on “people” and aims at improving the performance of engineering systems. So, effective corrosion control requires a complete management strategy involving people as much as equipment. And it's aimed to reduce the corrosion rate to a tolerable level (or predictable limits).

Sheir, et al [9], presented an outline scheme of ‘Methods of Preventing Corrosion’ in which five categories were defined, Design, Materials selection, Coating, Modification of the environment (adding inhibitors), Electrochemical methods,

- Cathodic protection
- Anodic protection

1.6 Studies of Green Inhibitors

An inhibitor is a substance added in a very low concentration to protecting the surface of a metal that is exposed to a corrosive environment that terminates or diminishes the corrosion of a metal [1]. The use of inhibitors has been well documented as an effective method of protecting metallic materials from corrosion. Many industrial processes have been put to use. Most inhibitors have been developed by empirical experimentation, to be used effectively, the inhibitor must be:-

1. Compatible with expected environment.
2. Economical for operation.
3. Amenable to protecting .
4. Contribute the greatest desired effect.

Many factors including cost, amount, easy availability and most .important safety to environment need to be considered when choosing an inhibitor.

1.7 General Characteristics of Green Inhibitors

Green inhibitors possess adsorption properties that are similar to the‘non-green’ inhibitors. Most of the green inhibitors adsorb on the metal surface by means of both physical and chemical adsorption at room temperature. In general, at elevated temperatures, inhibition occurs mainly through chemisorption. On prolonged exposure of the green inhibitor towards the corrosive environment, inhibitor gains or losses its effectiveness during the process of corrosion inhibition. The evaluation of the effect of increased time on the inhibition efficiency provide information about the stability of inhibitive behavior of the green inhibitor on time scale. In general, the effectiveness of the inhibitor decreases upon increasing the time, Which means that the adsorption of the inhibitor molecules on the metal surface occurs predominantly via physical interactions [10,11].

1.8 Types of Corrosion Inhibitors

Inhibitors are classified in to two types:

1.8.1 Inorganic inhibitors

It's used for corrosion protection but as a result of cost and toxicity, attention is currently shifted towards the use of more eco-friendly inhibitors. Inorganic inhibitors like chromate, phosphates, molybdates etc.

1.8.2 Organic inhibitors

It's used for corrosion protection containing functional groups with oxygen, nitrogen and /or sulfur atoms in a conjugate system have been reported to exhibit good inhibiting properties. This has made plant extracts an important choice for environmentally friendly, readily available and renewable source for a wide range of inhibitors referred to as green inhibitors. Some of the advantages of green inhibitors are low cost of processing, biodegradability, and absence of heavy metals or other toxic compounds which pose great hazard to the environment [12]. Some investigations in recent time have been made into the focused on corrosion inhibiting properties of natural products of plant origin, which showed good inhibition efficiencies. Each inhibitor must be tailored to the specific corrosion problem that needs solution [6]. While the use of inhibitors for some types of corrosion can be similar to other, this similarity must be treated as coincidence. Organic inhibitors generally contain heteroatoms such as O, N, and S which are found to have higher basicity and electron density suitable to act as corrosion inhibitor. O, N, and S are the active centers for the process of adsorption on the metal surface. The inhibition efficiency follows the sequence O < N < S < P [1].

Using organic inhibitors containing oxygen, sulfur, and especially nitrogen to reduce corrosion attack on steel has been studied in some detail

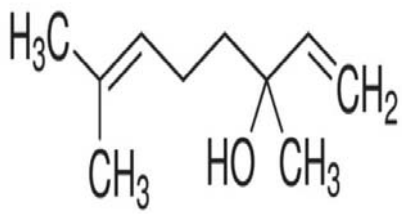
[1]. The use of inhibitor (*Citrus aurantium leaves* extract*) (CALE*), (*Rutaceae family*), also known as *sour orange* or *bitter orange*, is generally used as a rootstock and has a number of advantages, including resistance to several viral diseases, tolerance to cold, improvement in the fruit quality of the grafted plants, and it can be used as an ornamental tree [13].

1.9 Mechanism of Inhibitor

The inhibitors influence the kinetics of the electrochemical reactions which constitute the corrosion process, corrosion inhibitors adsorb on the metal surface and thereby change the structure of electrical double layer. Most of the efficient inhibitors used in industry are organic compounds that contain oxygen, sulfur, nitrogen atoms, which lead to the adsorption of the compounds on the metal surface [14]. Green or safe corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Corrosion inhibitors generally control corrosion by forming various types of films. Inhibitors form films in several ways: by adsorption, the formation of bulky precipitates, and /or the formation of a passive layer on the metal surface. Most of organic inhibitors retard corrosion by adsorption to form a thin, invisible film only a few molecules thick [15]. The existing data reveals that most organic inhibitors are adsorbed on the metal surface by displacing water molecules on the surface and forming a compact protecting barrier. Availability of no bonded (lone pair) and ∏-electrons in inhibitor molecules facilitate electron transfer from the inhibitor to the metal. A coordinate covalent bond involving transfer of electrons from inhibitor to the metal surface may be established.

1.10 Theoretical and Quantum Chemical Backgrounds

Quantum chemical calculations were used as a theoretical tool to support the experimental results and to explain the interaction between the inhibitor molecules and the steel surface, as well as the properties of this inhibitor concerning their reactivity. Linalool is the most important component which consists of than 58 % of *CAL* components [16, 17]. The chemical structure of these component were shown below



Linalool

According to PM3 theorem [18], the HOMO energy is related to the ionization potential (IP) whereas the LUMO energy is linked to the electron affinity (EA), as follows:

$$IP = -E_{HOMO} \quad E^{o} = -9.37 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.11)$$

$$EA = -E_{LUMO} \quad E^{o} = -0.38 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.12)$$

So, the electronegativity (χ), the chemical potential (μ) and the global hardness (η) were evaluated, based on the finite difference approximation, as linear combinations of the calculated IP and EA :

$$\chi = -\mu = \frac{IP + EA}{2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.13)$$

$$\eta = \frac{IP - EA}{2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.14)$$

The softness (σ) is the inverse of the global hardness.

$$\sigma = \frac{1}{\eta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.15)$$

The chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap. The global electrophilicity (ω) index was introduced as a measure of energy lowering due to maximal electron flow between donor and acceptor and is given by

$$\omega = \frac{\mu^2}{2}\sigma \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.16)$$

The fraction of transferred electrons (ΔN), evaluating the electronic flow in a reaction of two systems with different electro negativities, in particular case; a metallic surface and an inhibitor molecule was calculated according to Pearson theory [19] as:

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2\,(\eta_{Fe} + \eta_{inh})} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.17)$$

Where; χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and inhibitor molecule respectively, η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule respectively. In this study, we use the theoretical value of χ_{Fe}= 7.0eV and η_{Fe}= 0.0eV for the computation of number of transferred electrons. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance.

1.11 Parameters Effect on Wet Corrosion

1.11.1 Effect of temperature

Temperature increases the rate of almost all chemical reactions, lead to increase in corrosion rate but inhibitor efficiency decreases with increase it. Like most chemical reactions, the rate of corrosion of iron and steel in aqueous acid solutions increases with increasing temperature [6]. This effect can be expressed by Arrhenius equation in which the rate of corrosion reaction in correlated with temperature [20].

$$\text{Corrosion rate}(CR) = A \exp\left[-\frac{E_a}{RT}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.18)$$

Where; A is Frequency factor, E_a is Activation energy (kJ/mole), R is Gas constant (8.314 J/mole.K), T is Absolute temperature (K). From Arrhenius equation activation energy and frequency factor can be calculated by taking the natural (ln) of the previous equation lead to:

$$\ln(CR) = \ln A\left[-\frac{E_a}{RT}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.19)$$

So ln (CR) can be plotted against (1/T) with a slope of ($-E_a$ / R) and intercept of ln A. Temperature changes have the greatest effect when the rate determining step is the activation process. It is therefore not surprising that the activation energy of inhibited reactions at high coverages can be either larger or smaller than that of uninhibited reactions. Information contained in the literature shows that the relationship ln (CR) = f (1/ T) is quite frequently, although not always linear in the presence of inhibitor. While equation of transition state can be used to calculate enthalpy and entropy of activation as [21].

$$CR = \frac{RT}{Nh}\exp\left(\frac{\Delta S_{act}}{R}\right)\exp\left(-\frac{\Delta H_{act}}{RT}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.20)$$

$$\frac{CR}{T} = \frac{R}{Nh} \exp\left(\frac{\Delta S_{act}}{R}\right) \exp\left(-\frac{\Delta H_{act}}{RT}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.21)$$

$$\ln\left[\frac{CR}{T}\right] = \ln\left[\frac{R}{Nh} \exp\left(\frac{\Delta S_{act}}{R}\right) \exp\left(-\frac{\Delta H_{act}}{RT}\right)\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.22)$$

$$\ln\left[\frac{CR}{T}\right] = \ln\left(\frac{R}{Nh}\right) + \ln \exp\left(\frac{\Delta S_{act}}{R}\right) + \ln \exp\left(-\frac{\Delta H_{act}}{RT}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.23)$$

$$\ln\left[\frac{CR}{T}\right] = \ln \frac{R}{Nh} + \left(\frac{\Delta S_{act}}{R}\right) - \left(\frac{\Delta H_{act}}{RT}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.24)$$

Where; h is the Planck's constant (J.s), N is the Avogadro's number (mol), ΔS^* is the apparent entropy of activation ($kJmol^{-1}\ K^{-1}$), ΔH^* is the enthalpy of activation ($kJmol^{-1}$).

From equation (1.24) we can be plot ln (CR /T) against 1/T and the slope of the straight line show a value (- ΔH_{act} /R) and intercept show a value of (ΔS_{act} /R + ln R /Nh) from which ΔH_{act} and ΔS_{act} can be calculated.

1.11.2 Effect of acid concentration

As the concentration of a corrosive acid media is increased, the corrosion rate is likewise increased and this is primarily due to the fact that the amounts of hydrogen ions, which are the active species, are increased, as acid concentration is increased. Hydrogen ion activity is commonly expressed, for convenience in term of pH. At low pH values, hydrogen evolution usually predominate both in presence and absence of oxygen. Kinetic study of corrosion reactions of iron in H_2SO_4 by measuring the reaction rates in different molarity (0.5-1.5 M) at (30-60 °C). Development the kinetic observed that sulfuric acid because corrosive in (0.5M) lower than (1.5M). The dissolution rate and the amount of hydrogen absorbed by carbon steel in H_2SO_4, at different molarity (0.5-1.5 M) and different temperatures (30-60 °C). It was concluded that the dissolution rate of steel

in (1.5 M) of H_2SO_4 at 30 °C was much faster than the corresponding concentrations of the other [6].

1.11.3 Effect of reaction time

The rate of reaction can be obtained by plotting the concentration of carbon steel consumption against time and measuring the slope of the curve dW/dt (W is carbon steel consumption and t is time) at the required time. The rate of reaction obtained from such a method is known as instantaneous rate. For the determination of the instantaneous rate at any point, the slope of the curve is determined. The rate of reaction can be expressed by the following equation [22]:

$$\frac{dW}{dt} = k\,W^{n'} \quad \text{.....} \quad (1.25)$$

$$\ln\left(\frac{dW}{dt}\right) = \ln k + n' \ln W \quad \text{.....} \quad (1.26)$$

Where; k is rate constant and n` is order of reaction. Equation (1.26) can be drawn as ln(dw/dt) versus lnW and the values of slope and intercept can be obtained. However, the average rates calculated by concentration versus time plots are not accurate. This could be achieved by integrating the differential rate equation as below :

$$\int \frac{dW}{W^{n'}} = k\int dt \quad \text{.....} \quad (1.27)$$

Equation (1.27) can be integrated for different values of n`. Equations (1.28, 1.29 and 1.30) represent the rate equation for zero, first and second order, in order:

$$x = k_o\,t \quad \text{.....} \quad (1.28)$$

$$W_i = W_t \exp(k_1 t) \quad \text{..... (1.29)}$$

$$k_2 t = \frac{1}{a-x} - \frac{1}{a} \quad \text{..... (1.30)}$$

Where; W_i is the initial carbon steel consumption at t = 0 (gram), W_t is carbon steel consumption at any time (gram), a is the initial carbon steel consumption at t = 0 (gram), ($\Delta W = x$), x is the reaction concentration and $t_{1/2}$ is half-life (h). The half-life period is defined as the time necessary for the concentration of a reactant to decrease to half of its initial value. Half-life indicates the stability of reactants, the longer half-life the greater the stability of reactants.

1.11.4 Effect of inhibitor concentration

Investigators of acid corrosion soon learn that there is a characteristic relation between inhibitor concentration and loss in weight of the metal specimen. As the concentration of inhibitor increases, the weight loss decreases and tends to approach a low constant value, which depends on the properties of particular inhibitor [6].

1.12 Mechanism of Adsorption

Fundamentally, for solid–liquid adsorption system, adsorption largely depends on the charge and nature of the metal surface, electronic characteristics of the metal surface, properties of solvent and other ionic species, temperature of corrosion reaction and finally on the electrochemical potential at solution-interface. Adsorption of inhibitor involves the formation of two types of interaction. The physical adsorption is weak interaction and is due to electrostatic attraction between inhibiting organic ions or dipoles and the electrically charged surface of metal. The zero charge potential plays a key role in the electrostatic adsorption process. The second type of adsorption occurs when the directed forces

govern the interaction between the adsorbate and adsorbent. Chemical adsorption involves charge sharing or charge transfer from adsorbates to the metal surface atoms in order to establish a coordinate type of bond. Chemical adsorption has a free energy of adsorption and activation energy higher than physical adsorption and, hence, usually it is irreversible [23]. Adsorption isotherms are usually used to describe the adsorption process.

1.12.1 Adsorption of inhibitor and isotherm

The most frequently used isotherms are: Langmuir, Freundlich **,** Kinetic-thermodynamic models [24].

To obtain the adsorption isotherm, the degree of surface coverage (θ) for various concentrations of the inhibitor must be calculated and the various models must be tested to show the compatibility of the model with data through equations follows.

$$\theta = \frac{IE}{100} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.31)$$

Where; θ is the Surface coverage, IE is the inhibitor efficiency.

a. Langmuir adsorption isotherm

The model for the Langmuir isotherm is a set of uniform adsorption sites and many cases of strong adsorption do not fit this isotherm. Mathematically, this isotherm is given as:

$$\theta = \frac{K_L\ C_i}{1 + K_L\ C_i} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.32)$$

Where; K_L is the equilibrium constant (L/ml) for the Langmuir adsorption isotherm representing the degree of adsorption (i.e., the higher the value of K_L indicates that the inhibitor is strongly adsorbed on the metal surface,

C_i is the inhibitor concentration (ml/L), and θ is the surface coverage [6]. Rearranging equation (1.32) will give:

$$\frac{C_i}{\theta} = \frac{1}{K_L} + C_i \quad \text{.....} \quad (1.33)$$

$$K_L = \frac{1}{55.55} \exp\left(-\frac{\Delta G^o_{ads}}{RT}\right) \quad \text{.....} \quad (1.34)$$

Where; ΔG^o_{ads} is standard adsorption free energy (kJ mol^{-1}), The value of (55.5) is the water concentration in solution expressed in M. Equation (1.33) can be plotted as C_i/θ against C_i. From intercept the values of K_L. Can be calculated behavior of equilibrium constant of adsorption (K_L) was noticed decreased with increase in temperature as the same behavior was reported by Umoren et al [25].

b. Freundlich adsorption isotherm

This isotherm can be represented by the equation (1.35).

$$\theta = K_F\ C_i^{n''} \quad \text{.....} \quad (1.35)$$

Where; K_F and n`` are constant for a given system at a given temperature [25]. This isotherm can be written as:

$$\ln \theta = \ln\left(K_F\ C_i^{n''}\right) \quad \text{.....} \quad (1.36)$$

$$\ln \theta = \ln K_F + n'' \ln C_i \quad \text{.....} \quad (1.37)$$

Where; θ is surface coverage, K_F is the equilibrium constant for the Freundlich adsorption constant (L/ml), n" is slope. Equation (1.37) can be plotted as ln θ against ln C_i , where slope and intercept yield the values of n" and K_F respectively.

c. Kinetic-thermodynamic adsorption isotherm:

Recent researches have looked in to the action of adsorptive inhibitors from purely mechanistic kinetic point of view [26]. A kinetic-thermodynamic model for adsorption process at metal-solution interface has been suggested. In this model, (y') is the number of inhibitor molecules occupying one active site. This model can be given by the following equation;

$$\left(\frac{\theta}{1-\theta}\right) = K'\left(C_i\right)^{y'} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.38)$$

Where; θ is surface coverage, K` is the equilibrium constant for the kinetic-thermodynamic adsorption (L/ml), $C_i$ is inhibitor concentration (ml/L), y` is slope.

$$K_{ads} = K'^{\left(1/y'\right)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.39)$$

Rearranging equation (1.38) will give:

$$\ln\left(\frac{\theta}{1-\theta}\right) = \ln K' + y' \ln C_i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.40)$$

Equation (1.40) can be plotted as ln $\left(\frac{\theta}{1-\theta}\right)$ against ln C_i , where slope and intercept yield the values of y' and K' respectively.

1.13 Previous Studies

(Saratha et al. 2009) Observed the effect of acid extracted from *Citrus aurantiifolia leaves* plant which exhibited 97.51% inhibition efficiency on the corrosion of mild steel in 1 M HCl studied by weight loss technique. The nature of adsorption were proved by theoretical fitting of different isotherms, Frumkin , Freundlich, Temkin , Langmuir, Flory-Huggins and the kinetic thermodynamic model [27].

(Adnan and Hanan. 2009) Used economical and environmentally safe substances as inhibitor, the fresh leaves extract of *Zizyphus Spina – Chritis* were utilized as corrosion inhibitors by using weight loss procedure, The corrosion inhibition of carbon steel in HCl acid in the presence *Zizyphus Spina – Chritis leaves extract* showed the optimum inhibition efficiency for carbon steel be 99.5%, 75% and 66% at 1%, 1% and 2% concentration of the inhibitor at the temperatures 25 ^{o}C, 35 ^{o}C and 45 ^{o}C respectively [28].

(Dahmani et al. 2010) Corrosion inhibition effect of *black pepper extract* and its *piperine* isolated by ethanol from ground *black pepper* were investigated by weight loss technique on corrosion of C38 steel in 1 M HCl solution. The value attained showed higher efficiency reached above 95% at 2g/L inhibitor concertation which is tested for the natural compounds by weight loss measurements. It is observed that the corrosion rate decreases massively in the presence of *piperine*, and with increases of inhibitor concentration caused to increase the value of inhibition efficiency. Langmuir adsorption isotherm entrusted the mechanistic of adsorption process for *piperanine* on metal surface [29].

(Yaro et al. 2011) *Peach juice* were utilized as inhibitor of mild steel in 1 M of hydrochloric solution in the concentration range of 5-50 cm^3 /L and at temperature range of 30-60 ^{o}C by using both polarization and weight loss

procedure, the extreme inhibition efficiency reached about 91% at 50℃ ,when the concentration of inhibitor is 50 cm^3/L. Adsorption characteristics, the inhibition effect, mathematical and electrochemical modeling of *peach juice* were explained. The inhibitor adsorbed physically on metal surface through Langmuir isotherm [30].

(Iloamaeke et al. 2012) *Pterocarpus soyauxi, extract* were employed as the inhibitor substance of mild steel using weight loss technique at the temperature 30 ^oC and 60 ^oC, observed the inhibition efficiency increased with increase in inhibitor concentration but decreased with a raising temperature. The inhibition of corrosion of mild steel obey Freundlich and Tempkin adsorption isotherms and correspond into first order reaction kinetics. By calculating thermodynamics parameters; ΔH, Ea, and ΔG, inferred that inhibition of corrosion of mild steel occurred by physical adsorption mechanism in the presences of ethanol extract of *Pterocarpus soyauxi, extract* [31].

(Cang et al. 2013) *Aloes leaves extract* were utilized to prevent the corrosion of mild steel in 1.0 M Hydrochloric acid using weight loss procedures. Ones illustrated that the inhibition efficiency increases with the increase of the extract concentration. The influence of temperature on the corrosion actions of mild steel in 1M HCl as well varying the extract concentration was also investigated. The adsorption of the *Aloes leaves extract* molecules occurs spontaneously and conform Langmuir isotherm. The thermodynamic parameters and activation energy for the inhibition progression was calculated, for interaction between inhibitor and mild steel surface [32].

(Abdulkhaleq. 2013) Tried *Eucalyptus camaldulenis leaves extract* functioned as the inhibitor corrosion for low carbon steel in 3M

Hydrochloric acid using the gravimetric method. Different concentrations of (2, 4, 6, 8 and 10) g/L of extract were verified. Ones illustrated that inhibition efficiency increased rapidly with increasing the extract concentration at 25°C and increased with a raising temperature but progressively at 35 ^{o}C, 45 ^{o}C and less than other at 55 ^{o}C .the results which obtained from the experimental data showed that adsorption of *Eucalyptus camaldulenis leaves extract* molecules occurs spontaneously and conform Langmuir isotherm [33].

(Yaro et al. 2013) Studied the corrosion inhibition of mild steel in 1M H_3PO_4 solution by using *apricot juice* at various temperatures by weight loss procedure. Activation, adsorption and statistical investigated in this search had manifested that inhibitor adsorbed on metal surface correspond Langmuir isotherm. From the value of heat of adsorption of -14.93 kJ/mol inferred that inhibition of corrosion of mild steel occurred by physical adsorption, furthermore the inhibition efficiency reached 75 % at 30 ^{o}C where the concentration of the extract were 40 g/L [34].

(Hamdy and El-Gendy. 2013) Used aqueous extract from *henna leaves* with different concentration to restrain corrosion of carbon steel in 1M Hydrochloric acid by two methods; weight loss and potentiodynamic polarization. The influence of temperature on the corrosion actions of carbon steel was performed within temperature range of 293-333 K. The study showed that the inhibition efficiency increases with increased inhibitor concentration but is reduced with increasing temperature. The activation and free energies for the inhibition progression indicted the mechanism of physical adsorption. The adsorption of extract on carbon steel surface is endothermic, spontaneous and corresponded with the Langmuir isotherm. Surface of C-steel and protective layer analysis have been tested using; EDX (energy dispersive X-ray), SEM (scanning electron

microscopy), FT-IR spectroscopy (Fourier transforms infrared) and X-ray diffraction analysis [35].

(Aejitha et al. 2014) Explored the demonstration of inhibitor from extract *Antigonon Leptopus* on the corrosion of mild steel in 1M H_2SO_4 by using weight loss procedure. Results explained that the extract of *Antigonon Leptopus* behave as an efficient corrosion inhibitor in 1M H_2SO_4 acid medium. The inhibitor concentration of 0.7 % v/v at 6 hours inundation showed maximum inhibition efficiency reached to 92.6% [36].

(Anbarasi and Vasudha. 2014) Were functioned *peel of Cucurbita maxima extract* as a disincentive for mild steel corrosion in 1M HCl using weight loss and FTIR procedures. The calculated results of corrosion rates of mild steel and the inhibition efficiency of *peel of Cucurbita maxima extract* show that the extract utilized as a good corrosion inhibitor with inhibition efficiency increased with extract concentration. Extreme inhibition efficiency reached of 93 % at 2 % v/v concentration of the *peel of Cucurbita maxima extract* [37].

(Fouda et al. 2014) Utilized *Anise extract* had been used by to discouragement corrosion of carbon steel in 1 M HCl solution using weight loss procedure. Protecting film and surface morphology were verified using scanning electron microscope (SEM). The adsorption mechanism of the inhibitors on carbon steel surface corresponded with the Langmuir isotherm [38].

(Thilagavathy et al. 2015) Utilized different concentrations of the extract of *mirabilis jalapa flowers* to restrained the corrosion of mild steel in 1M HCl using weight loss technique, various immersion periods at certain elevated temperatures. The adsorption of the extract of *mirabilis jalapa flowers* molecules conform Langmuir and Temkin isotherms. The

result showed extreme maximum inhibition efficiency at 5 % v/v concentration of the extract and at 323 K [39].

(Olasehinde et al. 2015) Utilized *Alchornea laxiflora leaves extract* to prevent the corrosion of mild steel in acidic medium by using gravimetric technique. Research was conducted by varying the concentration of extract, immersion time and temperature. The extract exhibited a potential inhibitor for the corrosion of mild steel in the presence of 1M HCl, as the corrosion rate decreases with increase in the concentration of the extract. The inhibition efficiency increases gradually as the concentration of the extract increased but decreases with elevation in temperature and exposure time. The extreme inhibition efficiency reached to 96 % in the presence of the extract. Activation energy was found to be 21.81 kJ mol^{-1} for the blank and increases to 82.57 kJ mol^{-1} in the presence of the extract. Thermodynamic parameters such as, entropy change, enthalpy change and Gibb's free energy were calculated. Kinetics of the reaction in the presence of the extracts indicated to match a first order reaction and the half-life increase as the concentration of the extract increases, furthermore the adsorption showed that Langmuir isotherm is the perfect adsorption form to conform the adsorption of the extract on mild steel surface [40].

(Kulandai and Vasudha. 2015) Studied the adsorption and inhibitive efficiency of *Millingtonia hortensis leaves extract* on mild steel in 1M HCl and 1M H_2SO_4 at a temperature range of (303 to 343K) by mass loss measurements. The value of inhibition efficiency increased with the increase of inhibitor concentration and decreased at 333K. The value of inhibition efficiency in H_2SO_4 at 323K was (97.10 %) and the value of inhibition efficiency in HCl at 333K was (97.41%). ΔG_{ads} adsorption value of 12 – 24 KJ/ mol is suggestive of physisorption process. Adsorption of inhibitor on the metal surface was found to obey Langmuir and Temkin

isotherm. The values of activation energy (ΔE_a), enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS) were calculated [41].

(Muthukrishnan et al. 2015) Prevent corrosion by *Ficus hispida leaf extract* were in 1M HCl by using weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. The extreme Inhibition efficiency reached 90 % in 250 ppm of extract at 308 K. in the presence of the extract, an increase in inhibition efficiency was observed with decrease in temperature and the value of activation energies increased. The adsorption of *Ficus hispida leaf* on mild steel surface conforms to Langmuir isotherm. The morphology overlay coating which is formed on the mild steel surface tested by SEM and the surface synthesis verified by using EDX, diffuse reflectance fourier transform infrared spectroscopy (DRFT-IR) and X-ray diffraction (XRD) tests. [21].

(Abdulrahman et al. 2015) Utilized *Africa parquetina leaves extract* to prevent the corrosion of mild steel in sulphuric acid solution using gasometric, gravimetric and thermometric techniques. The chemical characterizations of the leaves extract were also performed using gas chromatography mass spectroscopy (GCMS) and fourier transformation Infra-Red (FTIR) analysis. Experiments showed the maximum inhibition efficiency 87.78 % at 0.5 g/L concentration of extract, and it was increased with the increases in concentration of extract but reduced with the increase in temperature. The adsorption of inhibitor conformed Langmuir isotherm and the thermodynamic parameters calculations indicated that it was physisorption [42].

(Noor et al. 2016) Were investigated the inhibitor action of red onion seeds and peels extracts (ROSE & ROPE) and comparing on the corrosion of steel in 0.75 M H_3PO_4 using chemical measurements, (hydrogen

evolution and mass loss) and SEM technique. The effect of temperature on the corrosion of steel in 0.75 M H_3PO_4 without and with certain concentration of each extract was studied in the temperature range of 303–333 K. The inhibition efficiency of both extracts increases with increasing concentration and gives powerful fitting to the Langmuir adsorption isotherm with the highest adsorption affinity for ROSE. The values of E_a without and with inhibitor revealed chemisorption and physical adsorption behavior for ROSE and ROPE, respectively, on the steel surface [43].

1.14 Objectives (aims of study)

1. Studying the corrosion rates of carbon steel in different concentrations of sulfuric acid and temperatures.

2. Extraction and evaluating a natural and environmental friendly corrosion inhibitor.

3. Studying the kinetics of reaction of carbon steel in H_2SO_4 solutions at different operating conditions.

4. Studying the steel surface morphology by scanning electron microscope.

5. Studying the active group in the inhibitor by fourier transform infrared spectroscopy.

6. Correlating of dependent variable (corrosion rate) and independent variables (temperature, inhibitor and acid concentration) in a mathematical models.