CORROSION INHIBITION OF MILD STEEL IN ACIDIC SOLUTIONS USING MORINGA OLEIFERA AS INHIBITOR

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CERTIFICATION

This is to certify that this work Titled "Corrosion Inhibition of Mild Steel in Acidic Environment using Moringa Oleifera as Inhibitor" was carried out by ONYIMA CHUKWUMA L. with (Reg No. 20114832948) in partial fulfillment for the award of the degree of M.Sc. in Analytical Chemistry in Department of Chemistry, Federal University of Technology Owerri.

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DEDICATION

This project is dedicated to the Almighty God for his love and protection.

To my lovely wife Onyima Obiajulu Agatha and the rest of my family.

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ABSTRACT

The corrosion behavior of mild steel in 1 M HCl and 0.5 M H_2SO_4 acidic environments was investigated using gravimetric and electrochemical techniques. The results obtained from both gravimetric and polarization experiments showed that mild steel is more susceptible to acid corrosion in 0.5 M H_2SO_4 than in 1 M HCl, with higher mass loss (gravimetric) and current density (polarization) obtained with sulphuric acid system compared to hydrochloric acid system. The effects of ethanol, sulphuric acid and water extracts of *Moringa oleifera* on the corrosion behavior of mild steel in the acid solutions were also analyzed. Generally, the different extracts exerted appreciable inhibition performance with sulphuric acid and water exhibiting higher inhibition efficiency than ethanol but ethanol exhibited higher stability in hydrochloric acid system. The trend of inhibition efficiency changed in sulphuric acid system with ethanol extract having the best performance than other extracts according to the polarization and temperature results, although, gravimetric data contradicted. Polarization studies revealed that the plant extracts functioned as mixed inhibition mechanism. Inhibition efficiency in general, increased with increase in the concentration of the extracts but decreased with prolonged exposure time. The discrepancies in the inhibition efficiencies exerted by the different extracts was attributed to the differences in the extracting abilities of the solvents, while discrepancies observed with the methods was attributed to time and instrumental effects. The *Moringa oleifera* leaf ethanol extract was characterized using gas chromatography / mass spectrometry (GC/MS). The analysis confirmed that the extract contained more than 29 active constituents including; 28.55% 9,12-Octadecadienoic acid (Z,Z)methyl ester; 11.24% n-Hexadecanoic acid; 9.31% 9,12,15-Octadecatrienoic acid methyl ester; 6.32% Benzeneacetonitrile,4-hydroxy-;5.6%2-Furancarboxaldehyde,5(hydroxyme- thyl)-

;4.85%Heptadecane; 3.49% and others. Since the presence of some organic species in the extract has been confirmed by GC/MS, selected constituents of the extract were modeled in order to assess their adsorbability using the density functional theory (DFT) and the result revealed remarkable high interaction energies, which corroborate the experimental findings.

Keywords: Characterisation of *moringa oleifera*; efficiency performance of different leaf extract of moringa, ethanol, sulphuric acid and water; electrochemical masurements and gravimetric measurement.

CHAPTER ONE

INTRODUCTION

1.1. Background Information

1.1.1 Definition and Description of Corrosion

Corrosion is the phenomenon of spontaneous destruction of metallic surfaces or alloys by chemical or electrochemical reaction with its environment. It is a natural phenomenon and results from the tendency of refined metals to revert back to their natural state (ore) by reacting with oxygen and water in their environment. The most common example is the rusting of iron and steel structures such as pipelines, machinery, buildings, bridges etc, which often have catastrophic consequences including environmental degradation and even loss of lives. One of the most serious problems in modern societies is that caused by corrosion, and it affects these sectors: oil and gas, chemical allied industries, utilities transportation, medical, etc. (DOE, 2003).

1.1.2. FORMS OF CORROSION.

We have different types / forms of corrosion briefly explained below:

i. Uniform Corrosion

This type of corrosion is characterized by corrosive attack proceeding evenly over the entire surface area, or a large fraction of the total area. General thinning takes place until failure.

ii. Crevice Corrosion

This occurs when water or other fluid is concentrated in a crack or crevice in the material. For example, aircraft fuselages are susceptible to water seeping into lap joint and rivet holes and staying there, causing corrosion and weakening the material, leading to crack growth.

iii. Intergranular Corrosion

This occurs within the grain structure of a metal, particularly in metal alloys. Stainless steel is susceptible to intergranular corrosion if heat treatment is not performed correctly or under the intense heat of welding operations. This effect is similar in many ways to galvanic corrosion.

iv. Pitting Corrosion

It often occurs in metals that have a passivation layer. If the passivation is prevented in a local location, such as a crevice, corrosion can occur.

v. Galvanic Corrosion

Corrosion of a metal that is in electrical contact with another metal and immersed in an electrolyte is known as galvanic corrosion. One of the most common locations for galvanic corrosion is in structures immersed in sea water. However, galvanization is also a process widely used to purposely protect metals from corrosion.

vi. Microbial Influenced Corrosion

As the name implies, is caused by microorganisms, which generates byproducts, such as acids, as part of their metabolic processes, and cause corrosion of the base metals. (Jerome, 2001).Microbially influenced corrosion (MIC) is a costly problem that impacts hydrocarbon production and processing equipment, water distributionsystems, ships, rail cars and other types of metallic infrastructure (Charles H.D Williamson, Luke A. Jain,2015).

1.1.3 IRON (Fe) CORROSION MECHANISM

Mild steel finds application in many industries due to its easy availability, ease of fabrication, low cost and good tensile strength besides various other desirable properties. It suffers from severe corrosion when it comes in contact with acid solutions during acid cleaning, transportation of acid, de-scaling, storage of acids and other chemical processes (Antroprove, 1977). The actual mechanism in the

corrosion of iron and steel is extremely complex and embraces the fields of chemistry and electrochemistry. Iron will corrode only in the presence of both water and oxygen, forming iron oxide. There are always two distinct chemical reactions in corrosion process the anodic and the cathodic reactions or processes (Hurlin, *et al* 1984).

Whether the corrosion takes form of red rust(ferric oxide, Fe_2O_3) or black stain (ferrous oxide, Fe_3O_4), the process is similar: Oxidation of the metal is linked to reduction of other constituents in the process, including the metal working fluids (Susan Conley's 'he Tube & Pipe Journal October/November 2013).

The anodic process.

The anodic dissolution of iron in acidic solution has been reported to proceed according to the mechanism below (Hurlen *et al*, 1984: Mounium, et al 2005; Olivares, *et al* 2006). If we assume that the electrochemical reaction of iron corrosion involves transfer of two electrons, then there are two steps , each one represents transfer of one electron and one of them may be considered the rate determining step. This is in good agreement with the mechanisms that are suggested for iron dissolution (Ehteram, 2008). The steps are represented according to the following equations below:

(a) In aqueous solutions

$Fe + H_2O \rightarrow [Fe\,OH]_{ads} + H^+ + e^-$ (1.1)

$[Fe\,OH]_{ads} \rightarrow H^+ + e^-$ (1.2)

$[Fe\,OH]^+_{ads} + H^+ \rightarrow Fe^{2+} + H_2O$ (1.3)

(b) In aqueous solutions containing chloride ions (Cl^-)

$Fe + H_2O + Cl^- \rightarrow [FeClOH]_{ads} + H^+ + e^-$ (1.4)

$[FeClOH]_{ads} \rightarrow [FeClOH]_{ads} + e^-$ (1. 5)

$[FeClOH] + H^+ \rightarrow Fe^{2+} + Cl^- + H_20$ (1.6)

Where $[FeOH]_{ads}$, and $[FeClOH]^-_{ads}$ are the adsorbed intermediates which each of them is involved in the rate determining step of mild steel dissolution. It must be pointed out that the presence of Cl- ions does not exclude dissolution through the $[FeOH]_{ads}$ intermediate in chloride free acid media, as the two mechanisms can proceed simultaneously (Ehteram , *et al* 2008) .

As a consequence of these reactions, including the high solubility of the corrosion products the metal loses weight in solution.

The Cathodic Process.

In acid solutions electrons can react with hydrogen ions, adsorbed on the metal surface from the solution to produce hydrogen gas (Oguzie, *et al* 2007). This is represented by the reactions shown below.

$2H^+_{ads} + 2e^- \longrightarrow H_{2(g)}$ (1.7)

For steel in contact with water at lower (pH), the cathode reaction is:

$O_2 + 2H_2O + 4e^- \longrightarrow 4OH$(1.8)

1.1.4 CORROSION CONTROL METHODS

Iron and its alloys are widely used in many applications, which have resulted in research into the corrosion resistance in various aggressive environments (Oguzie, 2004). In efforts to reduce electrochemical corrosion the primary strategy is to isolate the metal from corrosive agents.

1.1.4.1 DIFFERENT METHODS OF CORROSION CONTROL

i. Galvanizing: This is a process of applying another metal over the surface of an existing one using a chemical process to form a bond between them; for example galvanized steel is coated with iron or zinc. The iron or zinc will corrode leaving the steel protected for some time.

ii. Surface Coating: When the surface of the metal is covered with some impermeable layer like paint, this prevents access of damp air (Atkins *et al*, 2008). Unfortunately, this protection fails disastrously if the paint becomes porous. The oxygen then has access to the exposed metal and corrosion continuous beneath the paint work.

iii. Use of Corrosion Resistant Materials.

There are no materials that are immune to corrosion in all environments. Materials must be matched to the environment that they will encounter in service. Corrosion resistance data are used to assess the suitability of a material in an environment.

1.1.5 CORROSION INHIBITORS

Corrosion inhibitors are substances which when added in small concentrations to a corrosive medium reduce the rate or prevent the reaction between the metal and the medium (Pandian, 2008). It can also be defined as chemical products

which when added to water or to any other process fluid, slow down the rate of corrosion (SUEZ's degrement^{R} water handbook;2018).Use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent metal dissolution and acid consumption. If the correct inhibitor is selected then it is possible to achieve high efficiency up to 90-99%. The modes of action of some inhibitors are:

(i) Formation of a passivation layer, which is a thin film on the surface of the material that stops access of the corrodent to the metal, inhibiting either the oxidation or reduction part of the redox reaction.

(ii)Adsorption of the inhibitor on the surface of the metal.

Adsorption inhibitors are usually organic substances containing polar functions with nitrogen, sulphur and or oxygen in the conjugated system. (Hackerman,

et al, 1950; Gomma, 1998; Ashass, et al, 2000;Ateya, *et a*l, 1981;Ebenso, 2002; Ikeda,

et al 1981).

Such substances function by adherence to the metal surface through metal ions still in place in the lattice and thereby retard metal dissolution by virtue of adsorption, with the polar group acting as the reaction centre for the adsorption process (Oguzie *et al,* 2004: Ferrieira, *et al*, 2004: Chakrabarty, et al, 1983).

The absorption bond strength is dependent on: The composition of the metal and corrodents, inhibitor structure, concentration as well as temperature (Oguzie *et al,* 2005).

Generally, inhibitor molecules may either physically or chemically adsorb on a corroding metal surface. It has been suggested (Hackerman, *et al* 1950: Ahiberg, *et al* 1989), that physorbed molecules are attached to the metal at local cathodes and essentially retard metal dissolution by inhibiting the cathodic reaction, whereas chemisorbed molecules protect anodic areas and reduces the inherent reactivity of the metal at the sites where they are attached. The more efficient inhibitors appear to protect anodic areas preferentially by chemisorptions (Deberry *et al,* 1981).

In any case, adsorption is generally over the metal surface and the resulting adsorption layer functions as a barrier, isolating the metal from the corrodent (Oguzie *et al,* 2005).

1.1.6 CLASSIFICATION OF INHIBITORS

i. Inorganic inhibitors

Inorganic inhibitors typically function without oxygen by passivation. These include chromates and nitrate ions, which can be reduced while they oxidize the metal surface to form a passive oxide film (Satyanarayana-Gupta, 2004). Other inorganic compounds require oxygen to work. These include phosphates, silicates, borates, tungstates and molybdates but unfortunately most of these inorganic substances are toxic for example chromate is carcinogenic to human beings. Eliminating the use of more environmentally toxic compounds like chromates and dichromates and replacing them with more environmentally friendly chemicals has been the major directional change. Most inorganic corrosion inhibitors are being replaced with more environmentally friendly organic corrosion inhibitors.

ii. Organic Inhibitors.

A number of organic compounds have been found to be corrosion inhibitors for different metals in different aggressive environment such compounds contain-electron donating groups that decrease the corrosion rate by adsorption on the corroding metal surface. (Rajappa *et al*, 2003).

The efficiency of these organic corrosion inhibitors is related to the presence of polar functions with S, O or N atoms in the molecule, heterocyclic compounds and p electrons. The polar function is usually regarded as the reaction centre for the establishment of the adsorption process.

All the studies of corrosion inhibition potential of organic compounds revealed that organic compounds especially those with N, O, S showed an effective corrosion inhibition (Bendiss *et al*, 2000; Schimitt, 1984). Nevertheless, most of these compounds are not only expensive but also toxic.

iii. Plant extracts

The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. Recently plant extracts are viewed as an incredibly rich source of naturally occurring chemical compounds that are environmentally acceptable, biodegradable in nature, readily available and renewable source for a wide range of needed inhibitors. The extracts of their leaves, peels, seeds, fruits and roots have been reported as effective corrosion inhibitors in different aggressive environments. [Oguzie, 2008; Abiola *et al*, 2009; Loto, 2001; Quraishi *et al,* 1999; El-Etre, 2008]. The natural products extracted from fruits have been widely studied as corrosion inhibitors. A large number of scientific studies have been devoted to the inhibitive action of some plant extracts on the corrosion of C-steel in acidic media, showing that these extracts

could serve as good corrosion inhibitors. The actual inhibitors in the plant extracts are usually alkaloids and other organic nitrogen bases, as well as carbohydrates, proteins and their acid hydrolysis products. Several investigations have been reported using such economic plant extracts (El Hosary *et al,* 1972).

1.1.7 BRIEF DESCRIPTION OF *MORINGA OLEIFERA*

Moringa, native to parts of Africa and Asia, is the solegenus in the flowering plantfamily Moringaceae. The name is derived from the Tamil word Murungai. It contains 13 species from tropical and subtropical climates that range in size from tiny herbs to massive trees. Aberra Melesse 2011 and Bamishaiye, *et al,* 2011 performed proximate analysis on the plant and reported that Moringa contains numerous phytocompounds ranging from amino acids, sugars saponnins, tannins etc.

1.2 Problem Statement

The impact of corrosion is felt in three areas of concern; economics, safety (including health) and environmental damage. Some of the consequences of corrosion includes mechanical damages to pumps and other infrastructural facilities, reduction in the value of goods due to deterioration of appearance, contamination of fluids in pipes and vessels, perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings, hazards or injuries to people arising from structural failure or breakdown (examples,

bridges, cars, etc) and reductions of metal thickness leading to loss of mechanical strength and structural failure.

Different corrosion methods have been used in order to control the impact of corrosion (**Galvanizing, Surface coating, Modifying the environment Use of corrosion resistant materials, Inorganic inhibitors).** Studies have showed that most of these method are not only expensive but also toxic.

Due to the known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. Recently plant extracts are viewed as an incredibly rich source of naturally occurring chemical compounds that are environmentally acceptable, biodegradable in nature, readily available and renewable source for a wide range of needed inhibitors. The extracts of their leaves, peels, seeds, fruits and roots have been reported as effective corrosion inhibitors in different aggressive environments.

1.3 Objectives of Study

The main objective of this study is characterization, investigation of the mechanisms of corrosion inhibition of different leaf extracts of *Moringa oleifera.* The specific objectives are:

i. To characterize the leaf extract of *Moringa oleifera* so as to identify its major constituents that can render corrosion inhibition (as a green additive).
ii. To investigate the mechanisms of corrosion inhibition of different leaf extracts of *Moringa oleifera* for mild steel in 0.5 M H_2S0_4 and 1 M HCl

iii. To evaluate the effect of extraction solvents (different extractant) on the inhibition efficiency of the extracts.

1.4 Justification of study

Plant extracts contain several phytochemical compounds with molecular and electronic structures bearing close similarities with those of conventional organic inhibitor molecules.

1.5 Scope of study

Corrosion inhibitors are the compounds that are added in very small quantities in the aggressive medium. Due to the presence of these compounds in the medium, the corrosivity of the medium is reduced significantly. Enough literature is available on the varieties of inhibitors, which have been developed according to the metal/environment combinations. The inhibitors are anodic or cathodic, oxidizing or non-oxidizing and organic or inorganic depending on the end use requirement. Majority of the effective inhibitors from this category are toxic or possess a hazard in their use. It would be advantageous if environment friendly compounds would be used instead,

This study covers the following areas:

i. Characterization of leaf extract of *Moringaoleifera* so as to identify its major constituents that can render corrosion inhibition (as a green additive).

ii. Investigation of mechanisms of corrosion inhibition of different leaf extracts of *Moringaoleifera*for mild steel in 0.5 M H_2S0_4 and 1 M HCl

iii. Evaluation the effect of extraction solvents (different extractant) on the inhibition efficiency of the extracts

CHAPTER TWO

LITERATURE REVIEW

2.1 CORROSION INHIBITION BY ORGANIC MOLECULES.

Research has been done on the corrosion behavior of mild steel in 2M Sulphuric acid solution in the presence and absence of Methylene blue dye (MB) using gravimetric and thermometric techniques. The result proved that the inhibition efficiency of MB increased with concentration and synergistically increased in the presence of the halide additives, the trend of inhibition efficiency with temperature suggest that inhibitor molecules are physically adsorbed on the corroding metal surface at lower concentration, and chemically adsorbed at higher concentration. (Oguzie, 2005).Work has been carried out on the inhibitive capabilities of some organic dyes namely; safranine –o (SO), thymol blue (TB) and Fluorescein –Na(F-Na) on the electrochemical corrosion of mild steel in sulphuric acid solution, using gasometric technique. The result indicates that all of the studied compounds act as inhibitors in the acidic corrodent. Inhibition efficiency increased well with increase in concentration for so and TB but decreased with concentration for F.Na. (Oguzie, 2005).

The effect of diphenyl glyoxal and its dihydrazone derivative on the corrosion of mild steel in hydrochloric acid has been investigated over a wide range of

conditions using gravimetric technique. The results showed that both compounds were found to function as corrosion inhibitors in the acidic environment, with the dihydrazone derivative exhibiting higher efficiency. Inhibition efficiency generally increased with concentration of the additive. Corrosion inhibition is attributed to chemisorptron of inhibitor molecules on the corroding metal surface. (Oguzie *et al,* 2005). Eight diazoles were investigated by Propova et al, as corrosion inhibitors of mild steel in IM HCl acid using gravimetric and polarization techniques. It was found that the inhibition efficiency increased with increase of organic substrate concentration. (Popova *et al*, 2004). Tang demonstrated that the synergistic effect between 4-(2-pyridylazo) resoain and chloride ion on the corrosion of cold rolled steel in 0.5M sulphuric acid, their findings agreed with the fact that increase in concentration leads to an increase in inhibition efficiency likewise the synergistic effect of chloride ion (Tang *et al*, 2006).

Moretti et al (2004) studied tryptamine as a green corrosion inhibitor in 0.5M deareated sulphuric acid and found that it was effective in inhibiting ARMACO iron in the acid media in the 25-55^{0}C temperature range. (Moretti *et al*, 2004). Oguzie *et al,* studied the effect of surface nanocrystallization on corrosion and corrosion inhibition of low carbon steel, including the synergistic effect of methionine and iodide ion and found that surface nanocrystallization increased the corrosion.

Susceptibility of low carbon steel but methionine inhibited the corrosion of both specimens with comparable inhibition efficiencies and iodide ions synergistically increased the inhibition efficiency. (Oguzie *et al,* 2007).

Investigation has been carried out on the corrosion inhibition of aluminum alloy 2024-T3 by aqueous vanadate species and it was discovered that the inhibition of vanadates occurred mainly in alkaline solutions where tetrahedrally coordinated vanadate, metavanadate and pyrovanadate were abundant. (Balston *et al*, 2008).

Investigation has been carried out on the effect of saccharides (reducing sugars-fructose and mannose) on the corrosion of aluminum and zinc in alkaline media. His results showed positive inhibition efficiency (Muller, 2002). Anthony et al. has studied the effect of caffeine against chloride corrosion of carbon steel (Anthony, 2004). Adallah, worked on the corrosion behaviour of 304 stainless steel in sulphuric acid solutions and it's inhibition by some substituted pyrazolones. (Adallah, 2003).

Investigation has been done on the evaluation of the inhibitory effect of methylene blue dye on the Corrosion of aluminum in hydrochloric acid. (Oguzie *et al*, 2004a). Oguzie, worked on the influence of halide ions on the inhibitive effect of Congo red dye on the corrosion of mild steel in sulphuric acid solution. (Oguzie, 2004). Quaraishi et al carried out research on the inhibition of mild steel

corrosion by some macrocyclic compounds in hot and concentrated hydrochloric acid.

All of these studies indicate that organic molecules inhibit metal corrosion by adsorption on the metal/corrodent interphase.

2.2. CORROSION INHIBITION OF METALS BY PLANT EXTRACTS IN DIFFERENT MEDIA

The inhibitive effect of *Jasminum nudiflorum* (Lindl) leaves extracts on the corrosion of cold rolled steel (CRS) in I M HCl was investigated (Li, *et al*, 2010) by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. The results showed the extracts as a very good inhibitor, and the inhibition efficiency increased with concentration. Adsorption of the extract obeyed Langmuir adsorption isotherm. The aqueous extract of the leaves of henna (*lawsonia*) was found to be a corrosion inhibitor of carbon steel, nickel and zinc in acidic, neutral and alkaline solution, using the polarization technique(EI-Etre,2000).

The inhibitive effect of the extract of Khillah (*Ammi-visnaga*) seeds, on the corrosion of 3X 316 steel in HCl solution was determined (EL-Etre, 2006) using weight loss measurements as well as potentiostatic techniques. It was found that the presence of the extract reduces markedly the corrosion rate of steel in the acid solution. Also noticed was the increase in inhibition efficiency as the extract

concentration was increased the aqueous extract of the leaves of henna (*lawsonia*) was found to be a corrosion inhibitor of carbon steel, nickel and zinc in acidic, neutral and alkaline solution, using the polarization technique(EI-Etre,2000). Inhibition of aluminum corrosion in 2 M sodium hydroxide solution in the presence and absence of 0.5 M NaCl using damisissa (*Ambrosia Maritime, L.*) extract has been reported (Abdel-Gaber, *et al,* 2008) employing different chemical and electrochemical techniques, chemical gasometrical technique showed that addition of chloride ions or damsissa extract to sodium hydroxide solution decreased the volume of the hydrogen gas evolved while potentiodynamic results manifested that chloride ion retard the anodic dissolution of aluminum, below the pitting potential, in sodium hydroxide solution. Damsissa extract in presence or absence of chloride ion, influenced both the anodic dissolution of aluminum and the generated hydrogen gas at the cathode indicating that the extract behaved as mixed type inhibitor.

Occimum basilicum extract has been established to inhibit aluminum corrosion in the acidic and alkaline environments (Oguzie et al, 2006a). Inhibition efficiency was found to increase with extract concentration but decreased with rise in temperature, suggesting physical adsorption of the organic matter on the metal surface. (Oguzie, 2006b) also studied the corrosion inhibition of mild steel in 2 M HCl and 1 M H_2SO_4 by leaf extracts of Occimum Virdis via the gasometric technique. Aluminum, zinc and mild steel were subjected to influence of wild

strain *Bacillus mycoides* for 2 years under laboratory conditions at controlled temperature and humidity. Result obtained from the electrochemical impendance measurements performed for both biotic and abiotic samples indicated microbially influenced corrosion inhibition for aluminum corrosion acceleration for zinc and indifference for steel.

(Oguzie, *et al*, 2007) studied the effectiveness of *Gongronema latifolium* extract in strong acid (2 M HCl) and alkaline (2 M KOH) environments. The results showed that the extract was well adsorbed on the metal surface and significantly repressed aluminum corrosion in both environments.

The inhibitive effect of *Jasminum nudiflorum* (Lindl) leaves extracts on the corrosion of cold rolled steel (CRS) in I M HCl was investigated (Li, et al, 2010) by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. The results showed the extracts as a very good inhibitor, and the inhibition efficiency increased with concentration. Adsorption of the extract obeyed Langmuir adsorption isotherm. Inhibition of aluminum corrosion in 2 M NaOH solution in the presence and absence of 0.5 M NaCl using damisissa (*Ambrosia Maritime, L.*) extract has been reported (Abdel-Gaber, et al, 2008) employing different chemical and electrochemical techniques, chemical gasometrical technique showed that addition of chloride ions or damsissa extractto sodium hydroxide solution decreased the volume of the hydrogen gas evolved while potentiodynamic results manifested that chloride ion retard the

anodic dissolution of aluminum, below the pitting potential, in sodium hydroxide solution. Damsissa extract in presence or absence of chloride ion, influenced both the anodic dissolution of aluminum and the generated hydrogen gas at the cathode indicating that the extract behaved as mixed type inhibitor.

Abdel *et al* (2007) studied the inhibition of aluminium corrosion in alkaline solutions by some natural products using both electrochemical and gasometric techniques. They discovered from the gasometric results that corrosion rate decreased with increase in the damsissa extract at 25^{o}C. The potentiodynamic data showed that increase in the extract concentration decreases the corrosion current density ($i_{corr.}$) and consequently increases the % inhibition. Impedance data showed that increase in the extract concentration increases the capacitive semicircles indicating decreasing corrosion rate. Obi-Egbedi *et al* (2010), studied the use of *Spondias mombin* as a green corrosion inhibitor for aluminium in sulphuric acid using gravimetric technique at 30-60^{o}C, and density functional theory. They observed that inhibition efficiency of the extract increased with an increase in concentration of the extract but decreased with temperature increase. Furthermore, the inhibition efficiency synergistically increased on addition of potassium iodide. The DFT data showed that the inhibitive effect of extract constituent correlated with their electronic properties. Guy et al (2003), studied the use of tobacco plant extracts as environmentally benign corrosion inhibitor of aluminium and steel in saline water, using weight loss technique and physical

examination. The result showed that the extract provides corrosion protection to steel and aluminium metals.

Mejeha, *et al* (2011), assessed the inhibiting action of *Aspilia africana* extract on corrosion of aluminium alloy (AA3003) in hydrochloric acid using gasometric, electrochemical, quantum chemical computations and molecular dynamics simulation. Their result showed that the extract constituent inhibited corrosion by physisorption and chemisorptions of extract constituent on the aluminium surface. The Quantum chemical computation data showed the contribution of some of the extract constituent to the total observed inhibition

2.3 CORROSION INHIBITION OF MILD STEEL BY PLANT EXTRACTS IN ACIDIC MEDIA

Several investigations have focused on the corrosion inhibition of mild steel by plant extracts as corrosion inhibitors. (Oguzie et al, 2006c) studied the corrosion inhibition of mild steel in 2 M HCl and I M H_2S0_4 solutions with aqueous extracts from *Garcinia kola* seed using the gasometric technique. The results indicated that the extract inhibited mild steel corrosion in the acidic environment, and inhibition efficiency increased with concentration. Temperature studies revealed a decrease in efficiency with rise in temperature and corrosion activation energies increased in the presence of the extract. The inhibition effect of *Zenthoxylum alutum* plant extract on the corrosion of mild steel in 5% and 15% aqueous hydrochloric acid solution has been investigated (Chauhan *et al*, 2007)

by weight loss and electrochemical impedance spectroscopy (EIS). The plant extract was able to reduce the corrosion of steel more effectively in 5% HCl than in 15% HCl. The adsorption of this plant extract on the mild steel surface was observed to obey the Langmuir adsorption isotherm.

Oguzie 2005, investigated the efficacy of *Telfaria occidentalis* extracts as a corrosion inhibitor for mild steel in 2 M HCl and I M H_2S0_4 solutions, *Telfaria occidentalia* extracts was found to inhibit mild steel corrosion in 2 M HCl and I M H_2S0_4 solution. Inhibition efficiency increased with extract concentration but decreased with rise in temperature. The inhibition effect of *Zenthoxylum alatum* plant extract on the corrosion of mild steel in 20, 50 and 88% aqueous orthophosphoric acid was investigated (Gunasekaran et al, 2004) by weight loss and electrochemical impedance spectroscopy (EIS). Observation showed that the plant extract was able to reduce the corrosion of steel more effectively in 88% phosphoric acid than in 20% phosphoric acid. The effectiveness of guar gum as an inhibitor for carbon steel corrosion in sulphuric acid environment has been exterblished (Abdallah, 2004). (Oguzie, 2006d) studied the protective effect and adsorption behavior of *Azadirachta indica* extract in controlling mild steal corrosion in I M H_2S0_4 and 2 M HCl. *Azadirachta indica* extract effectively inhibited mild steel in the acidic media studied by virtue of adsorption. The inhibitor adsorption characteristics were approximated by Langmuir isotherm.

Oguzie, 2008, investigated the corrosion inhibition of selected plants on mild steel corrosion in 2 M HCl and I M H_2S0_4 using a gasometric technique. The studied plants materials include *Occimum virides, Telferia occidentalis, Azadirachta indica andHibiscus sabdariffa* as well as extracts from the seeds of Garainic, kola. The results indicated that all the extracts inhibited the corrosion process in both media by virtue of adsorption and inhibition efficiently improved with concentration of the extracts studied. The corrosion inhibitive effect of the extract of black pepper on mild steel in I M H_2S0_4 media was evaluated by conventional weight loss method using electrochemical studies viz. Tafel polarization on impedance and scanning electron microscope (SEM) studies (Raja and Sethuraman, 2008). Results from weight loss study revealed that black pepper extract acts as a good inhibitor even at high temperatures. The inhibition is through adsorption which is found to follow Termkin adsorption isotherm. Tafel polarization revealed the mixed mode inhibition of black pepper extract.

Inhibition of the corrosion of mild steel by ethanol extract of *Musa* species peel has been studied (Eddy, *et al,* 2009) using hydrogen evolution and thermometric methods of monitoring corrosion. The result of the study revealed that different concentration of ethanol extract of *Musa* species peel inhibited mild steel corrosion.

The inhibition efficiency of the extract was found to vary with concentration, temperature, period of immersion, PH and electrode potentials. A study of

rosemary oil as a green corrosion inhibitor has been carried out (Bendahou, *et al*, 2006). The oil was found to be a good inhibitor for steel corrosion, but its efficiency decreased with temperature. Polarization measurements showed that rosemary oil acted essentially as a cathodic inhibitor.

2.4 QUANTUM CHEMICAL CONSIDERATIONS IN CORROSION INHIBITION RESEARCH.

Ma et al., (2006) attempted to find theoretical parameters to characterize inhibition property of three nitrogen-heterocyclic compounds, namely 3,5-dimethyl-1H-pyridine and 2-(3-methyl-1H-pyrazol-5-yl)pyridine against steel corrosion by using an ab initio method employing the HF/LANL2DZ basis set. According to their results, corrosion inhibition efficiency is related to the HOMO energy. They also investigated the interaction between inhibitor molecules and one iron atom and found that the lower the value of combined energy, the more stable they formed complex is, and the inhibitor has better inhibitive property. Li et al., (2008), computed the HOMO and LUMO energies, energy gap, molecular orbital densities and dipole moment of newly synthesized three triazole derivarives:4-chloro-acetophenone-O-1´-(1´,3´,4´-triazoly)-metheneoxime (CATM),4-methoxyl-acetophenone-O-1´-(1´,3´,4´-triazoly)-metheneoxime (MATM) and 4-fluoro- acetophenone-O-1´-(1´,3´,4´-triazoly)-metheneoxime (FATM) as corrosion inhibitors of mild steel in acid media by ab initio method employing 3-21G basis set.

The effects of thiourea (TU), methylthiourea (MTU) and phenylthiourea (PTU) on the corrosion of mild steel in 0.1 M H_2SO_4 were also investigated in relation to the concentration of thioamides. The electronic properties of these compounds were calculated by ab initio RHF/6-31G(d) method.

Lebrini *et al.,* (2006) investigated the effect of 2,5-bis(4-pyridyl)-1,3,4-thiadiazole(4-PTH) and its derivatives (n-PTH; for n = 2 and n = 3) on the corrosion of mild steel in acidic media by the HF/3-21G method. The energies of HOMO and LUMO and dipole moments were computed. They developed a linear resistance model (LR) relying on dipole moment, E_{HOMO} and E_{LUMO}. They obtained a significant multiple correlation coefficients (R > 0.93) that indicated the variation of the corrosion inhibition with the structure of the inhibitors.

Sahin *et al*., (2008) investigated the dependence of inhibition efficiencies of three heterocyclic compounds, 3-amino-1,2,4-triazole (3-ATA), 4-hydroxy-2H-1-benzopyran-2-one (4-HQ) and 4-hydroxy-3-(1H-1,2,4-triazole-3-ylazo)-2H-1-benzopyran-2-one (3-ATA), by using the B3LYP/6-31G(d) method. Such parameters as the HOMO and LUMO energies, energy gap, net atomic charges, dipole moments, total and interaction between energies were calculated. A good agreement was found between experimental and theoretical data.

Bentiss et al., (2002) performed theoretical calculations of 2,5-bis(n-methoxyphenyl)-1,3,4-oxadiazoles (n-MOX) as corrosion inhibitors for mild steel

in 1 M HCl and 0.5 M H_2SO_4 to understand if any structural differences induced by different positions of the methoxy group may be related to the experimentally observed differences of corrosion efficiency.

Mohammed et al., (2009), studied the influence of glycine and one of its derivatives namely 2-(bis (2-aminoethyl(amino) acetic acid on the corrosion of cooled rolled mild steel. Their findings showed that the protection efficiencies of these compounds showed a certain relationship to highest occupied molecular orbital (HOMO) energy, Mulliken atomic charges and Fukui indices calculated using density functional theory (DFT) and quantum chemical calculations.

Interestingly, computational studies in the framework of the density functional theory (DFT) have recently been adapted to ascertain the individual contributions of different constituents of plant extracts to the overall corrosion inhibiting action of such extracts. Oguzie, *et al*., (2010), studied the adsorption and corrosion inhibiting effect of *Dacryodis eludes* extract on low carbon steel corrosion in acidic media using both the electrochemical and quantum chemical computations. The inhibiting potentials of some selected components of the extract was assessed from the parameters associated with the electronic structures of the selected compounds obtained from the DFT-based quantum chemical computations.

Chidiebere*et al*., (2011), used theoretical studies to study the corrosion inhibition and adsorption behavior of *Punica granatum*extract on mild steel in acidic environments. Their results showed that the higher the value of E_{HOMO} and the lower the value of energy gap (ΔE) of any compound, the better the inhibition of that compound.

Eddy*et al.,* (2010), Performed quantum chemical studies on the inhibition potentials of some Penicillin compounds for the corrosion of mild steel in 0.1 M HCl. From their DFT results, the sites for nucleophilic attacks in the inhibitors are the carboxoylic acid functional group, while the sites for electrophillic attacks are in the phenyl ring. And their theoretical and experimental results showed a strong correlation which further affirms the usefulness of theoretical modeling in corrosion inhibition testing of organic compounds.

CHAPTER THREE

MATERIALS AND METHOD

3.1 MATERIALS

3.1.1 Metal specimen

Mild steel (MS) specimens containing C = 0.01%, Mn = 0.34%, P = 0.08% and Fe = 99.51% was used for this study. Each sheet, which was 0.1cm in thickness, was mechanically pressed-cut into coupons of dimension 3cm x 3cm. These coupons were used as procured without further polishing, but were degreased in absolute ethanol, dried in acetone, weighed and stored in moisture free desiccators prior to use.

3.1.2 Reagents

All reagents were BDH analytical grade, and used as source without further purification. Distilled water was used for all solutions preparations. 1M HCl (hydrochloric acid) and 0.5M H_2SO_4(sulphuric acid)solutions were employed as corrodents.

3.1.3 Extraction process: The aqueous extracts from Moringa oliefera (M.O) used as inhibitor was obtained by sun drying the fresh leaves to constant weight.

The dried leaves were ground into powder using an electric blender. 20 g of the ground leaves were added into 400ml of ethanol contained in a 500ml round-bottom flask. The resulting solution was heated under reflux for 3hrs; allowed to cool to room temperature and then filtered. The filtrate obtained was measured, and stored in air tight container and kept away from the sun. The residue obtained was dried and weighed. Thereafter, it was used in the determination of the amount of dissolved plant material in the ethanol. The concentrations of the stock solutions are 400 mg/L, 800 mg/L, and 1600mg/L. These procedures were repeated with water and 0.5 M H_2SO_4.

3.2 METHOD

3.2.1 Gravimetric measurements

Gravimetric experiments were conducted on test coupons of dimension 3 x 3 x 0.14cm, under total immersion conditions in 200ml of test solutions at room temperature. All tests were made in aerated and unstirred test solutions. Test coupons retrieved at 24hrs intervals progressively for 120 h, immersed in 20% NaOH solution containing 200g/L of zinc dust, scrubbed with bristle brush, washed, dried and reweighed. The weight loss was taken as the difference between the initial and final weights of the coupons. Measurements were undertaken using a FAJA weighing balance of range 0.0001 to 200g.

3.2.2 Temperature measurements

Gravimetric experiments were also conducted on test coupons of dimension 3 x 3 x 0.14cm, under total immersion conditions in 200ml of test solutions at the temperatures of 333K, 323K, and 313K respectively. Test coupons were retrieved after 3 hrs, immersed in 20% NaOH solution containing 200g/L of zinc dust, scrubbed with bristle brush, washed, dried and reweighed. The weight loss was taken as the difference between the initial and final weights of the coupons.

3.2.3 Electrochemical measurements

Test metal samples of mild steel for electrochemical experiment were machined into cubic specimens and fixed in polytetrafluoroethylene (PTFE) rods by epoxy resin in such a way that only one surface of area $1cm^2$ was left uncovered. The electrodes (cubic specimen of metal samples) used were polished with emery papers (from 800 to 1200 grits), rinsed with distilled water, degreased by ethanol, dried in acetone. Electrochemical experiment was conducted in a three electrode corrosion cell using PAR Model 263 corrosion system, with power suite software (Princeton Applied Research) for potentiodynamic polarization experiments. A graphite rod was used as counter electrode and a saturated calomel electrode (SCE) was used as reference electrode. The latter was connected via a luggins capillary. Potentiodynamic polarization (PDP) studies

were carried out in the potential range ± 250 mV versus corrosion potential at a scan rate of 0.5mVs^{-1}.

Each test was run in triplicate to verify the reproducibility of the data. All experiments were carried out in freshly prepared solution at constant temperature 30 ± ^{o} C using a thermostatic water bath. In the both techniques the results were monitored and extracted from the computer through the help of the earlier mentioned software.

3.2.4 Extract Characterization

3.2.4.1 Gas Chromatography - Mass Spectrometry (Gc/Ms) Analysis

About 10µL of the plant extract, was analyzed by GC/MS using GC model : 7890A Agilent technologies (Tech) and MS model :5975C Agilent Tech. coupled with a HP-5 capillary fused silica column (30m x320µm x0.25µm). The temperature was programmed as follows: Initial temperature was 60^{0}C for 4 min.,Final temperature 310^{o}C for 5 min., at the rate of 78^{0}C from the final time of 48.25 min. Other operating conditions were as follows: Carrier gas is Helium (99.999%), Pressure 3.1325 Psi, Flow rate 1.626ml/min., Average velocity 46.699 cm/sec.

3.2.5 Quantum Chemical Computations

Alltheoretical calculation were performed using the density functional theory (DFT) electrode structure programs, forcite and VAMP as contained in materials studio 4.0 software (Accelrys, Inc.) **.** The approach used with the plant extracts in view of their complex chemical composition involved qualitative characterization of the phytochemical constituents coupled with their molecular structures. The electronic structure of some of the compounds, including the distribution of frontier molecular orbital's E_{HOMO} and E_{LUMO}, were estimated using the DFT program with a view to establishing the active sites as well as local reactivity of the molecule. The simulation was performed by means of the Density Funtional Theory (DFT) electronic program (VAMP)using the Mulliken population analysis in the Material Studio 4.0 software. VAMP permits analysis of the electronic structure and energetic of the molecules, solids and surfaces using DFT.

3.2.6 Molecular Dynamics Simulation.

Molecular dynamics (MD) simulation of the interaction between single molecule of interest and Fe surface was performed using Forcite quench molecular dynamics in the Material Studio (MS) modeling 4.0 software to sample many different low energy configurations and identify the low energy minima. Calculations were carried out using COMPASS force field. The Fe crystal was

cleaved along the (110) plane with a fractional dept of 3.0. The (110) plane was chosen because it is more densely packed and has the most stabilization, compared to Fe(110) and Fe(100) surface with relatively open structures. The geometry of the bottom layers are constrained before optimizing the Fe(110) surface, which is subsequently enlarged into 12 x 9 super cell. Temperature was fixed at 350K which represents a tradeoff between a system with too much kinetic energy, where the molecules desorbs from the surface and a system with not enough kinetic energy for the molecule to move around the surface. Temperature was fixed with the NVE (microcanonocal) ensemble with a time step of 1fs and 5ps (software specification). The system is quenched every 250 steps. Forcite optimized structures of compounds and the Fe surface were used to sample the different interactions of the molecule with the surface. The slab of Fe constructed for the docking process was significantly bigger than the organic molecules docked in order to avoid edge effects.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 RESULTS

GRAVIMETRIC RESULTS

The influence of acidic environments (1 M HCl and 0.5 M H_2SO_4) on the corrosion behavior of mild steel was investigated using gravimetric and electrochemical techniques. The results for the gravimetric experiment for mild steel corrosion in 1 M HCl without and with different (ethanol, sulphuric and water) extracts for different immersion times (24-120 h) are presented Table 4.1 – 4.15. While the respective plots showing the following: weight loss over exposure time, influence of concentration of M.O on the weight loss, inhibition performances of the extracts over time and the effect of concentration increase on inhibition efficiency of the different extracts of M.O are presented in Figures: 4.1 - 4.22.

The results for the gravimetric experiment for mild steel corrosion in 0.5 M H_2SO_4 without and with different (ethanol, sulphuric and water) extracts for different immersion times (24 - 120 h) are presented Tables: 4.16 – 4.30. While the corresponding plots; weight loss over time, weight loss versus inhibitor concentration, inhibition efficiency over time and effect of extract's concentration

on the inhibition efficiency for the different extracts(ethanol, sulphuric and water) are presented in Figures: 4.13 -4.24.

ELECTROCHEMICAL RESULTS

Electrochemical experiments were undertaking to identify the effect of the acidic environments on the anodic and cathodic current reactions as well as to determine how the extracts modify the electrochemical behaviour/processes (anodic and cathodic reactions).

The results of the potentiodynamic polarization (PDP) for mild steel in 1 M HCl without and with the highest concentration of different (ethanol, sulphuric and water) extracts of M.O are presented in Table 4.31, while the corresponding polarization curves are presented in Figures; 4.25, 4.26, 4.27 for ethanol, sulphuric acid and water respectively.

The polarization results for mild steel in 0.5 M $H_2SO_4$are presented in Figures; 4.28, 4.29 and 4.30 for ethanol, sulphuric and water extracts respectively. While the corresponding polarization parameters are presented in Tale 4.32.

TEMPERATURE/KINETIC CONSIDERATION

In order to evaluate the effect of temperature variations on the corrosion and corrosion inhibition processes, and to afford insights on the mechanism of

inhibition of the different M.O extracts, gravimetric tests were further undertaken at 313–333K in bothuninhibited and inhibited systems.

The results for the Weight loss versus temperature (at 313-333K) and inhibition efficiency versustemperature (at 313-333K) values for mild steel corrosion in 1 M HCl without and with ethanol, sulphuric and water extracts of M.O after 3 h are presented in Tables: 4.33-4.35, 4.36-4.38 and 4.39-4.41 respectively. While, the variation of weight loss with temperature and inhibition efficiency with temperature are presented in Figures: 4.31- 4.32, 4.33-4.34, 4.35- 4.36 for ethanol, sulphuric acid and water respectively.

Accordingly, the effects of temperature on the weight loss and inhibition efficiency for the different M.O extracts for mild steel in 0.5 M H_2SO_4 are presented in Tables: 4.22 - 4.44, 4.45 - 4.47 and 4.48 - 4.50 for ethanol, suphuric acid and water respectively. While the corresponding plots for weight loss versus temperature and inhibition efficiency versus temperature for mild steel corrosion in 0.5 M $H_2SO_4$are presented in Figures: 37-38, 39-40 and 4.41 -42 for ethanol, sulphuric acid and water respectively.

Arrhenius plots for mild steel corrosion in 1 M HCl without and with different extracts (ethanol, acid and water) of M.O are presented in Figures: 4.43, 4.44, and 4.45 for ethanol, sulphuric and water respectively. While, the corresponding kinetic data (Ea) are presented in Table 4.51.

Arrhenius plots for mild steel corrosion in 0.5 M H_2SO_4 without and with different extracts (ethanol, acid and water) of M.O are presented in Figures: 4.46, 4.47, and 4.48 for ethanol, sulphuric and water respectively. While the corresponding kinetic data (Ea) are presented in Table 4.52.

COMPARING DATA

In order to compare the performances of the different extracting solvents (ethanol, sulphuric acid and water) for corrosion inhibition of M.S by M.O in 1 M HCl and 0.5 M H_2SO_4;the average weight loss and inhibition efficiency values per day were computed and the data were used to plots graphs that reflected the inhibition differences exerted by the different extracts in the both acidic media studied.

Fig. 4.9 A and B compares the difference in the gravimetric and potentiodynamic behaviours of mild steel in 1 M HCl and 0.5 M H_2SO_4. Fig. 4.50 A and B respectively compared the average weight loss and inhibition efficiency versus time for the different extracts (ethanol, sulphuric and water respectively) of M.O in 1 M HCl. Secondly, Figure 4.51 compares the polarization curves for the different extracts. Againg, Figure 4.52 compares the average activation energies exacted by the different extracts of M.O in hydrochloric acid environment.

On the other hand, Fig. 4.53 A and B respectively compared the average weight loss and inhibition efficiency versus time for the different extracts (ethanol, sulphuric and water respectively) of M.O in 0.5 M H_2SO_4. Secondly, Figure 4.54 compares the polarization curves for the different extracts in 0.5 M H_2SO_4. Againg, Figure 4.55 compares the average activation energies exacted by the different extracts of M.O in sulphuric acid environment.

Table 4.1 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with ethanol extract of MO after 24h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0054	4.9154	0.09	0.09	
	B	4.9859	4.8959	0.09		
400	**A**	5.1894	5.1429	0.0465	0.0413	54.05
	B	5.2199	5.1837	0.0362		
800	**A**	5.1742	5.0929	0.0313	0.0384	57.33
	B	5.1748	5.1364	0.0384		
1600	**A**	4.9914	4.9648	0.0266	0.0230	74.44
	B	4.9006	4.8811	0.0195		

Table 4.2 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with ethanol extract of MO after 48h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0054	4.8642	0.1412	0.140	
	B	4.9859	4.8471	0.1388		
400	**A**	5.1894	5.1135	0.0759	0.0644	54
	B	5.2199	5.1670	0.0529		
800	**A**	5.1742	5.1287	0.0455	0.0498	64.42
	B	5.1748	5.1207	0.0541		
1600	**A**	4.9914	4.9472	0.0442	0.0386	72.42
	B	4.9006	4.8675	0.0331		

Table 4.3 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with ethanol extract of MO after 72 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.005	4.8143	0.1911	0.1866	
	B	4.9859	4.8037	0.1822		
400	**A**	5.1894	5.0948	0.0946	0.0829	55.57
	B	5.2199	5.1486	0.0713		
800	**A**	5.1742	5.1117	0.0625	0.0673	63.93
	B	5.1748	5.1026	0.0722		
1600	**A**	4.9914	4.9345	0.0569	0.0619	66.82
	B	4.9006	4.8336	0.0670		

Table 4.4 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with ethanol extract of MO after 96 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0054	4.7542	0.2512	0.2327	
	B	4.9859	4.7716	0.2142		
400	**A**	5.1894	5.0740	0.1154	0.1013	56.46
	B	5.2199	5.1326	0.0873		
800	**A**	5.1742	5.1115	0.0627	0.0756	67.51
	B	5.1748	5.0862	0.0886		
1600	**A**	4.9914	4.9223	0.0691	0.0627	73.05
	B	4.9006	4.8442	0.0564		

Table 4.5 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with ethanol extract of MO after 120 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0054	4.9154	0.09	0.09	
	B	4.9859	4.8959	0.09		
400	**A**	5.1894	5.1982	0.0306	0.0310	65.55
	B	5.2199	4.9419	0.0315		
800	**A**	5.1742	5.0178	0.0316	0.0292	67.55
	B	5.1748	5.0989	0.0269		
`1600	**A**	1	4.9215	0.0196	0.0211	76.55
	B		4.8591	0.0227		

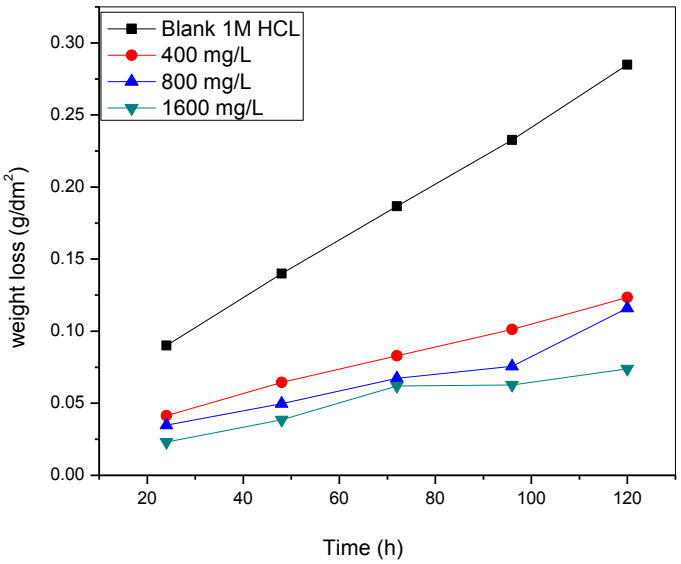


Figure 4.1 Variation of weight loss with time for mild steel in 1 M HCl without and with ethanol extract of MO

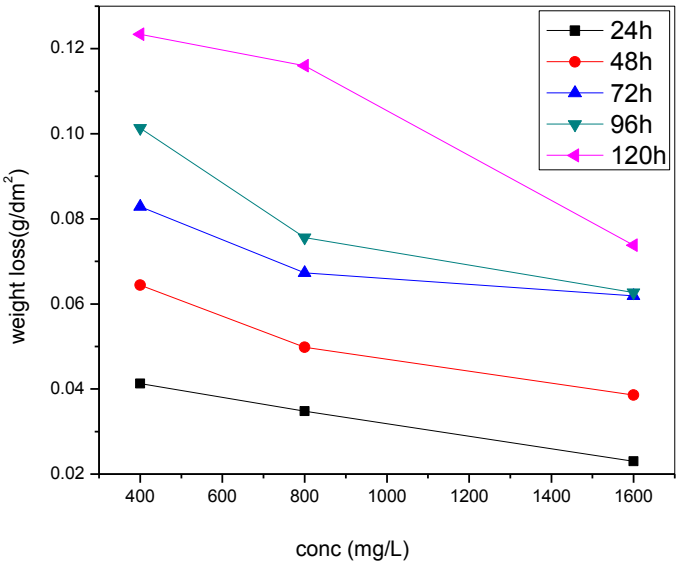


Figure 4.2 Variation of weight loss with concentration of ethanol extract of MO for mild steel in 1 M HCl

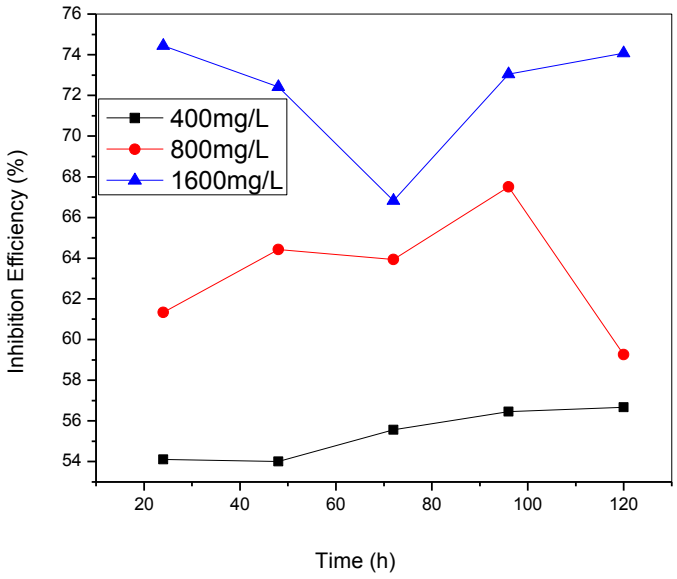


Figure 4.3 Variation of inhibition efficiency with time for mild steel with different concentration of ethanol extract of MO

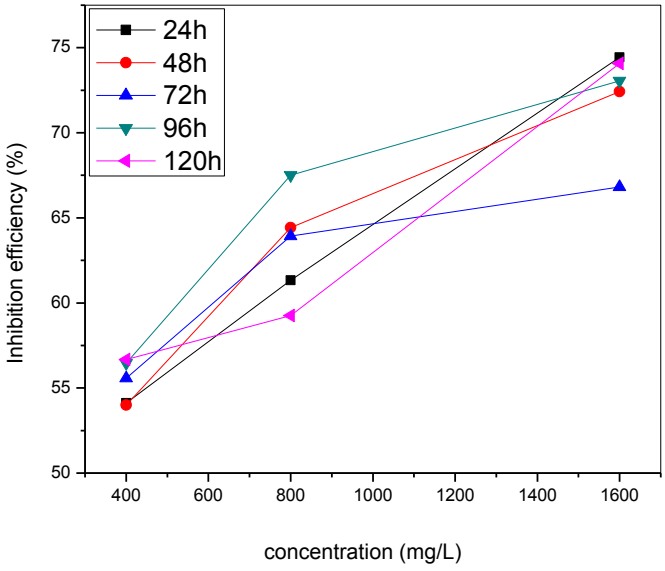


Figure 4.4 Variation of inhibition efficiency with concentration of ethanol extract of MO for mild steel in 1 M HCl

Table 4.6Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with H_2SO_4 extract of MO after 24h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0054	4.9154	0.09	0.09	
	B	4.9859	4.8959	0.09		
400	**A**	5.2288	5.1982	0.0306	0.0310	65.55
	B	4.9734	4.9419	0.0315		
800	**A**	5.0494	5.0178	0.0316	0.0292	67.55
	B	5.1258	5.0989	0.0269		
1600	**A**	4.9411	4.9215	0.0196	0.0211	76.55
	B	4.8818	4.8591	0.0227		

Table 4.7 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with H_2SO_4 extract of MO after 48 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0059	4.8642	0.1412	0.140	
	B	4.9859	4.8471	0.1388		
400	**A**	5.2288	5.1568	0.0720	0.0607	56.64
	B	4.9734	4.9239	0.0495		
800	**A**	5.0494	5.0036	0.0458	0.0424	69.71
	B	5.1258	5.0868	0.0390		
1600	**A**	4.9411	4.9086	0.0325	0.0353	74.78
	B	4.8818	4.8437	0.0381		

Table 4.8 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with H_2SO_4 extract of MO after 72 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0054	4.8143	0.1911	0.1866	
	B	4.9859	4.8037	0.1822		
400	**A**	5.2288	5.1686	0.0602	0.0598	67.95
	B	4.9734	4.9139	0.0595		
800	**A**	5.0494	4.9894	0.0600	0.0597	68.00
	B	5.1258	5.0664	0.0594		
1600	**A**	4.9411	4.9001	0.0410	0.0461	75.29
	B	4.8818	4.8306	0.0512		

Table 4.9 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with H_2SO_4 extract of MO after 96 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0054	4.7542	0.2512	0.2327	
	B	4.9859	4.7716	0.2142		
400	**A**	5.2288	5.1513	0.0775	0.0748	67.85
	B	4.9734	4.9012	0.0722		
800	**A**	5.0494	4.9721	0.0773	0.0757	67.46
	B	5.1258	5.0517	0.0741		
1600	**A**	4.9411	4.8877	0.0534	0.0579	75.11
	B	4.8818	4.8194	0.0624		

Table 4.10 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with H_2SO_4 extract of MO after 120 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0054	4.7028	0.3026	0.3026	
	B	4.9859	4.7189	0.2142		
400	**A**	5.2286	5.1394	0.0894	0.0872	69.38
	B	4.9734	4.8884	0.0850		
800	**A**	5.0494	4.9571	0.0923	0.0886	68.89
	B	5.1258	5.0409	0.0849		
1600	**A**	4.9411	4.8485	0.0926	0.0837	70.61
	B	4.8818	4.8069	0.0749		

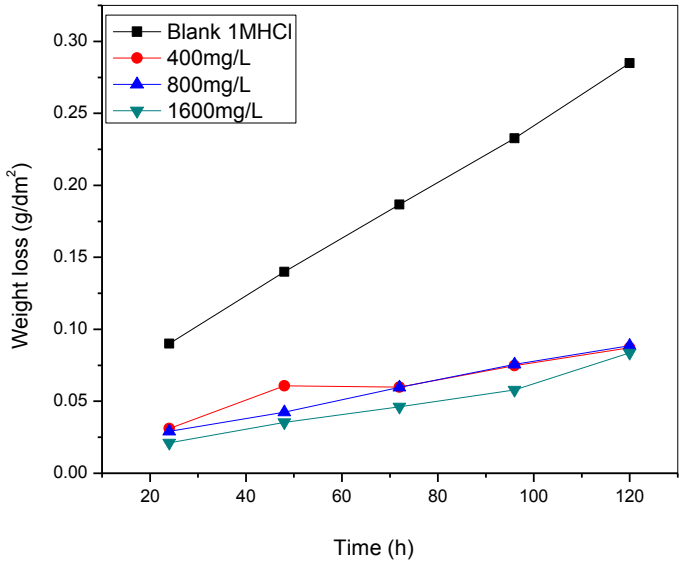


Figure 4.5 Variation of weight loss with time for mild steel in 1 M HCl without and with sulphuric acid extract of MO

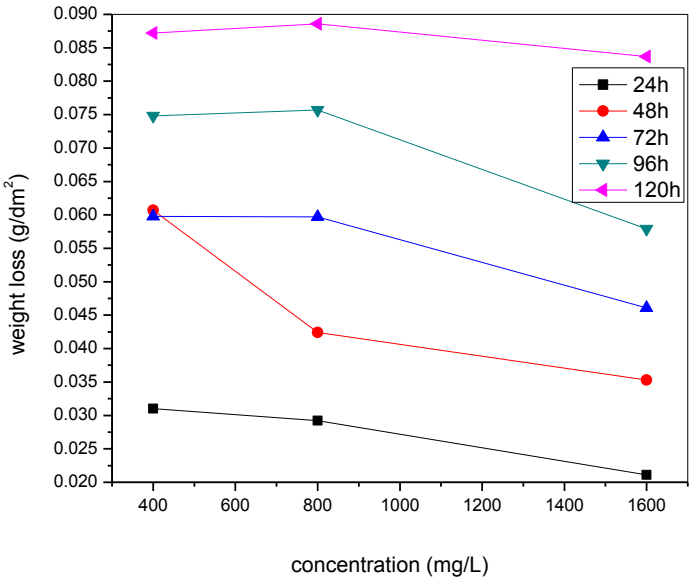


Figure 4.6 Variation of weight loss with concentration of sulphuric acid extract of MO for mild steel in 1 M HCl

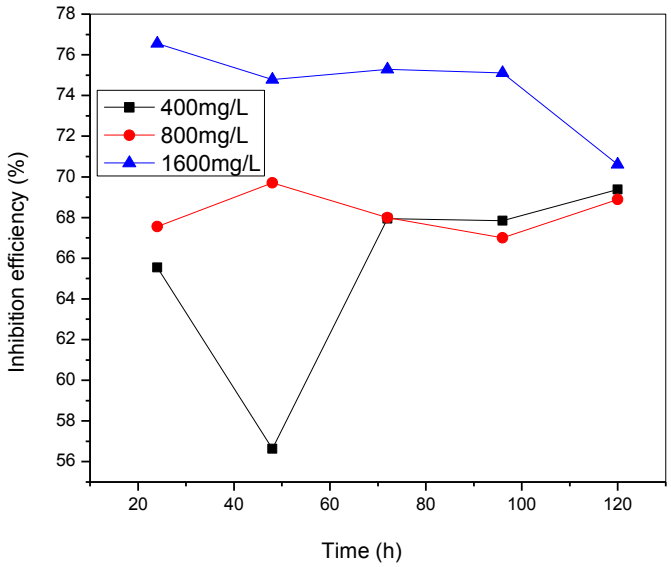


Figure 4.7 Variation of inhibition efficiency with time for mild steel with different concentration of sulphuric acid extract of MO

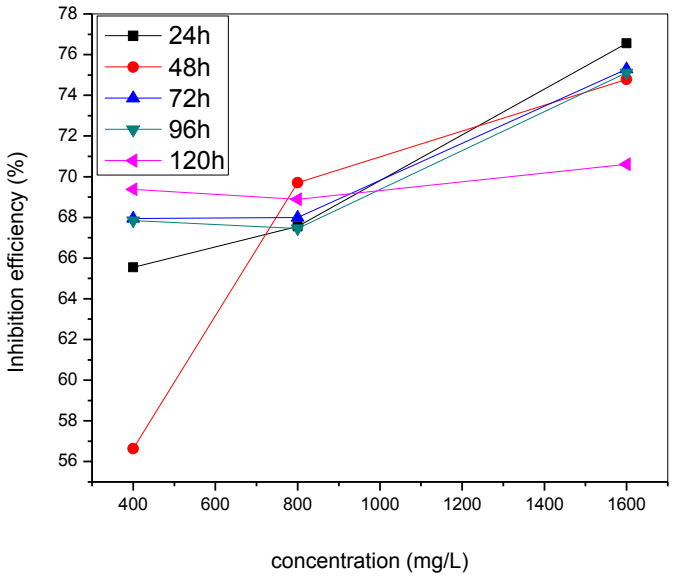


Figure 4.8 Variation of inhibition efficiency with concentration of sulphuric acid extract of MO for mild steel in 1 M HCl

Table 4.11Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with H_2O extract of MO after 24h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0054	4.9154	0.09	0.09	
	B	4.9859	4.8959	0.09		
400	**A**	4.4952	4.4654	0.0298	0.0312	65.33
	B	5.0677	5.0350	0.0327		
800	**A**	4.8737	4.8456	0.0281	0.0279	69.00
	B	4.7106	4.6829	0.0277		
1600	**A**	5.0663	5.0512	0.0151	0.0187	79.22
	B	4.8336	4.8113	0.0223		

Table 4.12 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with H_2O extract of MO after 48 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0054	4.8642	0.1412	0.140	
	B	4.9859	4.8471	0.1388		
400	**A**	4.4952	4.4488	0.0464	0.0497	64.5
	B	5.0677	5.0146	0.0531		
800	**A**	4.8737	4.8245	0.0492	0.0473	66.2
	B	4.7106	4.6651	0.0455		
1600	**A**	5.0663	5.0400	0.0263	0.0381	72.7
	B	4.8336	4.7837	0.0499		

Table 4.13 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with H_2O extract of MO after 72 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0054	4.8143	0.1911	0.1866	
	B	5.9859	4.9859	0.1822		
400	**A**	4.4952	4.4374	0.0578	0.0668	64.2
	B	5.0677	4.9919	0.0758		
800	**A**	4.8737	4.8051	0.0686	0.0640	65.7
	B	4.8737	4.6511	0.0595		
1600	**A**	5.0663	5.0060	0.0608	0.0562	69.88
	B	4.8336	4.7815	0.0521		

Table 4.14 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with H_2O extract of MO after 96 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0054	4.7542	0.2512	0.02327	
	B	4.9859	4.7716	0.2142		
400	**A**	4.4952	4.3779	0.1173	0.1016	56.33
	B	5.0677	4.9818	0.0859		
800	**A**	4.8737	4.7912	0.0825	0.0774	66.7
	B	4.7106	4.6383	0.0723		
1600	**A**	5.0663	4.9904	0.0759	0.0765	67.12
	B	4.8336	4.7564	0.0772		

Table 4.15 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with H_2O extract of MO after 120 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0059	4.7028	0.3026	0.2848	
	B	4.9859	4.7189	0.2142		
400	**A**	4.4952	4.3374	0.1578	0.1301	54.31
	B	5.0677	4.9652	0.1025		
800	**A**	4.7106	4.7774	0.0963	0.0938	67.06
	B	4.7106	4.6192	0.0914		
1600	**A**	5.0663	4.9732	0.0931	0.0926	67.48
	B	4.8336	4.7415	0.0921		

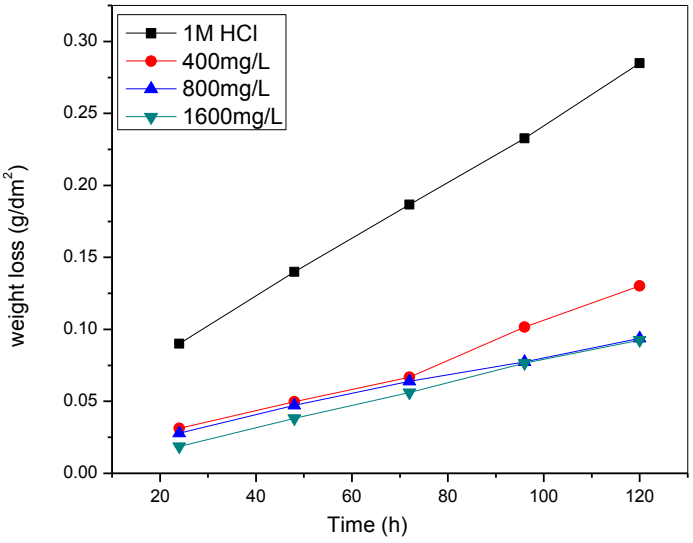


Figure 4.9 Variation of weight loss with time for mild steel in 1 M HCl without and with water extract of MO

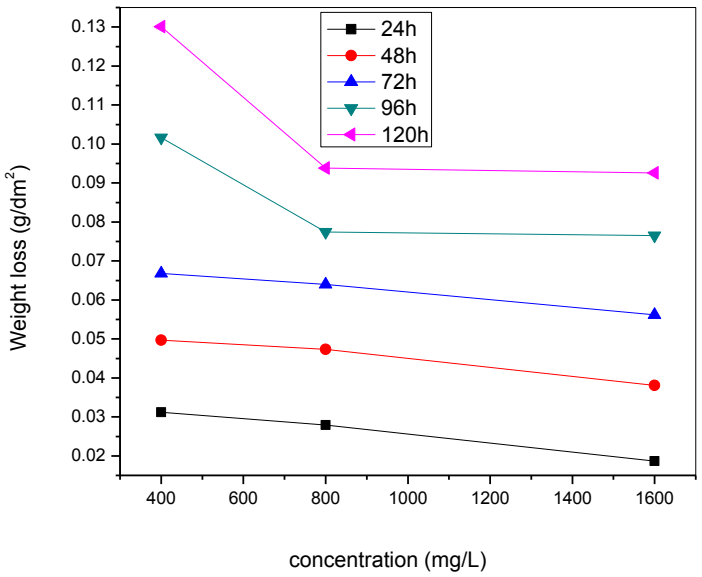


Figure 4.10 Variation of weight loss with concentration of water extract of MO for mild steel in 1 M HCl

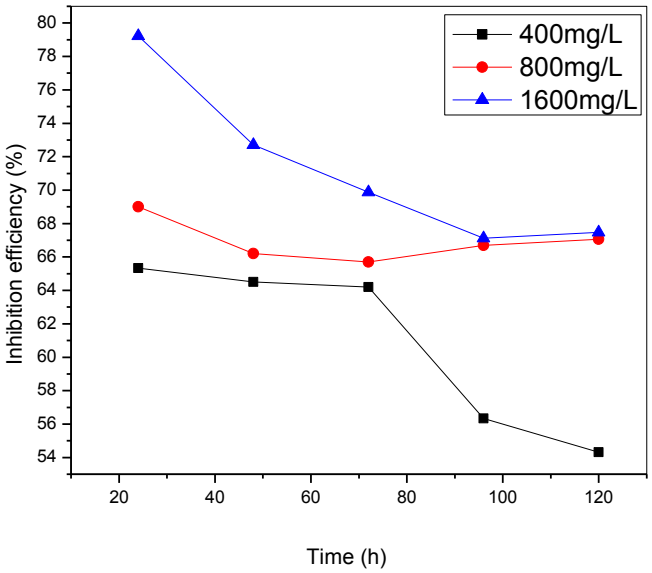


Figure 4.11 Variation of inhibition efficiency with time for mild steel with different concentration of water extract of MO

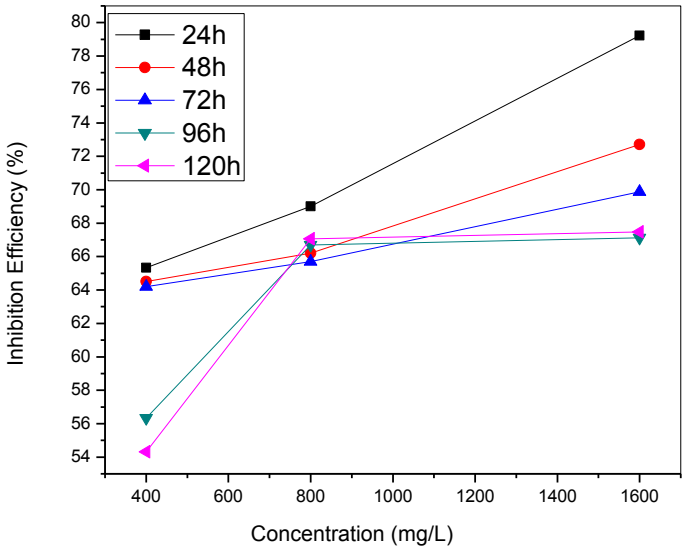


Figure 4.12 Variation of inhibition efficiency with concentration of water extract of MO for mild steel in 1 M HCl

Table 4.16 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with ethanol extract of MO after 24 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.9725	3.9237	1.0488	1.0748	
	B	5.0216	3.9207	1.1009		
400	**A**	5.0778	4.9022	0.1756	0.1587	85.22
	B	5.3306	5.1887	0.1419		
800	**A**	5.1331	5.0245	0.1106	0.0969	90.98
	B	4.5920	4.5097	0.0832		
1600	**A**	4.9025	4.8667	0.0358	0.0797	90.58
	B	4.9045	4.8606	0.0439		

Table 4.17 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with ethanol extract of MO after 48 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.9725	3.2304	1.7421	1.7642	
	B	5.0216	3.2352	1.7864		
400	**A**	5.0778	4.8248	0.2530	0.2337	86.75
	B	5.3306	5.1161	0.2145		
800	**A**	5.1351	4.9626	0.1725	0.1414	91.98
	B	4.5929	4.4826	0.1103		
1600	**A**	4.9025	4.8464	0.0561	0.0616	96.50
	B	4.9045	4.8374	0.0671		

Table 4.18 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with ethanol extract of MO after 72 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.9725	2.9673	2.0052	2.0708	
	B	5.0216	2.8851	2.1365		
400	**A**	5.0778	4.7446	0.3332	0.3074	85.15
	B	5.3306	5.0490	0.2816		
800	**A**	5.1351	4.9002	0.2349	0.2026	90.21
	B	4.5929	4.4226	0.1703		
1600	**A**	4.9025	4.8302	0.0723	0.0793	96.17
	B	4.9045	4.8182	0.0863		

Table 4.19 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with ethanol extract of MO after 96 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.9725	2.8731	2.0994	2.1716	
	B	5.0216	2.7777	2.2439		
400	**A**	5.0778	4.6192	0.4586	0.3849	82.27
	B	5.3306	5.0193	0.3113		
800	**A**	5.1351	4.8185	0.3166	0.2602	88.01
	B	4.5929	4.3890	0.2039		
1600	**A**	4.9025	4.8142	0.0883	0.0975	95.51
	B	4.9045	4.7978	0.1067		

Table 4.20 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with ethanol extract of MO after 120 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.9725	2.7984	2.1741	2.2756	
	B	5.0216	2.6444	2.3772		
400	**A**	5.0778	4.5694	0.5084	0.4933	78.32
	B	5.3306	4.8523	0.4783		
800	**A**	4.1351	4.2238	0.3113	0.2720	88.04
	B	4.5929	4.3601	0.2328		
1600	**A**	4.9025	4.7951	0.1074	0.1168	94.86
	B	4.9045	4.7782	0.1263		

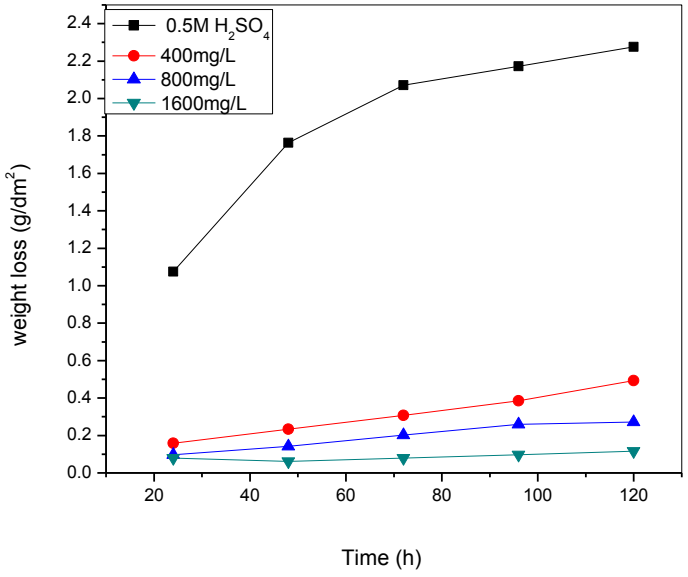


Figure 4.13 Variation of weight loss with time for mild steel in 0.5 M H_2SO_4 without and with ethanol extract of MO

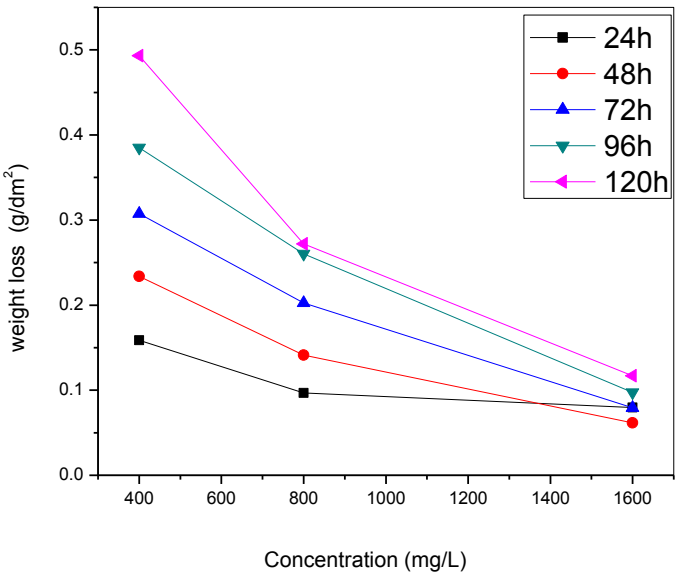


Figure 4.14 Variation of weight loss with concentration of ethanol extract of MO for mild steel in 0.5 M H_2SO_4

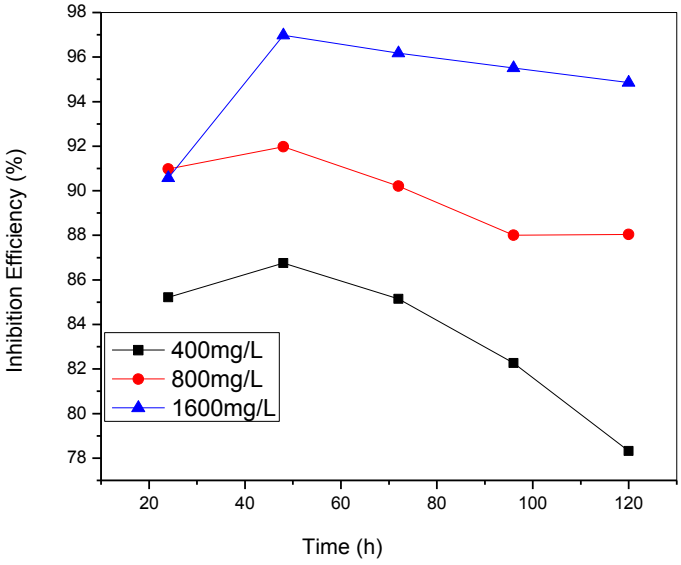


Figure 4.15 Variation of inhibition efficiency with time for mild steel in 0.5 M H_2SO_4 with different concentration of ethanol extract of MO

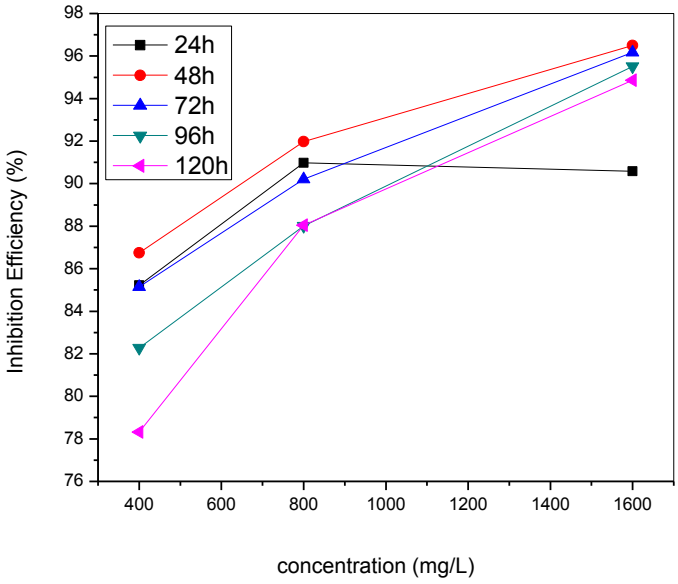


Figure 4.16 Variation of inhibition efficiency with concentration of ethanol extract of MO for mild steel in 0.5 M H_2SO_4

Table 4.21 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with H_2SO_4 extract of MO after 24h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.9725	3.9237	1.0488	1.0748	
	B	5.0216	4.9207	1.1009		
400	**A**	4.9663	4.9248	0.0415	0.0382	96.44
	B	5.2264	5.1915	0.0349		
800	**A**	5.1791	5.1430	0.0361	0.0365	96.60
	B	4.9312	4.8943	0.0369		
1600	**A**	5.0177	4.9835	0.0342	0.0318	97.04
	B	5.1098	5.0804	0.0294		

Table 4.22 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with H_2SO_4 extract of MO after 48 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.9725	3.2304	1.7421	1.7642	
	B	5.0216	3.2352	1.7864		
400	**A**	4.9663	4.8992	0.0671	0.0658	96.27
	B	5.2264	5.1618	0.0646		
800	**A**	5.1791	5.1120	0.0621	0.0658	96.27
	B	4.9312	4.8611	0.0695		
1600	**A**	5.0177	4.9596	0.0581	0.0637	96.38
	B	5.1098	5.0404	0.0694		

Table 4.23 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with H_2SO_4 extract of MO after 72 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.9725	2.9673	2.0052	2.0708	
	B	5.0216	2.8851	2.1365		
400	**A**	4.9663	4.9266	0.0397	0.1341	93.52
	B	5.2264	4.9978	0.2286		
800	**A**	5.1791	5.0646	0.1145	0.1136	94.51
	B	4.9312	4.8184	0.1128		
1600	**A**	5.0177	4.8714	0.1463	0.1243	93.99
	B	5.1098	5.0074	0.1024		

Table 4.24 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with H_2SO_4 extract of MO after 96 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.9725	2.8731	2.0994	2.1716	
	B	4.5601	2.7777	2.2439		
400	**A**	4.9663	4.7718	0.1945	0.2041	90.60
	B	5.2264	5.0127	0.2137		
800	**A**	5.1791	4.9614	0.2177	0.1329	93.88
	B	4.9312	4.8830	0.0428		
1600	**A**	5.0177	4.8362	0.1815	0.1005	95.37
	B	5.1098	5.0903	0.0195		

Table 4.25 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with H_2SO_4 extract of MO after 120 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.9725	2.7984	2.1741	2.2756	
	B	5.0216	2.6444	2.3772		
400	**A**	4.9663	4.7298	0.2365	0.2454	89.21
	B	5.2264	4.9720	0.2544		
800	**A**	5.1791	5.0496	0.1295	0.1263	94.44
	B	4.9312	4.8080	0.1232		
1600	**A**	5.0177	4.8511	0.1366	0.1233	94.58
	B	5.1098	4.9797	0.1101		

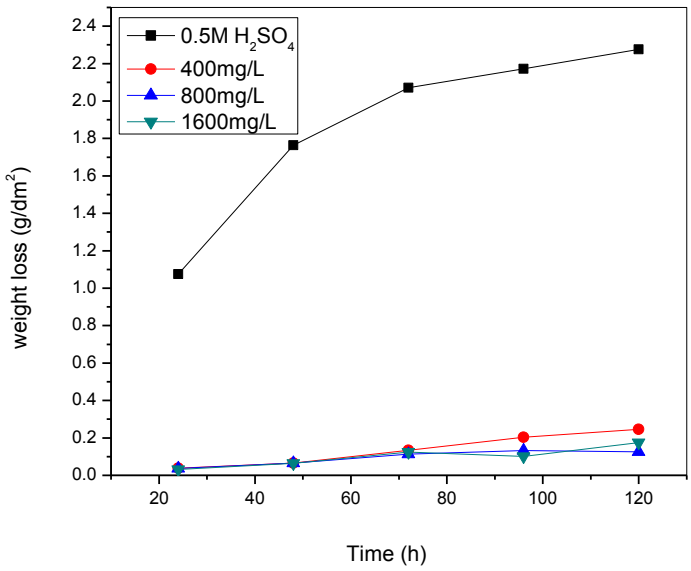


Figure 4.17 Variation of weight loss with time for mild steel in 0.5 M H_2SO_4 without and with sulphuric acid extract of MO

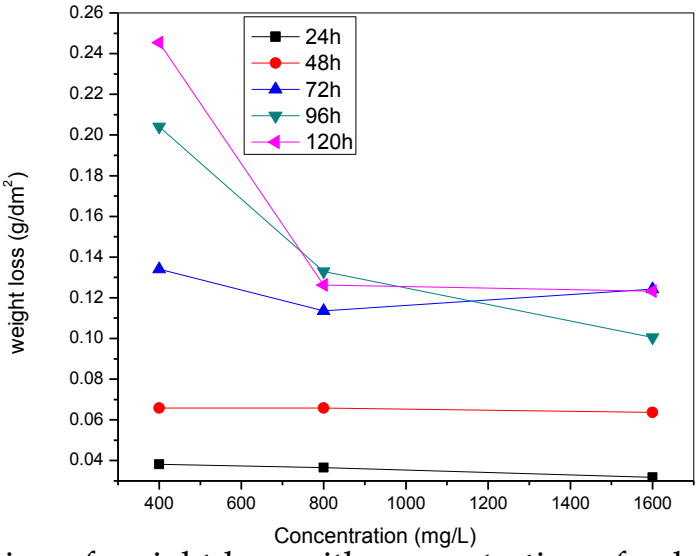


Figure 4.18 Variation of weight loss with concentration of sulphuric acid extract of MO for mild steel in 0.5 M H_2SO_4

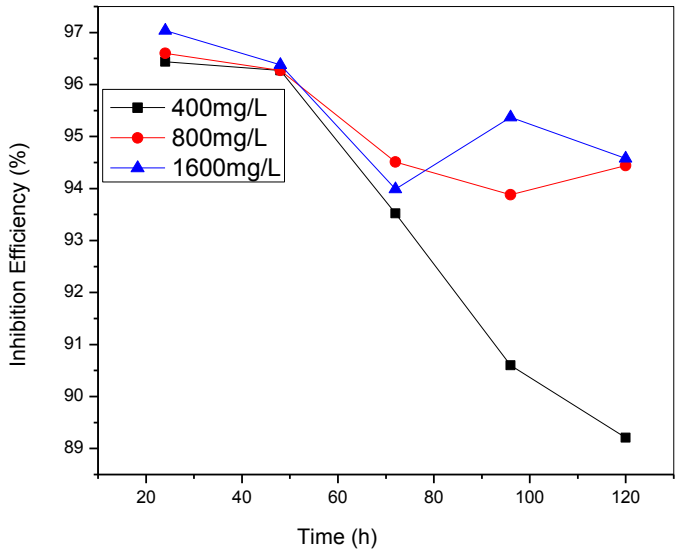


Figure 4.19 Variation of inhibition efficiency with time for mild steel in 0.5 M H_2SO_4 with different concentration of sulphuric acid extract of MO

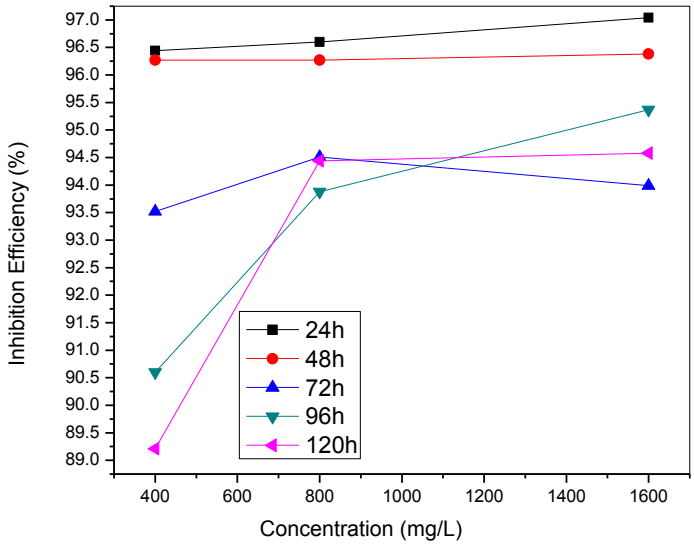


Figure 4.20 Variation of inhibition efficiency with concentration of sulphuric acid extract of MO for mild steel in 0.5 M H_2SO_4

Table 4.26 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with H_2O extract of MO after 24 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.9725	3.9237	1.0488	1.0748	
	B	5.0216	3.9207	1.1009		
400	**A**	5.0748	4.9897	0.0851	0.0908	91.55
	B	4.9505	4.8539	0.0966		
800	**A**	5.0941	5.0110	0.0731	0.0754	92.98
	B	4.9780	4.9002	0.0778		
1600	**A**	4.8152	4.7603	0.0549	0.0518	95.18
	B	4.9344	4.8857	0.0487		

Table 4.27 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with H_2O extract of MO after 48 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.9725	3.2304	1.7421	1.7642	
	B	5.0216	3.2352	1.7864		
400	**A**	5.0748	4.9380	0.1368	0.1588	90.99
	B	4.9505	4.7697	0.1808		
800	**A**	5.0941	4.9689	0.1252	0.1339	92.41
	B	4.9780	4.8353	0.1427		
1600	**A**	4.8152	4.7209	0.0943	0.0897	94.91
	B	4.9344	4.8493	0.0851		

Table 4.28 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with H_2O extract of MO after 72 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.9725	2.9673	2.0052	2.0708	
	B	5.0216	2.8851	2.1365		
400	**A**	5.0748	4.9021	0.1727	0.1723	91.67
	B	4.9505	4.7785	0.1720		
800	**A**	5.0941	4.9662	0.1279	0.1299	93.72
	B	4.9780	4.8460	0.1320		
1600	**A**	4.8152	4.7204	0.0948	0.1080	94.78
	B	4.9344	4.8131	0.1213		

Table 4.29 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with H_2O extract of MO after 96 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.9725	2.8731	2.0994	2.1716	
	B	5.0216	2.7777	2.2439		
400	**A**	5.0746	4.7838	0.2910	0.2860	86.82
	B	4.9505	4.8294	0.2811		
800	**A**	5.0941	4.8190	0.2751	0.2582	88.11
	B	4.9780	4.7367	0.2413		
1600	**A**	4.8152	4.6226	0.1926	0.2085	90.39
	B	4.9344	4.7099	0.2245		

Table 4.30 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with H_2O extract of MO after 120 h.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.9725	2.7984	2.1741	2.2756	
	B	5.0216	2.6444	0.3772		
400	**A**	5.0748	4.7436	0.3312	0.3365	85.21
	B	4.9505	4.6086	0.3419		
800	**A**	5.0941	4.7807	0.3134	0.3172	86.06
	B	4.9780	4.6569	0.3211		
1600	**A**	4.8152	4.5148	0.3004	0.3062	86.54
	B	4.9344	4.6223	0.3121		

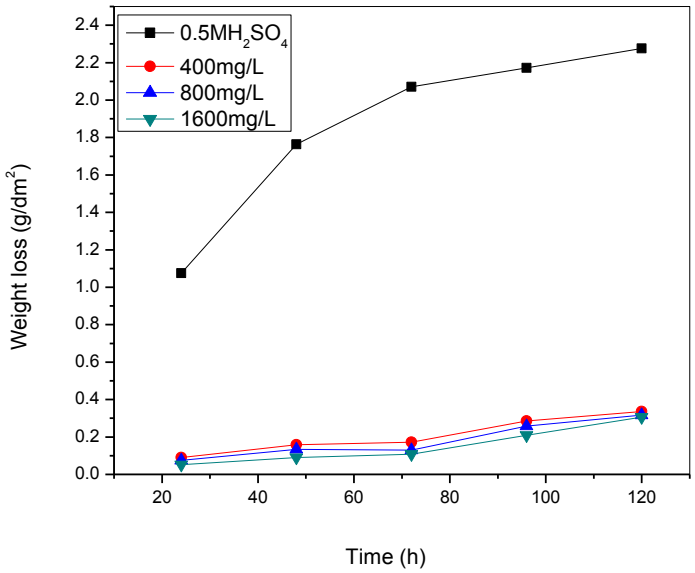


Figure 4.21 Variation of weight loss with time for mild steel in 0.5 M H_2SO_4 without and with water extract of MO

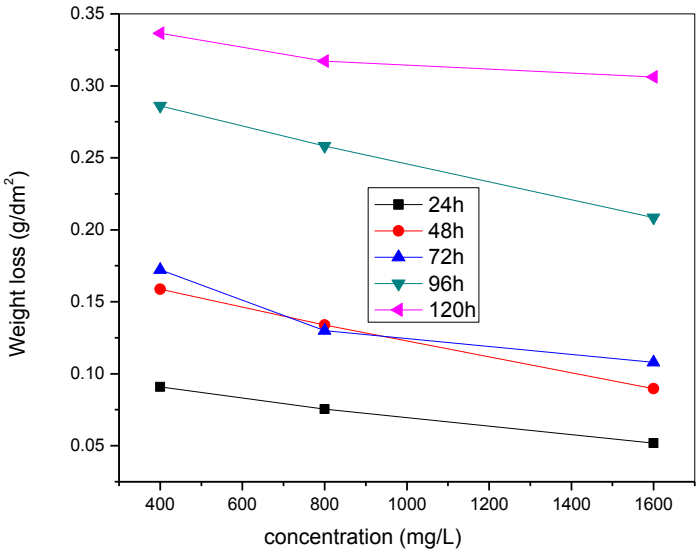


Figure 4.22 Variation of weight loss with concentration of water extract of MO for mild steel in 0.5 M H_2SO_4

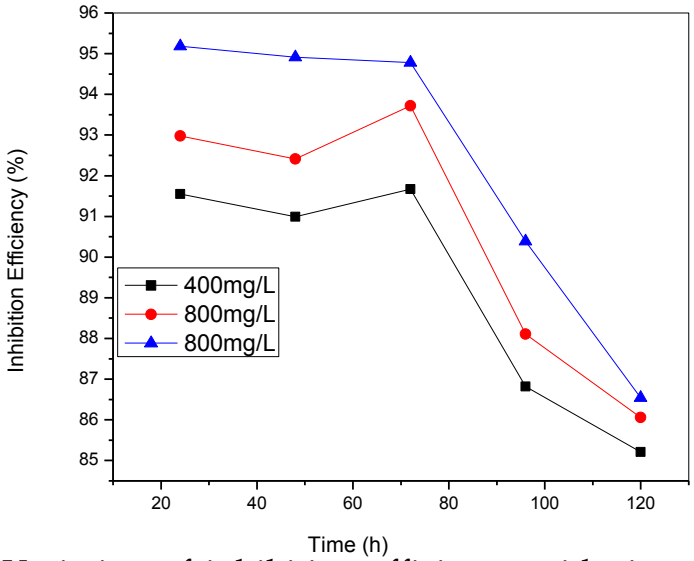


Figure 4.23 Variation of inhibition efficiency with time for mild steel in 0.5 M H_2SO_4 with different concentration of water extract of MO

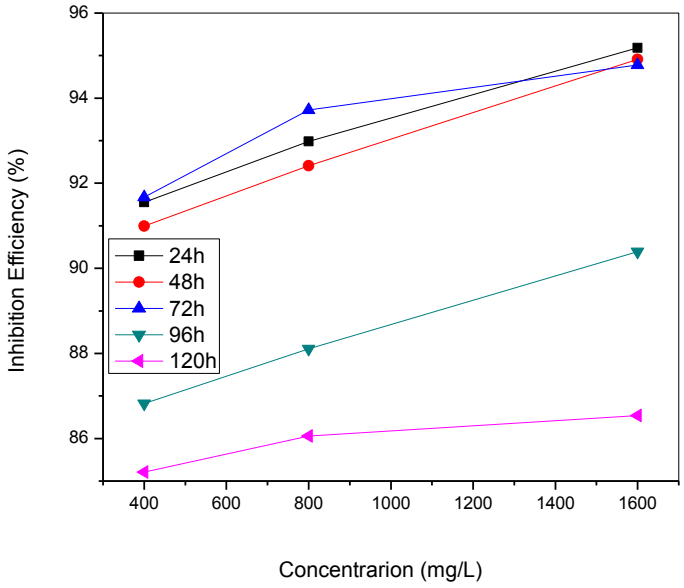


Figure 4.24 Variation of inhibition efficiency with concentration of water extract of MO for mild steel in 0.5 M H_2SO_4

ELECTROCHEMICAL RESULTS

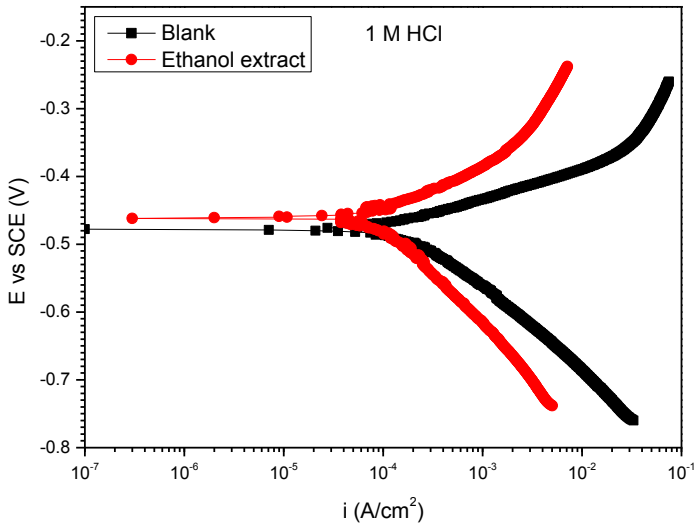


Figure 4.25 Potentiodynamic polarization curves of mild steel in 1M HCl solution without and with 1600 mg/L ethanol extract of M.O

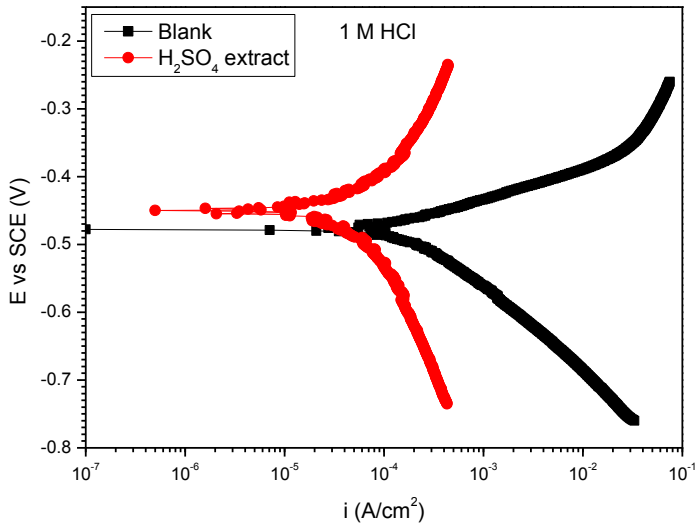


Figure 4.26 Potentiodynamic polarization curves of mild steel in 1M HCl solution without and with 1600 mg/L H_2SO_4 extract of M.O

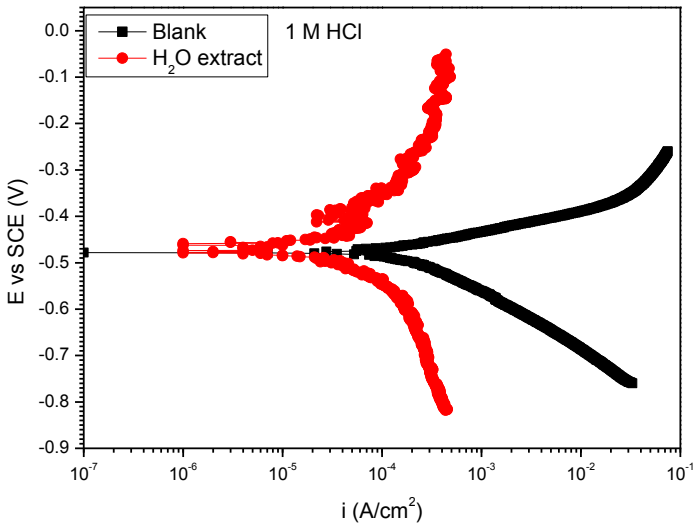


Figure 4.27 Potentiodynamic polarization curves of mild steel in 1M HCl solution without and with 1600 mg/L water extract of M.O

Table 4.31 Polarization parameters for mild steel in 1 M HCl in the absence and presence of 1600 mg/L of different extracts (ethanol, H_2SO_4, and water) of M.O

System	E corr. (mV)	I corr. $\mu A/cm^2$	Bc mV	Ba Mv	IE%
Blank 1 MHCl	-478	818.7	103	54	-
Ethanol Extract M.O (1600 mg/L)	-462	117	179	82	85.7
0.5 MH_2SO_4 Extract M.O (1600 mg/L)	-450	25	122	87	96.9
Water Extract M.O (1600 mg/L)	-471	35	348	141	95.7

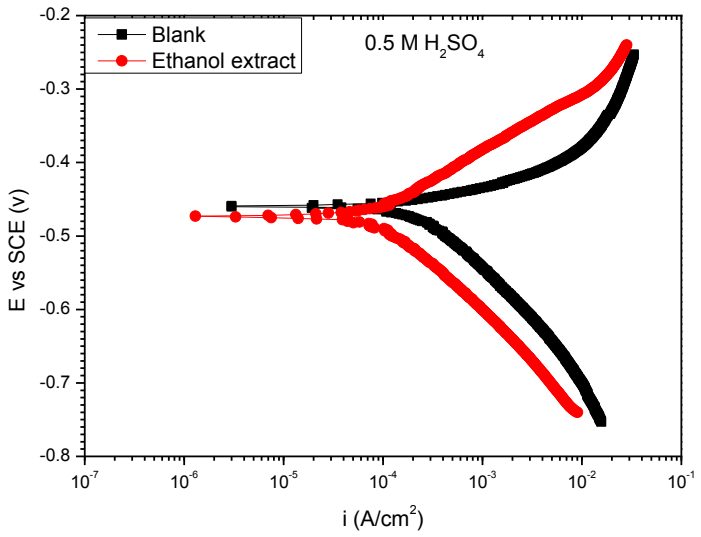


Figure 4.28 Potentiodynamic polarization curves of mild steel in 0.5 M H_2SO_4solution without and with 1600 mg/L ethanol extract of M.O

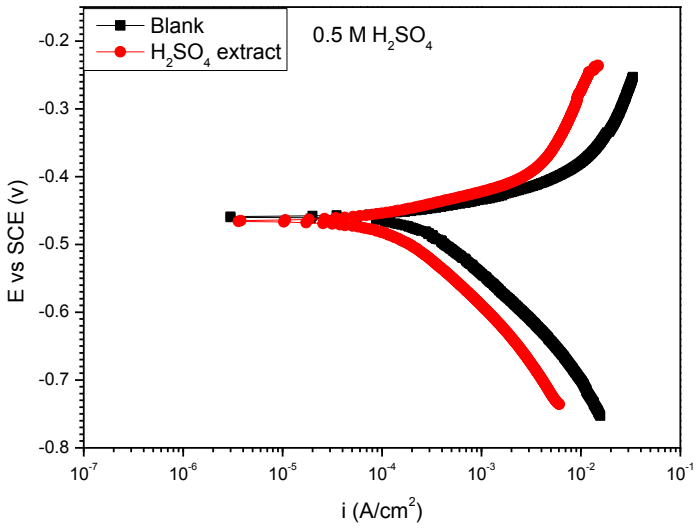


Figure 4.29 Potentiodynamic polarization curves of mild steel in 0.5 M H_2SO_4solution without and with 1600 mg/L H_2SO_4 extract of M.O

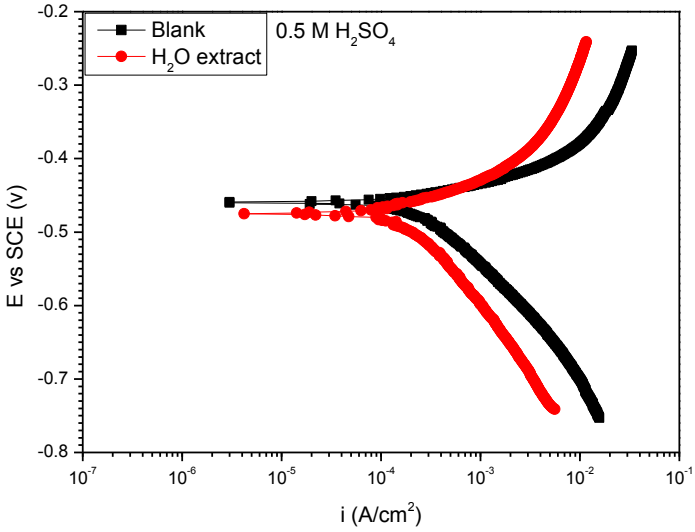


Figure 4.30 Potentiodynamic polarization curves of mild steel in 0.5 M H_2SO_4solution without and with 1600 mg/L water extract of M.O

Table 4.32 Polarization parameters for mild steel in 0.5 M H_2SO_4 in the absence and presence of 1600 mg/L of different extracts (ethanol, H_2SO_4, and water) of M.O

System	E corr. (mV)	I corr. $\mu A/cm^2$	Bc mV	Ba mV	IE%
Blank 0.5 M H2SO4	-460	1134	98	33	-
Ethanol Extract M.O (1600 mg/L)	-474	98	126	90	91.2
0.5 MH_2SO_4 Extract M.O (1600 mg/L)	-473	187	174	65	84.7
Water Extract M.O (1600 mg/L)	-464	104	119	44	90.8

4.32 TEMPERATURE AND KINETIC CONSIDERATION

Table 4.33Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with ethanol extract of MO after 3 h at 333K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0842	4.5814	0.5028	0.4429	
	B	5.0096	4.6266	0.3830		
400	**A**	4.6820	4.6328	0.1648	0.1631	63.17
	B	5.0323	4.8709	0.1614		
800	**A**	5.0464	4.9977	0.0487	0.0405	90.85
	B	5.1143	5.0819	0.0324		
1600	**A**	4.5263	4.5251	0.0012	0.0307	93.06
	B	4.5518	4.4916	0.0602		

Table 4.34 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with ethanol extract of MO after 3 h at 323K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0681	4.8035	0.2646	0.2611	
	B	4.5690	4.3115	0.2575		
400	**A**	5.1870	5.0980	0.0890	0.0949	63.65
	B	5.0826	4.9818	0.1008		
800	**A**	5.0433	5.0051	0.0382	0.0377	85.56
	B	5.0224	4.9852	0.0372		
1600	**A**	4.9104	4.8812	0.0292	0.0290	88.89
	B	4.7894	4.7605	0.0289		

Table 4.35 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with ethanol extract of MO after 3 h at 313 K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0633	5.0181	0.0452	0.0434	
	B	4.9537	4.9121	0.0416		
400	**A**	5.0683	5.0461	0.0222	0.0222	48.84
	B	5.1929	5.1707	0.0222		
800	**A**	4.9731	4.9573	0.0158	0.0156	64.05
	B	5.1411	5.1257	0.0154		
1600	**A**	5.1167	5.1033	0.0134	0.0141	67.51
	B	5.4426	5.4278	0.0148		

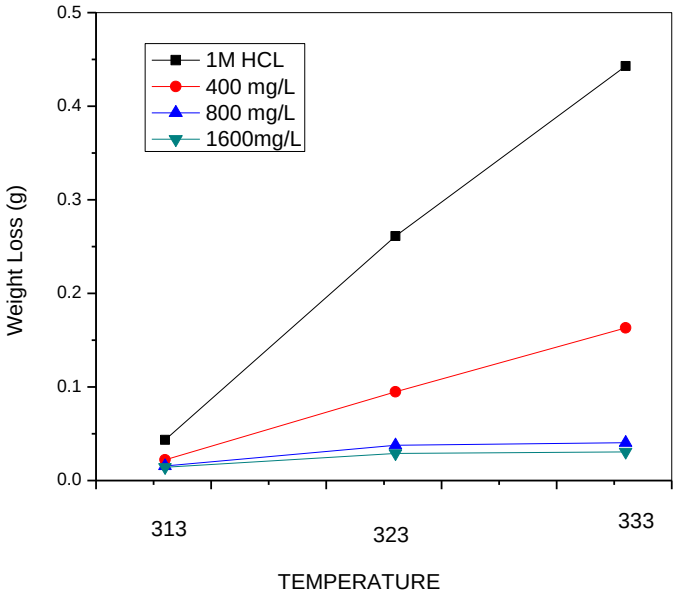


Figure 4.31 Variation of weight loss with temperature in 1M HCl without and with different concentration of ethanol extract of M.O

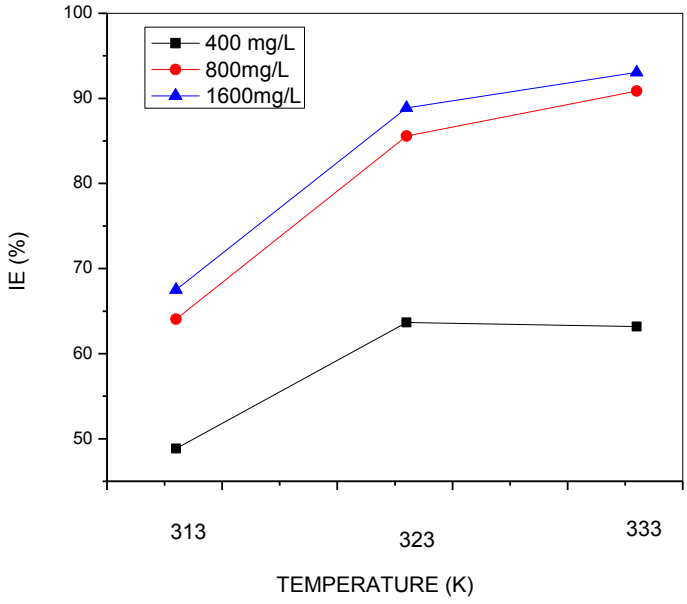


Figure 4.32 Variation of inhibition efficiency with temperature in 1M HCl in the presence of different concentration of ethanol extract of M.O

Table 4.36 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with acid extract of MO after 3 h at 333K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0842	4.5814	0.5028	0.4429	
	B	5.0096	4.6266	0.3830		
400	**A**	4.9397	4.8813	0.0584	0.0658	85.14
	B	5.2434	5.1702	0.0732		
800	**A**	4.4930	4.4716	0.0214	0.0251	94.33
	B	4.7337	4.7050	0.0287		
1600	**A**	4.8589	4.8346	0.0243	0.0248	94.40
	B	4.9958	4.9705	0.0253		

Table 4.37 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with acid extract of MO after 3 h at 323K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0681	4.8035	0.2646	0.2611	
	B	4.5690	4.3115	0.2575		
400	**A**	4.9339	4.8697	0.0642	0.0629	75.90
	B	4.8409	4.7792	0.0617		
800	**A**	5.0339	4.7902	0.0437	0.0423	83.79
	B	4.8366	4.7956	0.0410		
1600	**A**	4.9076	4.8844	0.0232	0.0251	90.38
	B	5.0952	5.0683	0.0269		

Table 4.38 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with acid extract of MO after 3 h at 313K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0633	5.0181	0.0452	0.0434	
	B	4.9537	4.9121	0.0416		
400	**A**	4.4413	4.4139	0.0274	0.0193	55.52
	B	5.0744	5.0632	0.0112		
800	**A**	4.9610	4.9479	0.0131	0.0135	68.89
	B	4.9884	4.9745	0.0139		
1600	**A**	5.0611	5.0486	0.0125	0.0112	74.19
	B	4.9342	4.9242	0.0100		

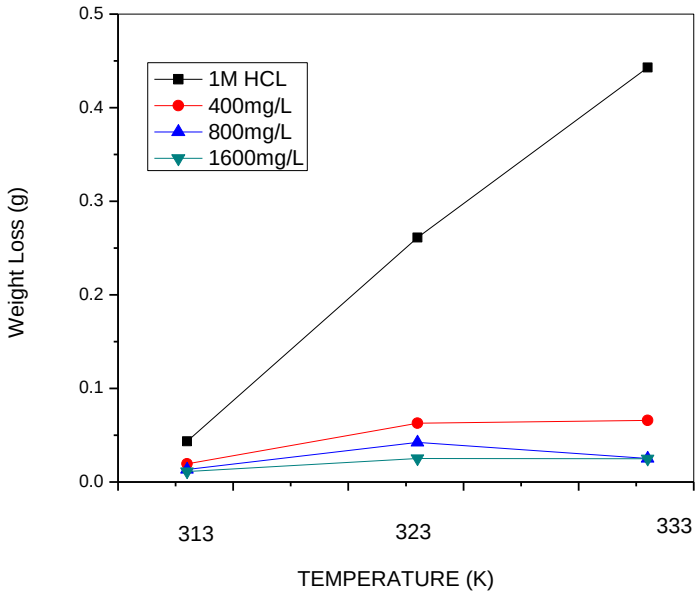


Figure 4.33 Variation of weight loss with temperature in 1M HCl withot and with different concentration of H_2SO_4 extract of M.O

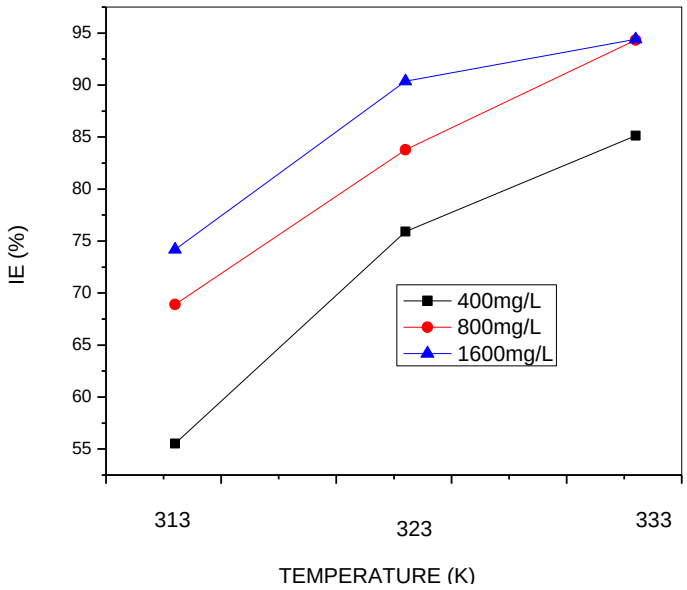


Figure 4.34 Variation of inhibition efficiency with temperature for 1M HCl in the presence of different concentration of H_2SO_4 extract of M.O

Table 4.39 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with water extract of MO after 3 h at 333K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0842	4.5814	0.5028	0.4429	
	B	5.0096	4.6266	0.3830		
400	**A**	4.6377	4.6045	0.0364	0.0348	92.14
	B	4.8750	4.8386	0.0257		
800	**A**	3.8397	3.8140	0.0257	0.0330	92.54
	B	4.6737	4.6334	0.0403		
1600	**A**	5.0811	5.0499	0.0293	0.0311	92.97
	B	5.1666	5.1355	0.0288		

Table 4.40 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with water extract of MO after 3 h at 323K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0681	4.8035	0.2646	0.2611	
	B	4.5690	4.3115	0.2575		
400	**A**	4.7641	4.7303	0.0338	0.0335	87.16
	B	4.9283	4.8951	0.0332		
800	**A**	4.8237	4.7926	0.0311	0.0311	88.08
	B	4.9963	4.9101	0.0312		
1600	**A**	4.5836	4.5535	0.0301	0.0300	88.51
	B	4.9230	4.8930	0.0300		

Table 4.41 Weight loss and inhibition efficiency values for mild steel corrosion in 1 M HCl without and with water extract of MO after 3 h at 313K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	5.0633	5.0181	0.0452	0.0434	
	B	4.9537	4.9121	0.0416		
400	**A**	5.2084	5.1877	0.0207	0.0199	54.14
	B	5.1204	5.1013	0.0191		
800	**A**	5.1021	5.0857	0.0164	0.0185	57.37
	B	4.8036	4.7830	0.0206		
1600	**A**	5.1056	5.0893	0.0163	0.0163	62.44
	B	4.9553	4.9391	0.0162		

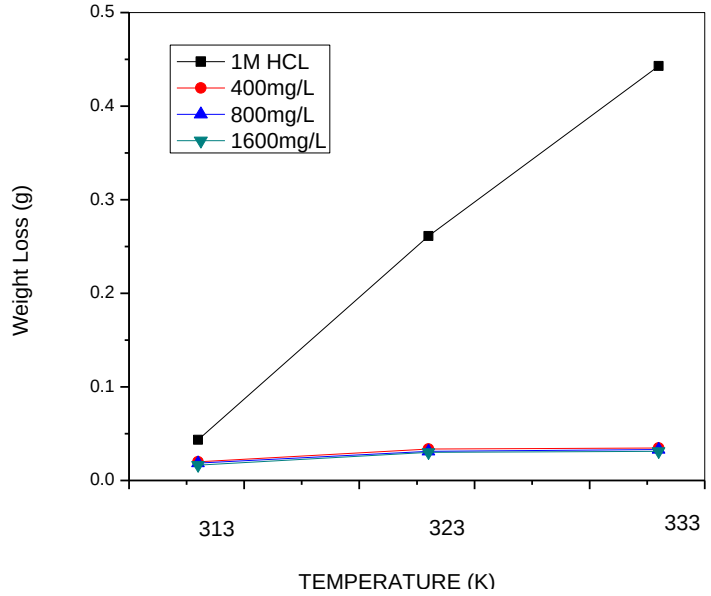


Figure 4.35 Variation of weight loss with temperature in 1M HClwithout and with different concentration of water extract of M.O

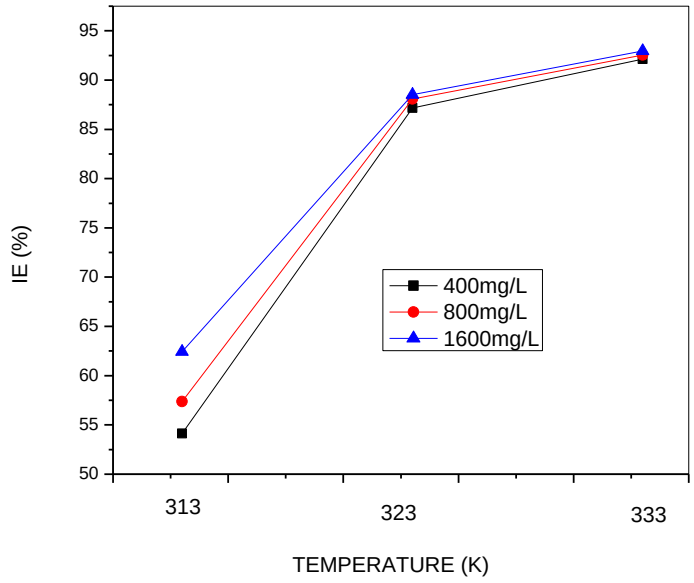


Figure 4.36 Variation of inhibition efficiency with Temperature in 1M HCl with different concentration of water extract of M.O

Table 4.42 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with ethanol extract of MO after 3 h at 333K

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.7174	3.6233	1.0941	1.0528	
	B	4.8495	3.8379	1.0116		
400	**A**	4.5493	4.4372	0.1121	0.1107	89.48
	B	4.7985	4.6891	0.1094		
800	**A**	5.1846	5.0857	0.0989	0.0761	92.77
	B	4.9130	4.8597	0.0533		
1600	**A**	4.7986	4.7356	0.0630	0.0689	93.45
	B	4.9773	4.9024	0.0749		

Table 4.43 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with ethanol extract of MO after 3 h at 323K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.8913	3.9446	0.9467	0.9963	
	B	4.9286	3.8827	1.0459		
400	**A**	5.0553	4.9091	0.1462	0.1340	86.55
	B	4.9272	4.8054	0.1218		
800	**A**	4.9182	4.8030	0.1152	0.1155	88.73
	B	5.0169	4.9010	0.1159		
1600	**A**	5.0443	4.9454	0.0989	0.0988	89.75
	B	4.6125	4.5137	0.0988		

Table 4.44 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with ethanol extract of MO after 3 h at 313K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.7567	4.7154	0.1413	0.1529	
	B	5.2789	5.1143	0.1646		
400	**A**	4.8813	4.7804	0.1009	0.1048	31.45
	B	5.1982	5.0894	0.1088		
800	**A**	5.9121	4.8422	0.0699	0.0673	55.98
	B	4.9733	4.9085	0.0648		
1600	**A**	5.6134	5.5718	0.0416	0.0398	73.96
	B	5.2199	4.1818	0.0381		

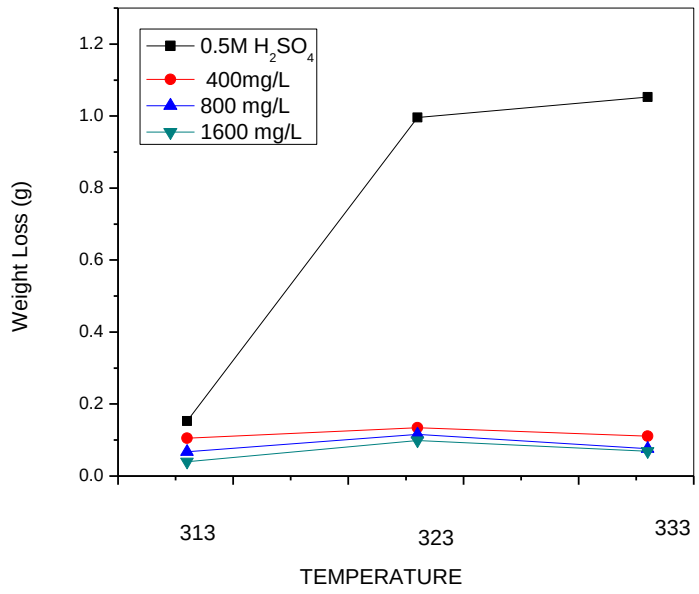


Figure 4.37 Variation of weight loss with temperature in 0.5M H_2SO_4 without and with different concentration of ethanol extract of M.O

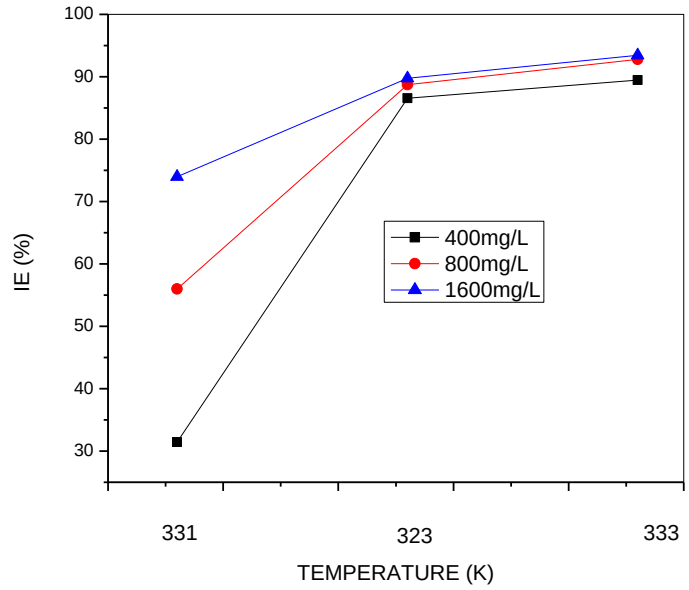


Figure 4.38 Variation of inhibition efficiency with Temperature in 0.5M H_2SO_4 with different concentration of ethanol extract of M.O

Table 4.45 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M acid without and with H_2SO_4 extract of MO after 3 h at 333K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.7174	3.6233	1.0941	1.0528	
	B	4.8495	3.8379	1.0116		
400	**A**	5.1334	4.9770	0.1564	0.1711	83.74
	B	4.8903	4.7044	0.1859		
800	**A**	4.9330	4.8841	0.0489	0.0583	94.46
	B	4.5866	4.5189	0.0677		
1600	**A**	4.7381	4.6948	0.0433	0.0474	95.49
	B	5.0904	5.0389	0.0515		

Table 4.46 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with acid extract of MO after 3 h at 323K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.8913	3.9446	0.9467	0.9963	
	B	4.9286	3.8827	1.0459		
400	**A**	5.1383	4.9429	0.1954	0.1923	80.69
	B	4.7785	4.5893	0.1892		
800	**A**	4.9847	4.8125	0.1722	0.1707	82.86
	B	4.8420	4.6728	0.1692		
1600	**A**	4.2951	4.1666	0.1285	0.1297	86.66
	B	4.9560	4.8250	0.1310		

Table 4.47 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with acid extract of MO after 3 h at 313K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.7567	4.6154	0.1413	0.1529	
	B	5.2789	5.1143	0.1646		
400	**A**	4.6707	4.6333	0.0374	0.0353	76.91
	B	4.8522	4.8189	0.0333		
800	**A**	4.3979	4.3551	0.0428	0.0320	79.07
	B	4.9305	4.9093	0.0212		
1600	**A**	4.5754	4.5534	0.0220	0.0217	85.80
	B	5.1037	5.0822	0.0215		

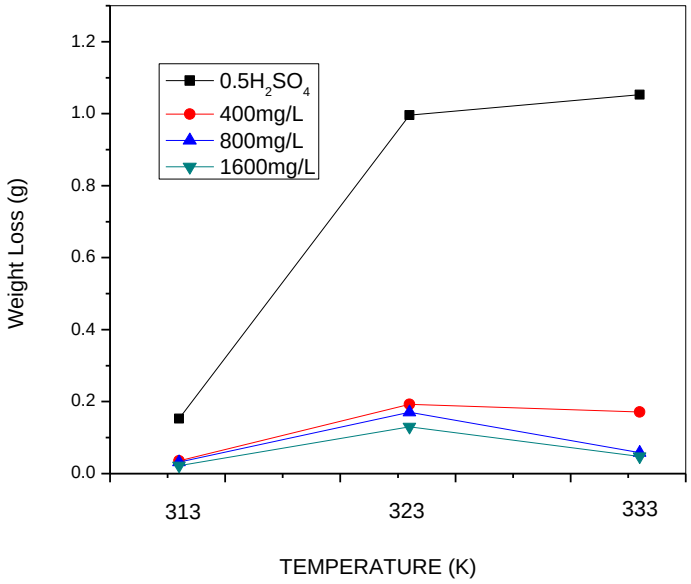


Figure 4.39 Variation of weight loss with temperature in 0.5M H_2SO_4 without and with different concentration of H_2SO_4 extract of M.O

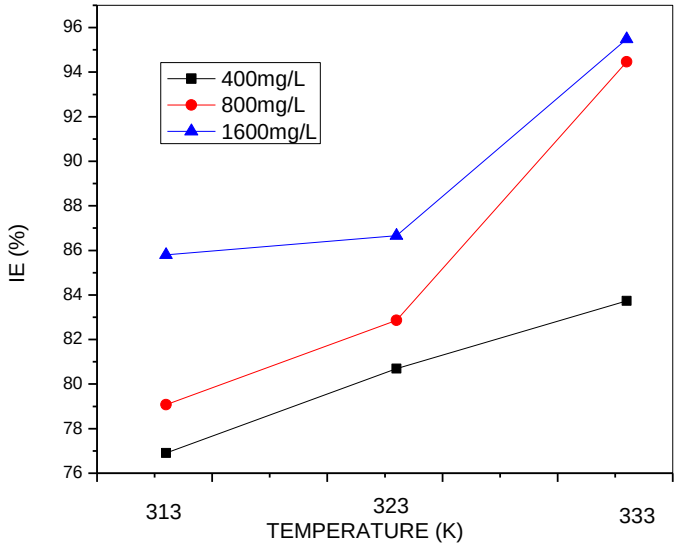


Figure 4.40 Variation of inhibition efficiency with temperature in 0.5M $H_2SO_4$with H_2SO_4 extract of M.O

Table 4.48 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with water extract of MO after 3 h at 333K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.7174	3.6233	1.0941	1.0528	
	B	4.8495	3.8379	1.0116		
400	**A**	4.8529	4.6213	0.2316	0.2769	73.69
	B	3.6235	3.3013	0.3222		
800	**A**	4.8499	4.5945	0.2554	0.2666	74.67
	B	4.8417	4.5639	0.2778		
1600	**A**	4.9890	4.8588	0.1302	0.1407	86.63
	B	4.4725	4.3212	0.1513		

Table 4.49 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with water extract of MO after 3 h at 323K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.8913	3.9446	0.9467	0.9963	
	B	4.9286	3.8827	1.0459		
400	**A**	4.8935	4.6245	0.2690	0.2735	72.54
	B	4.9832	4.7052	0.2780		
800	**A**	5.0742	4.8088	0.2654	0.2642	73.48
	B	4.9325	4.6694	0.2631		
1600	**A**	4.9977	4.8581	0.1396	0.1396	85.67
	B	4.9668	4.8271	0.1397		

Table 4.50 Weight loss and inhibition efficiency values for mild steel corrosion in 0.5 M H_2SO_4 without and with water extract of MO after 3 h at 313K.

System (mg/L)		Initial weight (g)	Final weight (g)	Weight loss (g)	Average weight loss (g)	IE%
Blank	**A**	4.7567	4.6154	0.1413	0.1529	
	B	5.2789	5.1143	0.1646		
400	**A**	5.1989	5.1187	0.0802	0.0779	49.05
	B	5.1009	5.0253	0.0756		
800	**A**	4.9216	4.8677	0.0539	0.0563	63.17
	B	4.9777	4.9189	0.0588		
1600	**A**	5.0946	5.0425	0.0521	0.0531	65.27
	B	4.9558	4.9016	0.0542		

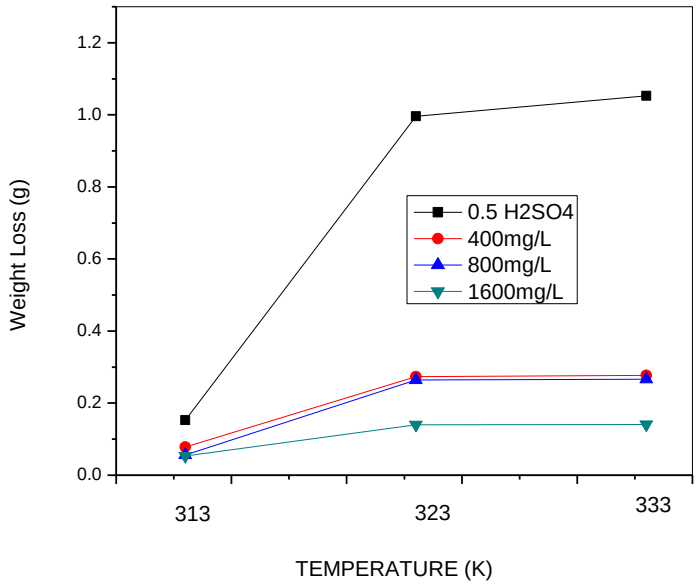


Figure 4.41 Variation of weight loss with temperature in 0.5M H2SO4 without and with different concentration of water extract of M.O

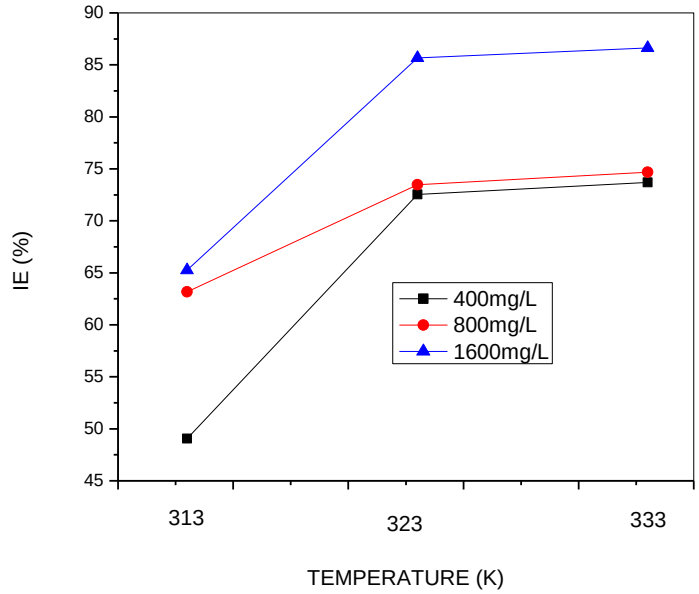


Figure 4.42 Variation of inhibition with temperature in 0.5M H_2SO_4 with different concentration of water extract of M.O

ARRHENIUS PLOTS AND KINETIC PARAMETERS FROM TEMPERATURE CONSIDERATION

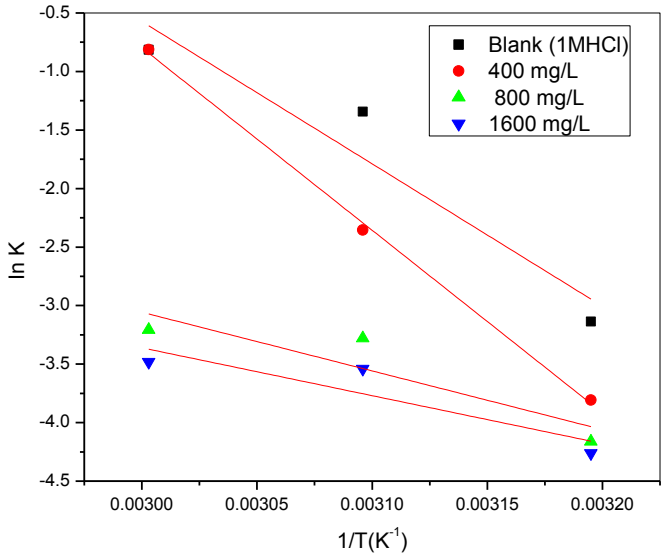


Figure 4.43 Arrhenius plots for mild steel corrosion in 1M HCl without and with ethanol extract of M.O

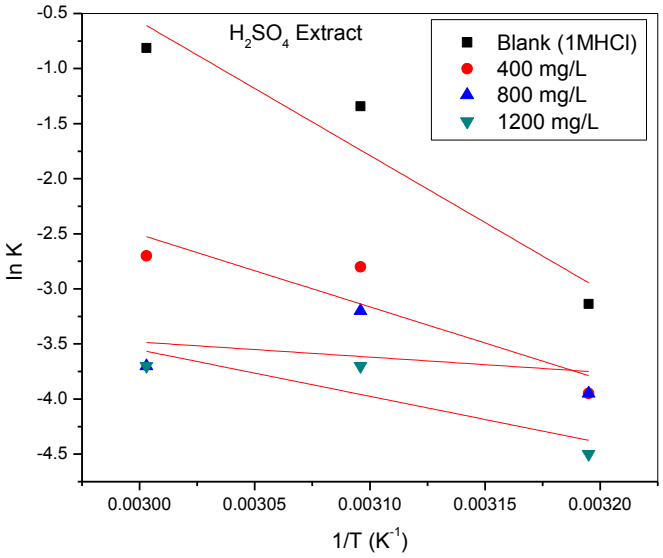


Figure 4.44 Arrhenius plots for mild steel corrosion in 1M HCl without and with H_2SO_4 extract of M.O

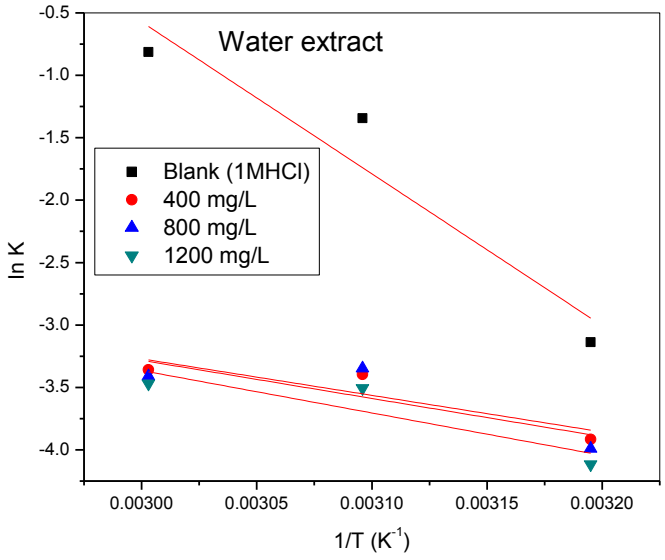


Figure 4.45 Arrhenius plots for mild steel corrosion in 1M HCl without and with Water extract of M.O

Table 4.51 Corrosion activation energies (Ea) for mild steel in 1M HCl without and with different extracts of M.O

System	Ea (kj mol-)		
	Ethanol extract	0.5 MH_2SO_4 extract	Water (H_20)extract
Blank (1 M HCl)	1463	1463	1463
400 mg/L M.O	970	789.7	351.98
800 mg/L M.O	602	163.5	367.8
1600 mg/L M.O	491	506.2	408.6

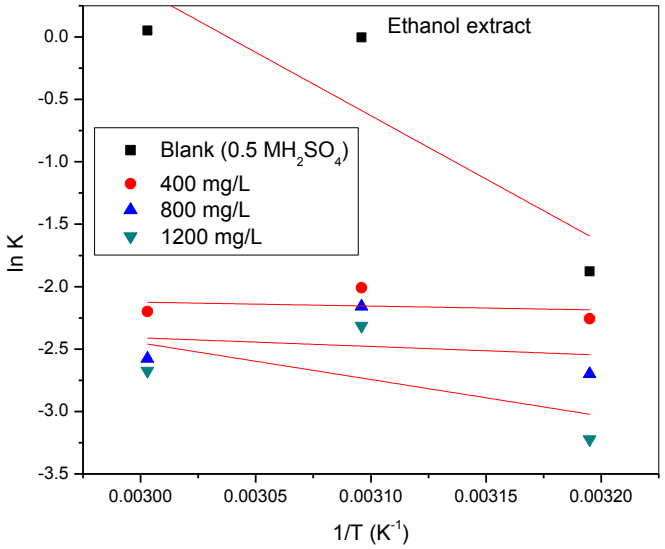


Figure 4.46 Arrhenius plots for mild steel corrosion in 0.5 M H_2SO_4 without and with ethanol extract of M.O

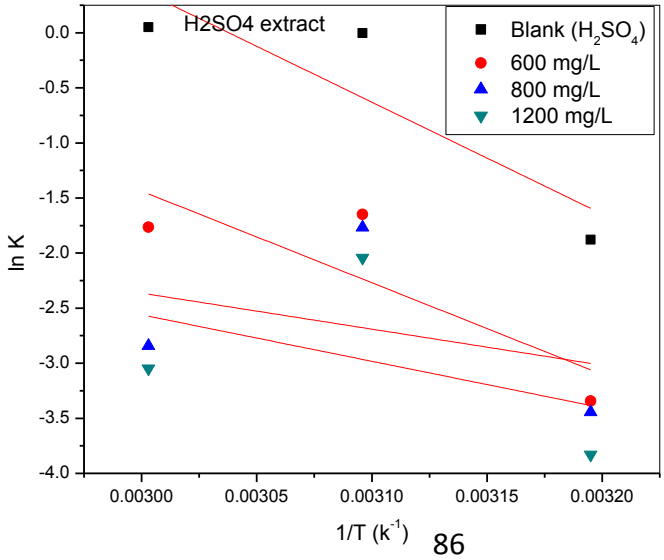


Figure 4.47 Arrhenius plots for mild steel corrosion in 0.5 M H_2SO_4 without and with H_2SO_4 extract of M.O

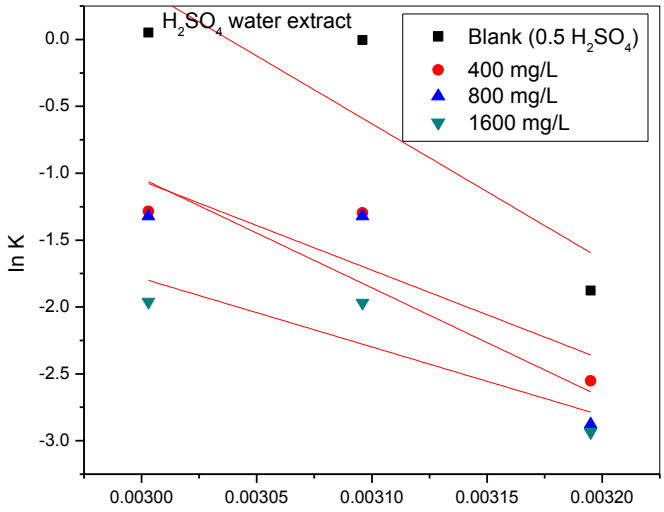
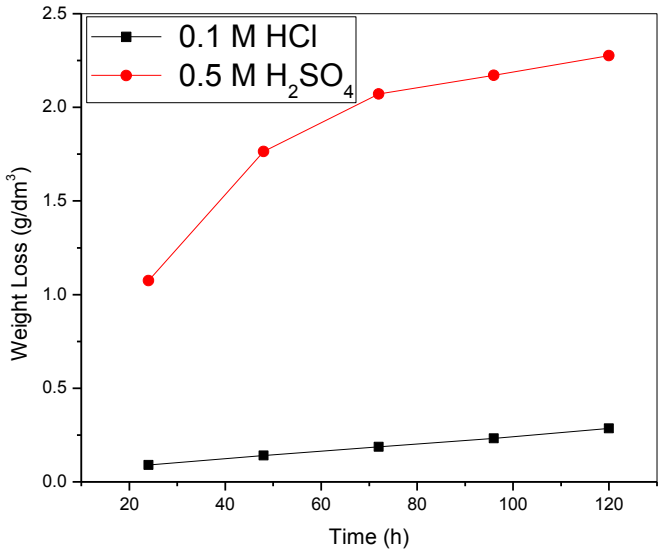


Figure 4.48 Arrhenius plots for mild steel corrosion in 0.5 M H_2SO_4 without and with Water extract of M.O

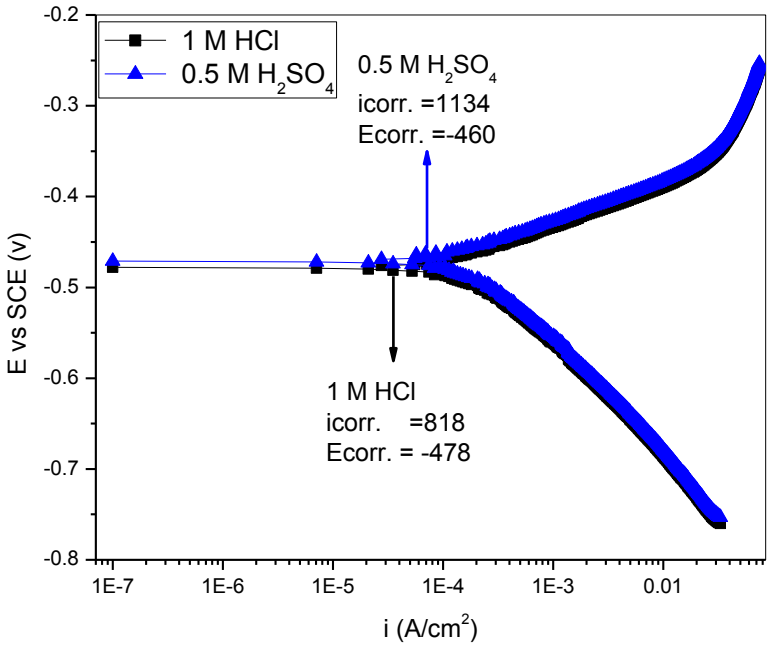
Table 4.52 Corrosion activation energies (Ea) for mild steel in 0.5 M H_2SO_4 without and with different extracts of M.O

System	Ea (kj mol-)		
	Ethanol extract	0.5 MH_2SO_4 extract	Water (H_20)extract
Blank (0.5M H_2SO_4)	1220.2	1220.2	1220.2
400 mg/L M.O	37.9	1000.3	802.3
800 mg/L M.O	83.2	393.6	984.02
1600 mg/L M.O	359.6	507.5	616.4

COMPARING THE BEHAVIOUR OF MILD STEEL METAL IN 0.1 M HCl AND 0.5 H_2SO_4



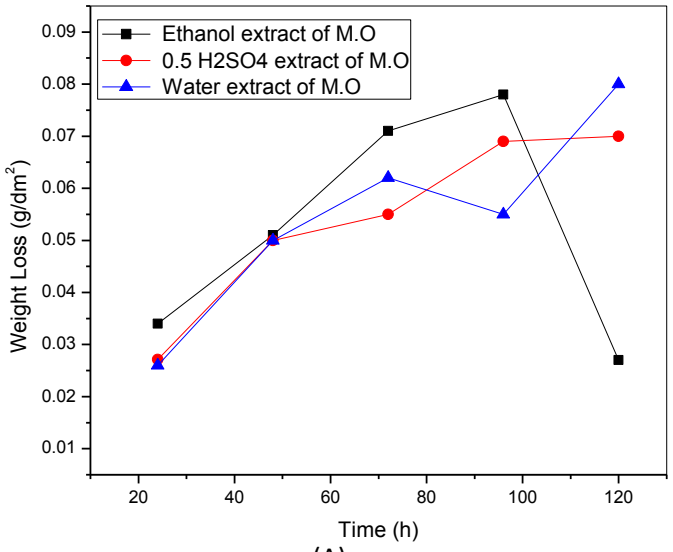
(A)



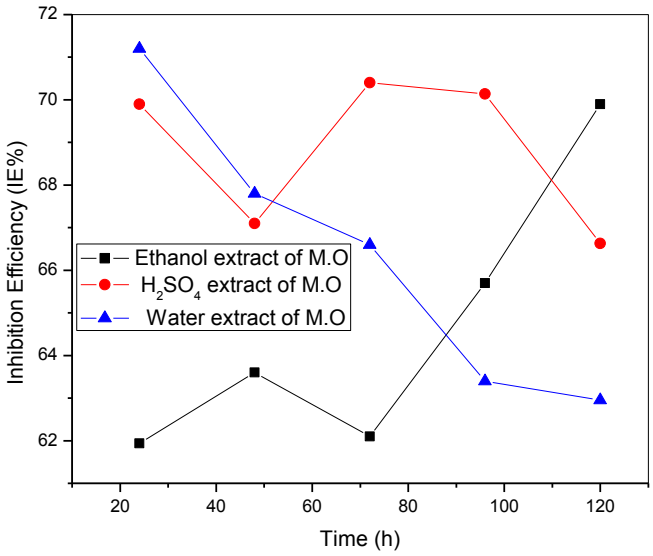
(B)

Figure 4.49 Comparing the Gravimetric (A) and potentiodynamic (B) behaviours of mild steel in 1 M HCl and 0.5 M H_2SO_4 solutions without inhibitors

COMPARING THE GRAVIMETRIC, POTENTIODYNAMIC AND KINETIC RESULTS OF DIFFERENT EXTRACTS IN 1 M HCl



(A)



(B)

Figure 4.50 Gravimetric plots comparing the average inhibition effects for the different extracts of M.O in 1 M HCl medium (A) weight loss over time, (B) inhibition efficiency over time

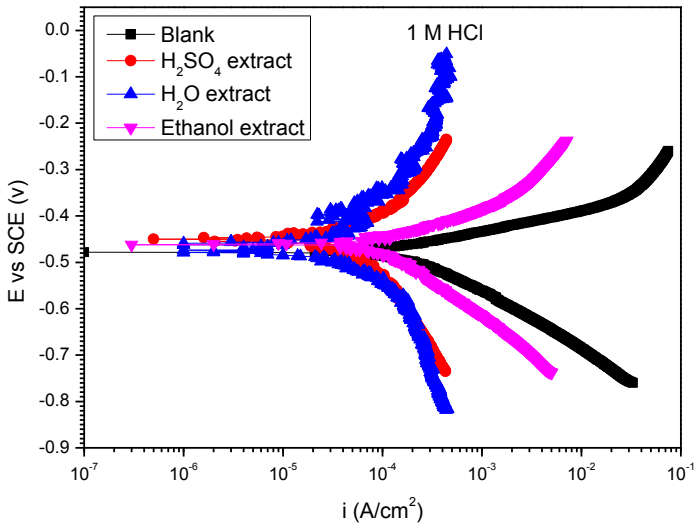


Figure 4.51 Potentiodynamic polarization curves comparing the inhibition performances of the different extracts of M.O (ethanol, 0.5 M H_2SO_4 and water) for mild steel corrosion in 1 M HCl

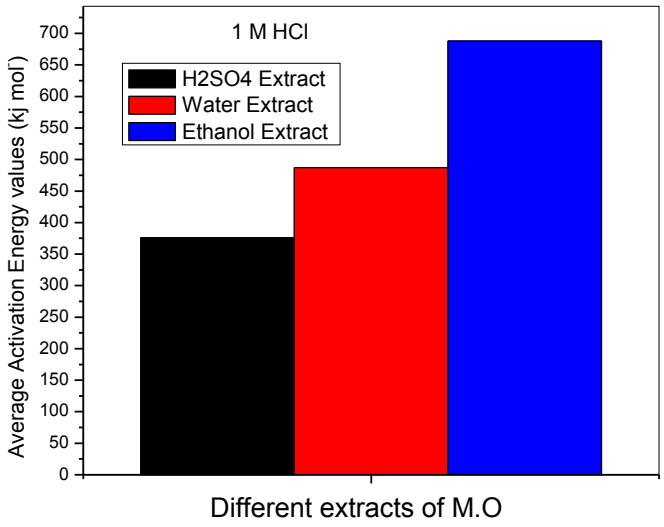
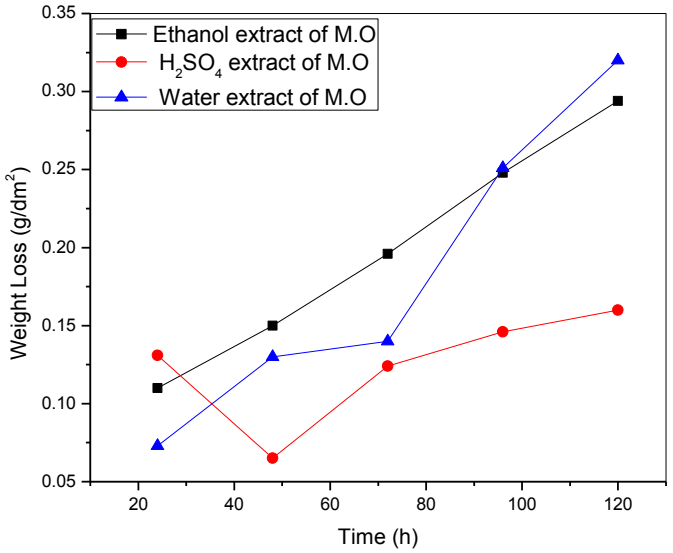
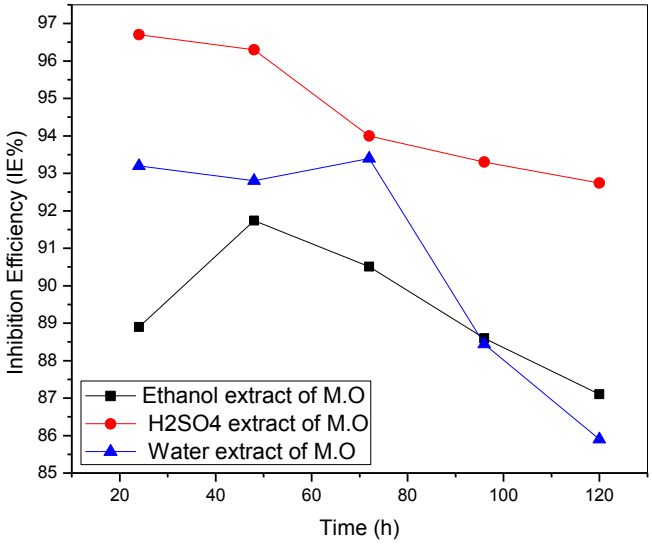


Figure 4.52 Bar chart comparing the average activation energies exacted by the different extracts of M.O in 1 M HCl



(A)



(B)

Figure 4.53 Gravimetric plots comparing the average inhibition effects for the different extracts of M.O in 0.5 M H_2SO_4 medium (A) weight loss over time, (B) inhibition efficiency over time

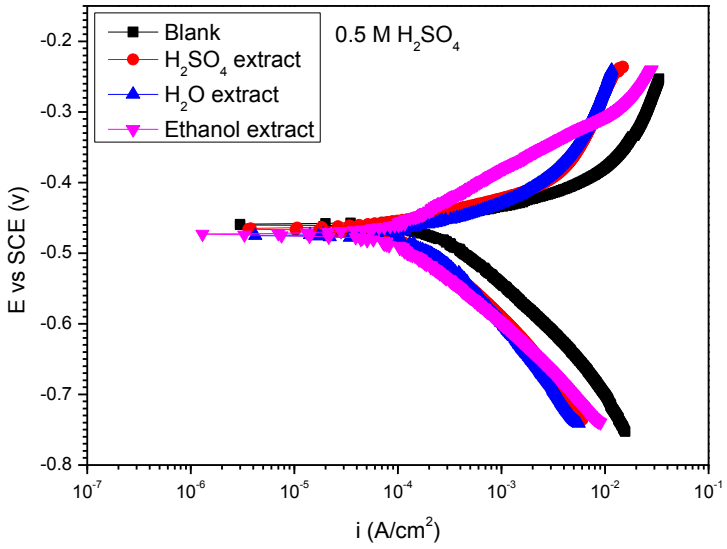


Figure 4.54 Potentiodynamic polarization curves comparing the inhibition performances of the different extracts of M.O (ethanol, 0.5 M H_2SO_4 and water) for mild steel corrosion in 0.5 M H_2SO_4

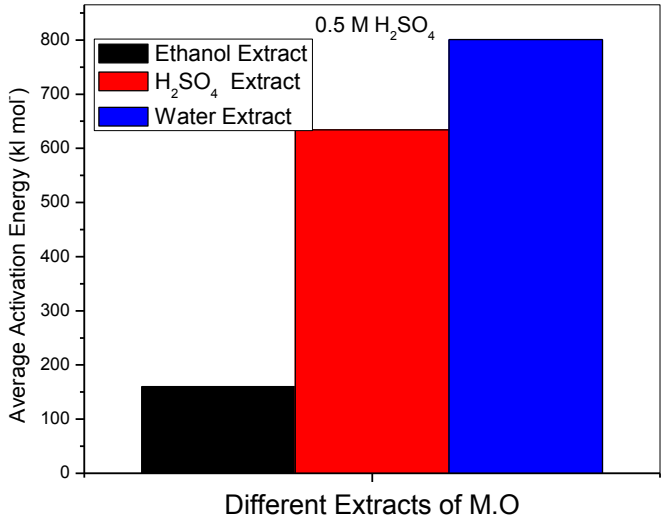


Figure 4.55 Bar chart comparing the average activation energies exacted by the different extracts of M.O in 0.5 M H_2SO_4

4.2 DISCUSSION

4.2.1 Gravimetric results for mild steel corrosion in 1 M HCl without and with different extracts (ethanol, acid and water) of M.O

Gravimetric measurement(Weight loss experiment) is a non- electrochemical butclassical technique for the determination of corrosion rates. It provides more reliable results than electrochemical technique because the experimental conditions are approached in a more realistic manner (Souza et al., 2009). However, it is a time consuming task (a disadvantage).

Gravimetric measurements were undertaken in this studyto assess the weight losses and hence corrosion rates of mildsteel test coupons immersed in 1M HCl for the total period of 120 (h) without and with different extracts; (ethanol, 0.5 M H_2SO_4, and water extracts) of Moringa oleifera (M.O) .

Tables 4.1 to 4.5 present the collected gravimetric data for the ethanol extract of M.O in 1 M HCl, while Figure 4.1 showed the variation of weight loss without and with different concentration of the ethanol extract. Also, Figure 4.2 showed the effect of the ethanol extract's concentration increase on the corrosion rate of mild steel (M.S) in 1 M HCl (blank). Again, Tables 4.6 to 4.10 and Tables 4.11 to 4.15 collected the gravimetric results for the corrosion of M.S in 1 M HCl without and with different concentrations of 0.5 M H_2SO_4 (acid extract) and water (H_2O) extracts respectively.

While Figure 4.5 and Figure 4.7 showed the variation of weight losses (corrosion rates) in 1 M HCl without and with different concentrations of acid and water extracts respectively. Again, Figures 4.5- 4.6 and 4.9-4.10 showed the effects of the acid's and water's extracts concentration increase on the rate of corrosion retardation.

Generally, from the results (Tables 4.1 to 4.15 and Figures 4.1-4.2, 4.5-4.6 and 4.9-4.10): corrosion rate increases with increasing immersion time and the introduction of the different extracts of M.O actually retarded the rate of corrosion reaction in the 1 M HCl. This depicts inhibition process. However, the inhibition contributions of the different extracts improved with increasing M.O concentration, implying a dependence of the inhibition process on the amount of inhibiting species present in the systems. Although, the degree of this effect varies slightly amongst the different extracting solvents. This however, could be related to the different extracting capabilities and the stability of the constituents of the biomass in the different solvents.

4.2.1.1 Inhibition Efficiency

The inhibition performance of the different extracts of M.O on mild steel corrosion in 1 M HCl was quantified (using weight loss data) by evaluating the inhibition efficiency IE (%) as follows: (Ebenso et al., 2008);

$$IE\% = \left(1 - \frac{W_1}{W_2}\right) x\ 100 \qquad (4.1)$$

Where, W_1 and W_2, are the weight losses in the presence and absence of M.O inhibitor. Tables 4.1-4.5, 4.6-4.10, 4.11-4.15 showed the experimentally determined inhibition efficiency values for M.S corrosion in 1 M HCl in the presence of ethanol, sulphuric acid and water extracts of M.O respectively.

Also, Figures 4.3-4.4, 4.7-4.8, 4.11-4.12 showed respectively the plots for the variation of inhibition efficiencies with increase in the extracts concentration and variation of the inhibition efficiency with lengthened immersion time for ethanol, sulphuric acid and water extracts respectively.

The results showed that inhibition efficiency improved with increase in the concentration of all the extracts (ethanol Fig. 4.4, sulphuric acid Fig. 4.8 and water Fig. 4.12). This phenomenon shows that increasing the concentration of the various extract actually increased the amount of inhibiting species extracted from the plant biomass leading to greater surface coverage of the substrate.

Interestingly, the inhibition efficiency was observed to improve slightly with increase in exposure time in ethanol extract (Fig. 4.3). This remarkable property is advantageously important to corrosion scientists because it depicts extra stability of the ethanol extract in the inhibition process. This observation was less stable in sulphuric acid extract (Fig. 4.7) and was not observed in water extract. These could be related to the different extracting capabilities and stabilities of the molecules in the different solvents. The decrease in the inhibition efficiency with

time was more pronounce in water extract than sulphuric acid extract indicating that the presence of ions from the acid (H^+ and SO_4^{2-}) affected the extracting ability of the acidic water. Finally, it is reasonable to say that ethanol serves as the better extractant amongst the three extract and thus better for extracting organic molecule than water which agrees with the literature.

4.2.2 Potentiodynamic Polarization results for mild steel corrosion in 1 M HCl without and with different extracts (ethanol, acid and water) of M.O

Potentiodynamic polarization experiments were carried out to understudy the influence of different extracts of M.O on the kinetics of the anodic ($Fe \rightarrow Fe^{2+} + 2e$) and cathodic ($2H^+ + 2e \rightarrow H_2$) of the corrosion process. Figures: 4.25, 4.26 and 4.27 showed respectively, the typical potentiodynamic polarization curves for the mild steel specimens in 1M HCl without and with 1600 mg/L of: ethanol, sulphuric and water extracts of M.O. The corresponding electrochemical parameters derived from the polarization experiments are presented in Table 4.31. The mild steel specimen is seen to exhibit active dissolution with no distinctive transition to passivation within the studied potential range in all the studied systems. The polarization curves (Figure 4.25 - 4.27) reflected that addition of the different extracts of M.O in the 1 M HCl environment did not notably altered the corrosion potentials (Ecorr. values) and inhibited both the anodic andcathodic partial reactions of the corrosion process (Table 4.31 and

Figures 4.25 to 4.27). This implies that M.O extract functioned therein as a mixed-typeinhibitor, reducing the rates of both anodic and cathodic corrosion reactions. The values of the corrosion current density in the absence ($i_{corr-blank}$) and presence ($i_{corr-inh)}$ of different extracts of M.O were used to estimate the inhibition efficiency from polarization as follows;

$$IE(\%) = (1 - i_{corr-inb} / i_{corr-blank}) \times 100 \quad (4.2)$$

Where $i_{corr-inb}$is corrosion current density in the presence of inhibitor and$i_{corr-blank}$is corrosion current density in 1 M HCl (blank). The computed inhibition efficiency values are presented in Table 4.31 and followed the order; sulphuric acid extract (97%)> water extract (96%)> ethanol extract (86%). These values showed appreciable corrosion inhibition with sulphuric and water having higher values than ethanol. However, from the gravimetric findings (Fig. 4.7 and 4.11respectively) sulphuric and water extracts could not stand the taste of time since the inhibition efficiency losses strength with time. Then, it is reasonable to say that the slight difference between the polarization and gravimetric results is attributed to time (exposure time) effect. This notwithstanding, the results from the polarization experiment are in close agreement with results from gravimetric experiment (Table 4.1 - 4.15).

4.2.3 Temperature / Kinetic results for mild steel corrosion in 1 M HCl without and with different extracts (ethanol, acid and water) of M.O

In order to evaluate the effect of temperature variation on the corrosion and corrosion inhibition processes, gravimetric tests were further undertaken for three hour (3 h) immersion time at 313–333K in both uninhibited (1 M HCl) and inhibited systems (400 mg/L, 800 mg/L and 1600 mg/L) for the different extracts (ethanol, sulphuric acid and water) of M.O.

The different M.O extract concentrations (mentioned before) were selected to appropriately reflect thetemperature effects at low and high surface coverage.

Figures: 4.31, 4.33 and 4.35 presented the variation of corrosion rates (weight loss) with temperature increase for M.S in 1 M HCl without and with different concentration of ethanol, sulphuric acid and water extracts respectively.

The results obtained showed that corrosion rates in both uninhibited and inhibited acids increased with rise in temperature. Also it is clear from the plots that addition of the different extracts actually retarded the corrosion reaction at all temperatures following however gravimetric and polarization trend.

Secondly, Figures: 4.32, 4.34 and 4.36 illustrated the trend of inhibition efficiency with temperature rise for the different concentrations of ethanol, sulphuric and water M.O extracts respectively. The results showed that inhibition efficiency increased rapidly with rise in temperature at low as well as high concentrations for all the studied extracts (Figure 4.32, 4.34 and 4.36). This suggests that some constituents of the extracts are chemically adsorbed on the mild steel surface (Oguzie wt al., 2013) and exerted a controlling influence on the corrosion

inhibition performance of the different extracts of MO. Chemisorption of such constituents is enhanced with rise in temperature, leading to greater surface coverage and hence inhibition efficiency.

The apparent activation energies (Ea) for mild steel corrosion in 1M HCl solution in the presence and absence of the different extracts of M.O were evaluated fromArrhenius equation as follows:

$$K = A \exp(-Ea / RT) \qquad 4.3$$

Where A is the pre-exponential factor and R; the universal gas constant. Plots showing variation of natural logarithm of corrosion rate (In K) with reciprocal of absolute temperature (1/T) for both uninhibited system (1 M HCl acid) and different concentrations of inhibited system are shown in Figures 4.43 (ethanol extract), 4.44 (sulphuric acid extract) and 4.45 (water extract) respectively. While the values of Ea (Activation energy) obtained from the plots are presented in Table 4.51.The data showed that the thermodynamic activation functions (Ea) of the corrosion of mild steel in 1 M HCl solution in the presence of the different extracts of M.O are lower than those in the free acid solution indicating that the extracts actually exhibited corrosion process. The increase in inhibition efficiency with rise in temperature with corresponding decrease in corrosion activation energy in the presence of inhibitor compared to systems without inhibitor is frequently attributed to the formation of an adsorption film on the substrate by organic molecules (Akalezi et al., 2013). These effects which are both

concentration and extract's nature dependent are in perfect agreement with the results obtained earlier from both gravimetric and polarization experimental results.

4.3 GRAVIMERIC RESULTS CONTINUED

4.3.1 Gravimetric results for mild steel corrosion in 0.5 M H_2SO_4without and with different extracts (ethanol, acid and water) of M.O

Tables: 4.16 – 4.20, 4.21-4.25, and 4.26 – 4.30 presented the values for weight loss and inhibition efficiency for mild steel corrosion in 0.5 M H_2SO_4 without and with different concentrations of ethanol, sulphuric acid and water extracts of M.O respectively for different immersion times (24 -120 h). The corresponding plots of the data are presented in Figures: 4.13 -4.16, 4.17 – 4.20 and 4.21 – 24 for ethanol, sulphuric and water extracts of M.O respectively.

The plots showed that corrosion rate increased with time in all the systems but was more pronounced in the blank corrodent (0.5 M H_2SO_4). The plots also indicated clearly that the introduction of the different concentration extracts of M.O actually inhibited dissolution of mild steel in the blank corrodent. Also the effect of M.O concentration to the rate of corrosion reaction retardation in 0.5 M H_2SO_4 is presented in Figures: 4.17, 4.22, and 4.27 for ethanol, sulphuric acid and water extracts respectively. The plots showed that increase in the concentration of M.O reduced progressively the weight loss rate. This meant that increasing the

concentration of M.O in this acid environment gradually enhanced the absorbability of the extract molecules, probably because certain constituents of the extract became available in sufficient amounts for chemical interaction with metal surface in this system also.

4.3.2 Inhibition Efficiency

The inhibition performance of the different extracts of M.O on mild steelcorrosion in 0.5 M $H_2SO_4$was also quantified (using weight loss data) by evaluating the inhibition efficiency IE (%) according to equation 4.2.

Tables: 4.16 – 4.20, 4.21 – 4.25, and 4.26 – 4.30 showed the experimentally determined inhibition efficiency values for M.S corrosion in 0.5 M H_2SO_4 without and with different concentrations of ethanol, sulphuric acid and water extracts of M.O respectively. While, Figures 4.15 - 4.16, 4.19 – 4.20 and 4.23 - 4.24 showed the plots depicting the effect of increasing the concentration of the different extracts of M.O on the inhibition efficiency and the variation of the inhibition efficiency with lengthened exposure time for ethanol, sulphuric acid and water extracts respectively.

Interestingly, the inhibition efficiency values increased steadily with the increase in M.O concentration in all the studied extracts in 0.5 M H_2SO_4 medium,with maximum inhibition efficiency (particularly at higher M.O concentrations) exceeding 96%, 97% and 95%(especially within the first few days of immersion)

for ethanol, sulphuric acid and water extracts respectively, and didnot fall below78% for ethanol extract, 90% for sulphuric acid extract and 85% for water extract (Tables 4.13 to 4.24) throughout the entire period of immersion. This remarkable stability of the inhibition performance of the different M.O extracts in 0.5 M H_2SO_4makes them rather attractive for actual practical applications.

4.3.3 Potentiodynamic Polarization results for mild steel corrosion in 0.5 M H_2SO_4 without and with different extracts (ethanol, acid and water) of M.O

Polarization experiments were also carried out to ascertain the influence of the different extracts of M.O on the kinetics of the anodic andcathodic partial reactions of the mild steel corrosion process in 0.5 M H_2SO_4 solution.

Figures: 4.28, 4.29 and 4.30 showed respectively, the typical potentiodynamic polarization curves for the mild steel specimens in 0.5 M H_2SO_4 without and with 1600 mg/L of: ethanol, sulphuric and water extracts of M.O. The corresponding electrochemical parameters derived from the extrapolation of Tafel straight line of the polarization curves are presented in Table 4.32. The mild steel specimens here also exhibited active dissolution with no distinctive transition to passivation within the studied potential range in all the studied systems (just like in HCl). The polarization curves (Figures 4.28 - 4.30) reflected that addition of the different extracts of M.O in the 0.5 M H_2SO_4environment did not notably altered the corrosion potentials (Ecorr. values) and inhibited both the anodic and cathodic

partial reactions of the corrosion process (Table 4.32 and Figures 4.28 to 4.29). This implies that M.O extract functioned therein as a mixed-typeinhibitor, reducing the rates of both anodic and cathodic corrosion reactions.

The values of the corrosion current densities in the absence ($i_{corr-blank}$) and presence ($i_{corr-inh)}$ of different extracts of M.O were used to estimate the inhibition efficiency from polarization results using equation 4.2.

The computed inhibition efficiency values are presented in Table 4.32 and followed the order; ethanol extract (91.2%) > water (90.8%) > sulphuric acid (84.7%). These values also showed appreciable corrosion inhibition with ethanol and water extracts exhibiting higher values than sulphuric acid extract. This does not really follow the trend in 1M HCl; but, the reduction in the inhibition efficiency of sulphuric acid extract in 0.5 M H_2SO_4could be related to the increase in the concentration of sulphuric acid anions, which must have aggravated the rate of corrosion attack. Notwithstanding however, all the extracts exhibited appreciable inhibition performance and are in close agreement with the results from gravimetric experiment except in sulphuric acid system (Table 4.16 – 4. 30).

4.3.4 Temperature / Kinetic results for mild steel corrosion in 0.5 M H_2SO_4 without and with different extracts (ethanol, acid and water) of M.O

In order to evaluate the effect of temperature variation on the corrosion and corrosion inhibition processes, gravimetric tests were also further undertaken for three hour (3 h) immersion time at 313–333K in both uninhibited (0.5 M H_2SO_4) and inhibited systems for the different extracts (ethanol, sulphuric acid and water) of M.O.

The different M.O extract concentrations (mentioned before) were selected to appropriately reflect the temperature effects at low and high surface coverage. Tables; 4.42-4.44, 4.45-4.47, 4.48-4.50 and Figures; 4.37, 4.39 and 4.41 presented the variation of corrosion rates (weight loss) with temperature increase for M.S in 0.5 M H_2SO_4 without and with different concentration (400 mg/L, 800 mg/L and 1600 mg/L) of ethanol, sulphuric acid and water extracts respectively.

The results obtained showed that corrosion rates in both uninhibited and inhibited acids increased with rise in temperature. Also it is evident from the plots that addition of the different extracts actually retarded the corrosion reaction at all temperatures following however gravimetric and polarization trend.

Secondly, Figures 4.38, 4.40 and 4.42 illustrated the trend of inhibition efficiency with temperature increase for the different concentrations of ethanol, sulphuric and water M.O extracts respectively. The results showed that inhibition efficiency increased rapidly with rise in temperature at low as well as high concentrations for all the studied extracts (Figure 4.32, 4.34 and 4.36). This

increase in the inhibition performance by certain plant extracts with rise in temperature has been duly attributed to chemisorptions of some of the organic constituents of the plant extract by many corrosion scientists (Oguzie et al., 2013 and Akalezi et al., 2013).

This shows that M.O is a good inhibitor that could render fascinating application potentials, since it exhibited this property for both acid media (HCl and H_2SO_4) studied. The apparent activation energies (Ea) for mild steel corrosion in 0.5 M H_2SO_4 solution in the presence and absence of the different extracts of M.O were evaluated from Arrhenius equation (Equation 4.3)

Plots showing variation of natural logarithm of corrosion rate (In K) with reciprocal of absolute temperature (1/T) for both uninhibited system (0.5 M H_2SO_4acid) and different concentrations concentration (400 mg/L, 800 mg/L and 1600 mg/L) of inhibited system are shown in Figures; 4.46 (ethanol extract), 4.47 (sulphuric acid extract) and 4.48 (water extract) respectively. While the values of Ea (Activation energy) obtained from the plots are presented in Table 4.52.The data showed that the thermodynamic activation functions (Ea) of the corrosion of mild steel in 0.5 M H_2SO_4solution in the presence of the different extracts (ethanol, sulphuric acid and water) of M.O are lower than those in the free acid solution indicating that extract inhibited corrosion process. An increase in inhibition efficiency with rise in temperature with analogous decrease in corrosion activation energy (Ea) in the presence of inhibitor compared to systems

without inhibitor has been attributed before to the formation of an adsorption film on the substrate by organic molecules. These effects which are both concentration and extract's nature dependent are in perfect agreement with the results obtained earlier from both gravimetric and polarization experimental results.

4.4. COMPARING THE PERFORMANCES OF THE DIFFERENT EXTRACTING SOLVENTS (ETHANOL, SULPHURIC ACID AND WATER) FOR CORROSION INHIBITION OF M.S BY M.O IN 1 M HCl AND 0.5 M H_2SO_4

4.4.1 Comparing the Corrosion behaviour of mild steel in 1 M HCl and 0.5 M H_2SO_4 without inhibitors (Corrodents) and the effects of the acidic (Cl^- and SO_4^{2-}) anions on the inhibition performance of the extracts

Figure 4.49 compares the plots of average weight loss from gravimetric experiments (A) and polarization curves from potentiodynamic polarization experiment (B) for mild steel in 1 M HCl and 0.5 M H_2SO_4 solutions without inhibitors respectively. From the Figures it is evident that mild steel was more susceptible to corrosion attack in 0.5 M H_2SO_4 than 1 M HCl. Similar observations have been made by other authors (Oguzie et al ., 2013, Akalezi et al., 2013). This somewhat affected the inhibition performance of the different extracts in the two acid solutions, although some authors (Oguzie et al.,2013; Oguzie et al 2012.,Akalize et al., 2013) have reported that mild steel possesses a

positive surface charge in both sulphuric and hydrochloric acid solutions. Since some of the organic constituents of M.O extract should be protonated in the both acid solutions, whilst the rest remain in the molecular form the observed inhibiting efficiency of M.O could be attributed to the participation of both protonated and molecular species in the adsorption process and the variation in inhibition efficiency of the extract in 1M HCl and 0.5M H2SO4 resulted from differences in the modes of adsorption in both acid solutions. The positive surface charge on mild steel in both sulfuricand hydrochloric acid solutions restricts adsorption of protonated species, due to electrostatic repulsions. On the other hand, chloride ions present in hydrochloric acid can become strongly adsorbed on the metal surface and hence facilitate adsorption of protonated species. This effect, which is not pronounced with the sulfate ion, ensures a significant adsorption of protonated inhibitor species on the mild steel surface immersed in 1M HCl, whereas the metal specimen immersed in 0.5M H_2SO_4 ismore predisposed to adsorption of non-protonated species, yielding the observed variations in inhibition efficiency from polarization experiments. Notwithstanding however, the higher inhibition efficiency observed in suphuric acid environment from gravimetric experiments showed that there are still enough non protonated molecules in M.O extract that could render corrosion inhibition. This explains why the extracts perform in the both acid media.

4.4.2 Comparing the inhibition performance exerted by the different extracts of M.O for mild corrosion in 1 M HCl acid solution

Figure 4.50 (A) compares the average weight loss over time in different extracts of ethanol, sulphuric acid and water extracts of M.O.

While Figure 4.50 (B) compares the variation of the average inhibition efficiency with lengthened exposure time. The average weight loss and inhibition efficiency values were calculated by summing the daily averages (calculated by taking the average of weight loss observed with all the concentrations of the extracts per day or 24 h) and reported.

Thus, the results reflected the overall performance of the different extracts over the entire experimental times. The results showed that the extracts exhibited approximately equal inhibition strength (Fig. 4.50), but the inhibition efficiency exerted by the ethanol extract tends to increase with increasing exposure time (Fig. 4.50 B), where that of sulphuric and water decrease with time. This remarkable inhibition performance exerted by ethanol extract is attributed to the extracting capability and the stability of the biomass molecules in the solvent which agrees with our initial report (gravimetric observation).

Figure 4.51 showed the differences between the polarization curves obtained from the corrosion of M.S without and with different extract of M.O. The curves showed that sulphuric acid and water extracts exerted better corrosion inhibition than ethanol within the experimental time. Also, Figure 4.52 which compares the

effect of the different extracts on the activation energy (Ea) values reflected that the average Ea increases in the order: sulphuric acid extract < water < ethanol (the smaller the better) which was in close agreement with both gravimetric and polarization experiments.

4.4.3 Comparing the inhibition performance exerted by the different extracts of M.O for mild corrosion in 0.5 M H_2SO_4 acid solution

The gravimetric plots comparing the average weight loss and inhibition effects observed for the different extracts of M.O in 0.5 M H_2SO_4 over lengthened exposure times are presented in Figure (A) and (B) respectively. On the average, sulphuric acid extract showed lower weight loss over time followed by water extract while the average inhibition efficiency exerted by the different extracts followed the trend; sulphuric > water > ethanol.

Figure 4.54 showed the differences on the differentpolarization curves for M.S corrosion in 0.5 M H_2SO4 without and with different extracts of M.O while, Figure 4.55 expressed the bar chats depicting the average Ea for the different extracts. The results showed that the trend of Ea followed the order: ethanol < sulphuric < water.

It is obvious that the average results in 0.5 M H_2SO_4 for polarization and temperature (Ea) followed the initial trend, although there a slight deviation from gravimetric result which is probably due to time effect as earlier argued.

Notwithstanding however, ethanol had the best inhibition performance in 0.5 M H_2SO_4.

4.4.4 GC-MS CHARACTERIZATION OF THE ETHANOL EXTRACT M.O

To account for thepresence of organic constituents responsible for the corrosion inhibiting effects, the extract of *Moringa oleifera was* duly characterized by gas chromatography mass spectrometry. Figure; 4.56 showed the GC-MS spectrumfor the ethanol extract of M.O. While Table 4.53 presented the identified individual organic molecules in M.O extract. The extracts of water and sulphuric acids were not characterized using this instrument due to test restriction compliance (the solvents could not pass through the GC column). The corresponding structures of some of the identified compounds are presented in Figure 4.57

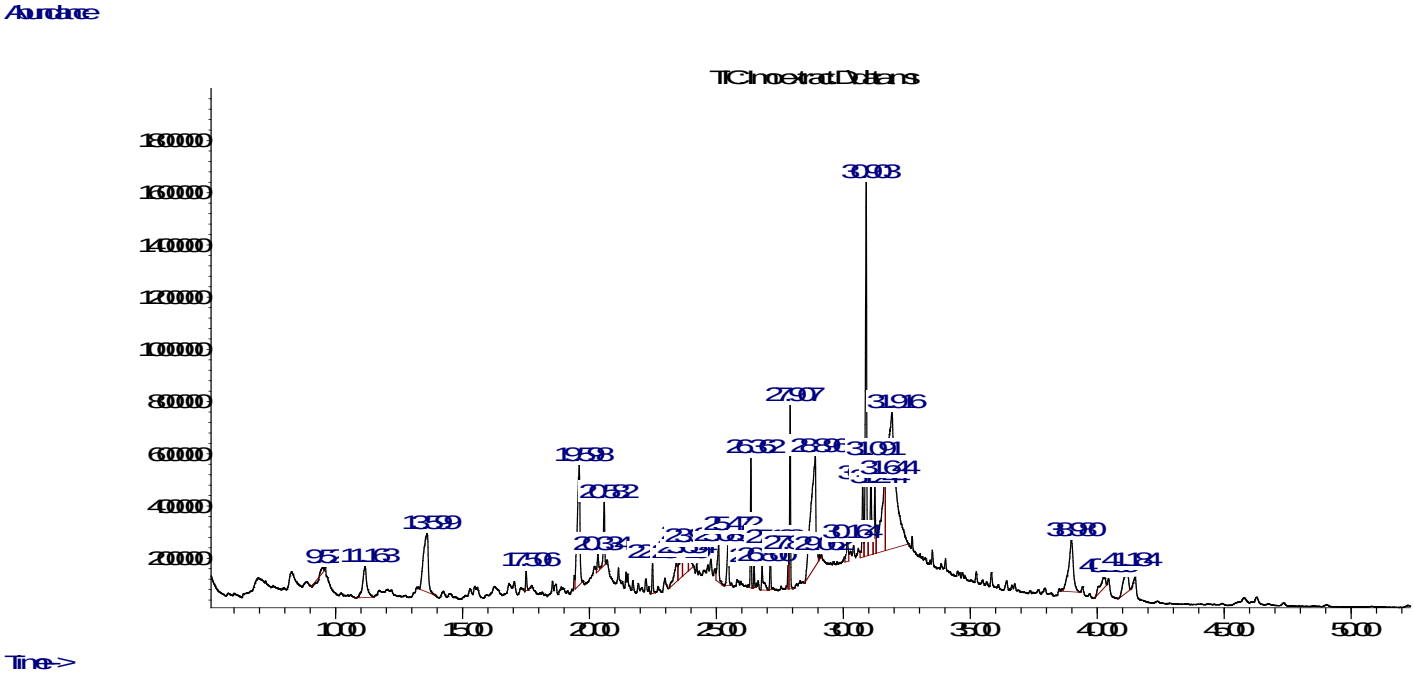
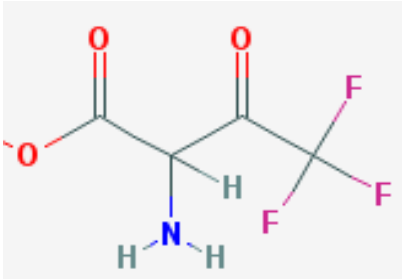


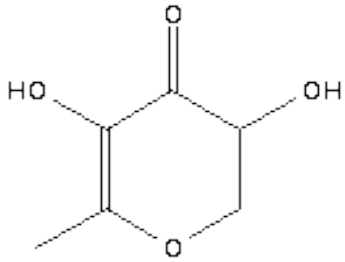
Figure 4.56 GC/MS Chromatogram for the ethanol extract of M.O

Peak S/N	R.T	Name of Coumpound	Molecular Formula	Molecular Weight	Peak Area %
1	9.521	Butanoic acid, 2-amino-4,4,4-trifl uoro-3-oxo-, methyl ester	$C_5H_6F_3NO_3$	185.1025	0.07
2	11.164	4H-Pyran-4-one, 2,3-dihydro-3,5-di hydroxy-6-methyl-	$C_6H_8O_4$	144.12532	2.59
3	13.601	2-Furancarboxaldehyde, 5-(hydroxymethyl)-	$C_6H_6O_3$	126.1100	5.60
4	17.503	1-(3,6,6-Trimethyl-1,6,7,7a-tetrah ydrocyclopenta[c]pyran-1-yl)ethanone	$C_{13}H_{18}O_2$	206.280807	0.43
5	19.598	Benzeneacetonitrile, 4-hydroxy-	C_8H_7NO	133.1473	6.31
6	20.336	Nonanoic acid	$C_9H_{18}O_2$	158.23	0.47
7	20.582	2(4H)-Benzofuranone, 5,6,7,7a-tetr ahydro-4,4,7a-trimethyl-	$C_{11}H_{16}O_2$	180.2435	1.57
8	22.487	Megastigmatrienone	$C_{13}H_{18}O_2$	190.2814	0.67
9	23.420	Tetrahydropyrrole-3-ol-5-carboxyli c acid, 1-acetyl-, methyl ester	$C_8H_{13}NO_4$	187.1912	1.31
10	33.655	2,4,4-Trimethyl-1-hexene	C_9H_{12}	126.24	3.66
11	23.958	Methoxyacetic acid, octyl ester	$C_{11}H_{22}O_3$	202.29058	1.03
12	25.091	Tetradecanoic acid	$C_{14}H_{28}O_2$	228.3709	1.37
13	26.474	5-Ethylcyclopent-1-ene-1-carboxyli c acid	$C_8H_{12}O_2$	140.17968	1.69
14	26.361	Bicyclo[3.1.1]heptane, 2,6,6-trime thyl-, (1.alpha.,2.beta.,5.alpha.)	$C_{10}H_{18}$	138.24992	2.31
15	26.487	2-Pentadecanone, 6,10,14-trimethyl	$C_{18}H_{36}O$	263.4778	0.38
16	26.802	1,2-Dihexylcyclopropene	$C_{15}H_{28}$	208.38282	0.88
17	27.128	Citronellyl isobutyrate	C14H26O2	226.36	0.81
18	27.832	E-2-Methyl-3-tetradecen-1-ol			

		acetate	$C_{17}H_{34}O_2$	268.434814	0.69
19	27.906	Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	270.4507	3.49
20	28.896	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	256.4241	11.24
21	28.896	Oleic Acid	$C_{18}H_{34}O_2$	282.40	0.79
22	30.767	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	$C_{19}H_{34}O_2$	294.4721	1.88
23	30.904	9,12,15-Octadecatrienoic acid, met-hyl ester, (Z,Z,Z)-	$C_{19}H_{32}O_2$	292.4562	9.31
24	31.093	Phytol	$C_{20}H_{40}O$	292.4562	2.92
25	31.242	Octadecanoic acid, methyl ester	$C_{19}H_{38}O$	298.50382	1.74
26	31.642	9,12-Octadecadienoic acid (Z,Z)-	$C_{19}H_{36}O$	296.4720	28.55
27	38.978	Heptadecane	C17H36	240.47	4.85
28	40.283	3H,6H-Thieno[3,4-c]isoxazole, 3a,4 -dihydro-6-(1-methylethyl)-	$C_7H_{13}N_3O$	-	1.21
29	41.181	1H-Indole-2,3-dione, 7-propyl-	$C_{16}H_{24}N_2O_2Si$	304.459503	2.18

Table 4.53 GC/MS analytical result for ethanol extract of M.O

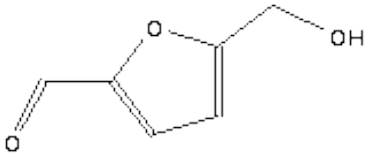


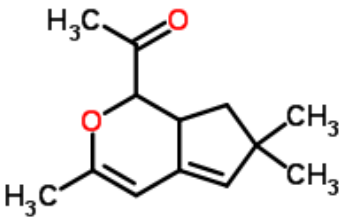


Methyl 2-amino-4,4,4-trifluoro-3-oxobutanoate

4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-

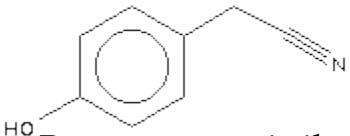
Table 4.53 GC/MS analytical result for ethanol extract of M.O



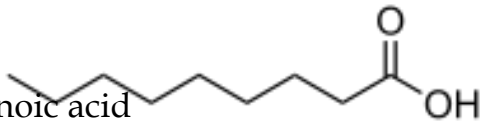


2-Furancarboxaldehyde, 5-(hydroxymethyl)-

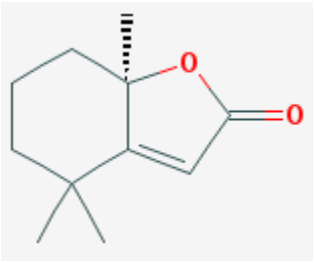
1-(3,6,6-Trimethyl-1,6,7,7a-tetrahydrocyclo-penta[c]pyran-1-yl)ethanone



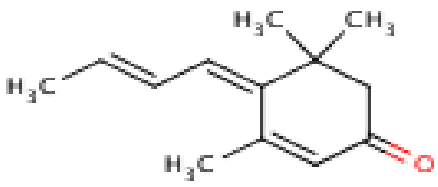
Benzeneacetonitrile, 4-hydroxy-.



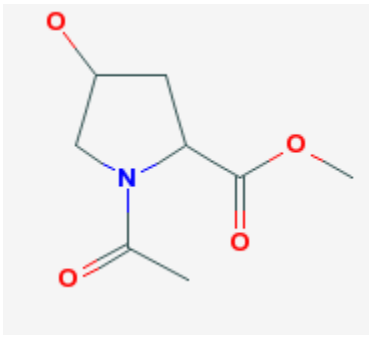
Nonanoic acid



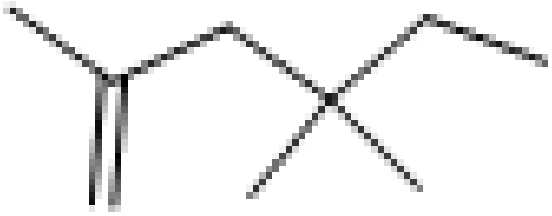
2(4H)-Benzofuranone, 5,6,7,7a-tetrahydro-4,4,7a-trimethyl-, (R)-



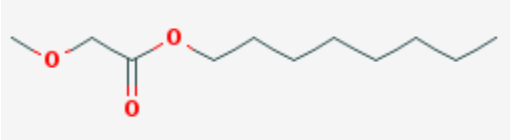
Megastigmatrienone

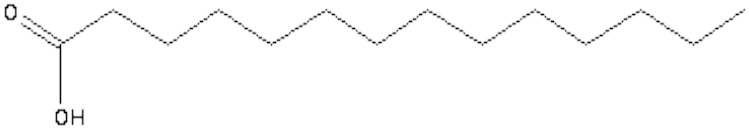


Tetrahydropyrrole-3-ol-5-carboxylic acid, 1-acetyl-, methyl ester

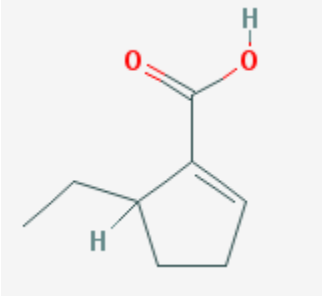


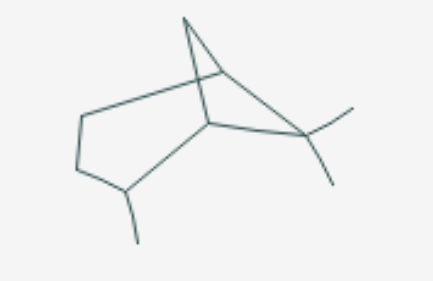
2,4,4-Trimethyl-1-hexene





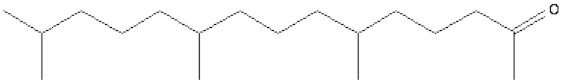
Methoxyacetic acid, octyl esterTetradecanoic acid

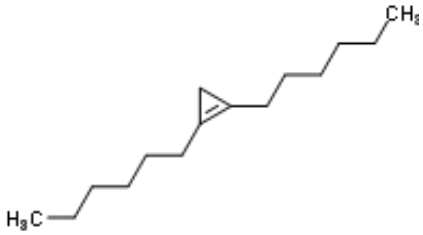




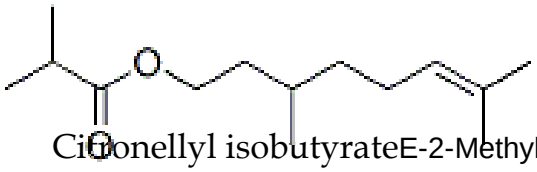
5-Ethylcyclopent-1-ene-1-carboxylic acid

Bicyclo[3.1.1]heptane, 2,6,6-trimethyl-, (1.alpha.,2.beta.,5.alpha.)

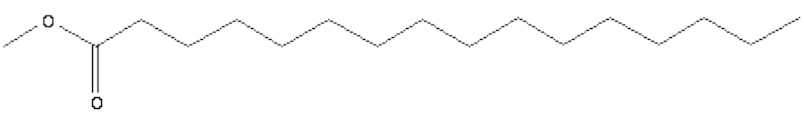




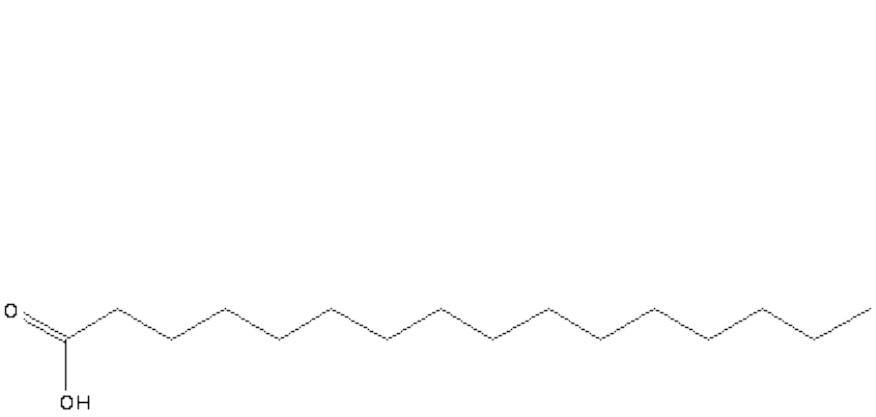
2-Pentadecanone, 6,10,14-trimethyl-1,2-Dihexylcyclopropene



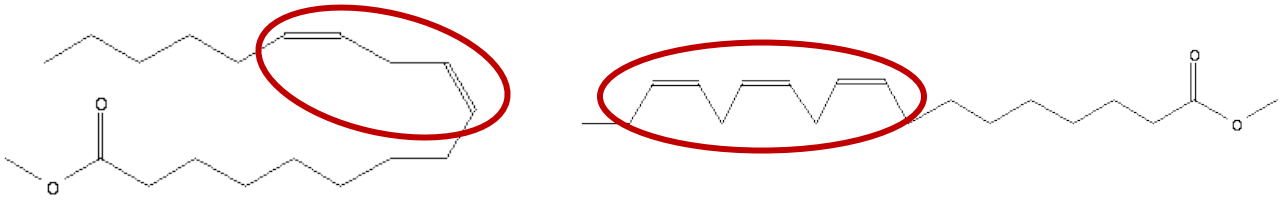
Citronellyl isobutyrateE-2-Methyl-3-tetradecen-1-ol acetate



Hexadecanoic acid, methyl ester



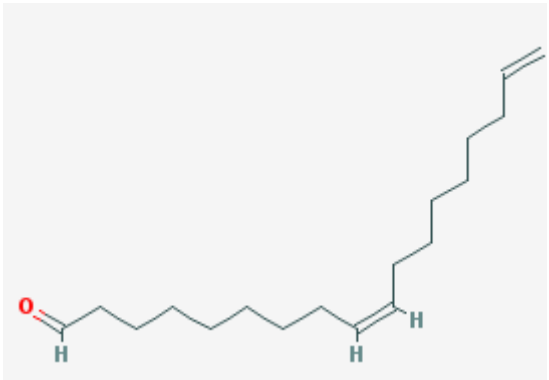
n-Hexadecanoic acidOleic acid



9,12-Octadecadienoic acid 9,12,15-Octadecatrienoic (Z,Z)-, methyl esteracid, methyl ester, (Z,Z,Z)-

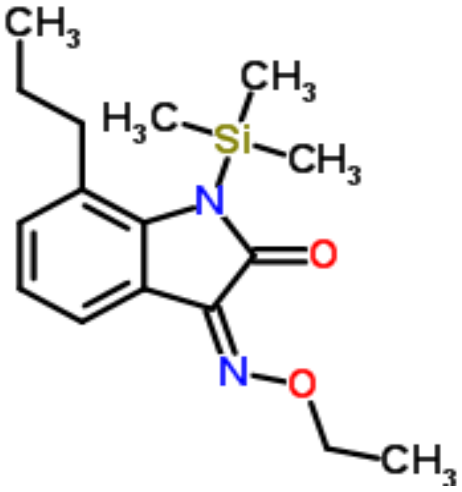
Phytol

Octadecanoic acid, methyl ester



(9Z)-9,17-Octadecadienal

Heptadecane



1H-Indole-2,3-dione, 7-propyl-1-(trimethylsilyl)-, 3-(O-ethyloxime)

Figure 4.57, Some of the organic molecules identified in the ethanol extract of M.O

4.4.4 Gas chromatography mass spectroscopy (GC/MS) analytical result for the ethanol extract of *Moringa oleifera* leaves

From the GC/MS data represented in Table 4.53; the extract contained;28.55% 9,12-Octadecadienoic acid (Z,Z)methyl ester; 11.24% n-Hexadecanoic acid; 9.31% 9,12,15-Octadecatrienoic acid methyl ester; 6.32%Benzeneacetonitrile, 4-hydroxy-; 5.6%2-Furancarboxaldehyde, 5-(hydroxymethyl)-; 4.85%Heptadecane; 3.49% Hexadecanoic acid; 2.91% Phytol; 2.59% 4H-Pyran-4-one, 2,3-dihydro-3,5-di hydroxy-6-methyl-; 2.31% Bicyclo [3.1.1] heptane,2,6,6-trimethyl (1.alpha.,2.beta.,5.alpha.); 2.98% 1H-Indole-2,3-dione, 7-propyl-; while the

remaining percentage were shared by the rest of the constituents as can presented in Table (4.53) and Figure (4.56).

The Table and the spectrum are similar to the results reported by Ostovari et al., 2009, Njoku et al., 2013 and Oguzie et al., 2014. A total of 29 phyto-constituents were detected by the equipment with the presence of many small peaks indicating that there are more phytocomponents far more than the number detected as can be seen in Figure (4.56)

It is important to mention herein that the constituents were identified after comparison with those available in the computer library attached to the instrument and reported. Therefore, the structural assignments are based on spectral matching with NIST library (National Institute of standards and Technology) and are shown in Figure 4.42. Similar approach has been recorded by (Nava et al., 2012 and Blustein et al., 2006). In summary the GC/MS experimental results confirmed the presence of many organic species in the M.O extract with structures similar to conventional organic inhibitors (Figure 4.57): which are responsible for the remarkable corrosion inhibition exhibited by the different extracts of M.O

4.5. THEORETICAL (COMPUTATIONAL) STUDIES.

Our experimental results so far showed that the corrosion inhibiting action of M.O extract resulted from adsorption of the organic matter on the corroding

mild steel surface. Such metal-inhibitor interactions have been theoretically investigated at the molecular level using computer simulations of suitable models in the framework of the DFT (Density Functional Theory). This quantum chemical method has already proven to be very useful in elucidating molecular structures and reactivity of compounds (Mohamed, et al 2010). It has therefore become a common practice to carry out quantum chemical calculations in corrosion inhibition studies. Thus, we have performed such computations to model the electronic and adsorption structures of some active constituents of M.O extract namely:Benzeneacetonitrile, 4-hydroxy-(BANH), 2-Furancarboxaldehyde, 5 (hydroxymethyl)- (FCDH), n-Hexadecanoic acid (NHDA), Hexadecanoic acid methyl ester (HAME), 9,12-octadecadienoic acid methyl ester (Z,Z) (ODMA), 9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-., (OTMA).

The motivation for the computational study is not so much as to provide in depth explanation for the adsorption of the extract, but rather to give a theoretical framework in which to recognize the relative contributions of different extract components vis-a`-vis their individual adsorption mechanisms and adsorption strengths.

The calculation was performed by means of the DFT electronic program VAMP as contained in MS modeling 4.0 programs. The structures of the selected phytoconstituents for M.O extract is contained in the structures in Figure 4.57,

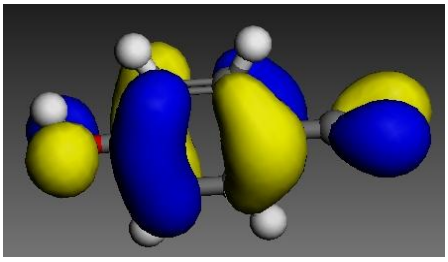
while the calculated quantum properties (E_{HOMO}, $E_{LUMO,}$ Total electron density, ΔE energy etc) are shown in Table 4.54.The regions of highest occupied electron molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (HUMO) in the selected organic constituents of the extract were calculated and are very important parameters that determine the reactivity, softness and corrosion inhibition capabilities of compounds.

The HOMO are the sites at which electrophiles attack and represent the active centers with the utmost ability to bond to the metal by donating electrons, whereas the LUMO orbital denotes regions with utmost ability to accept electrons from the orbital of the metals using anti-bonding orbital to form feedback bonds. Excellent corrosion inhibitors are usually those organic compounds that not only offer electrons to unoccupied orbital of the metals, but also accept free electrons from the metals (Obi – Egbedi, et al 2010). It is a well established fact in the literature that the higher the HOMO energy of the inhibitor the greater the trend of offering electrons to unoccupied orbital of the metal and the higher the corrosion inhibition efficiency. In addition the lower the LUMO energy the easier the acceptance of electrons from metal surface because the ΔE (LUMO – HOMO) or energy gap value would be decreased and the inhibition efficiency of the inhibitor improved.

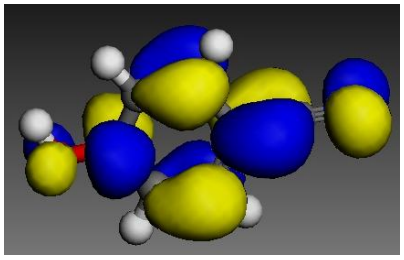
Secondly, Mohammed et al., 2009 reported that the energy of HOMO is directly related to the ionization potential and the susceptibility of the molecules toward

attack by electrophiles. Also, the energy of LUMO on the other hand is related to the electron affinity and the susceptibility of the molecule toward attack by necluophiles. The energy gap designated as ΔE given by $\Delta E = E_{HOMO}-E_{LUMO}$, which is another important parameter that gives information about the reactive behaviour of inhibitor moleculesis closely related to the polarizability; since decrease of the energy gap usually leads to easier polarization of the molecules. Thus, low values of ΔE will render good inhibition efficiencies since the energy needed to remove an electron from the last occupied orbital will be minimized (Visalovic et al., 2011). Therefore, species can be classified as soft if they are easy to polarize and vice verse.

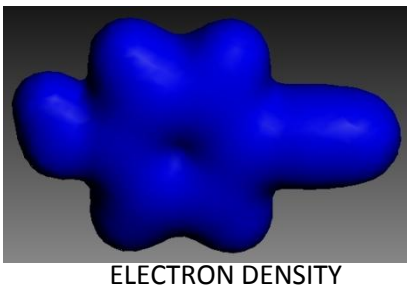
Results from quantum chemical computations and molecular dynamics simulations (Modeling) are presented in Figures 4.58 to 4.63 and the corresponding parameters presented in Table 4.54



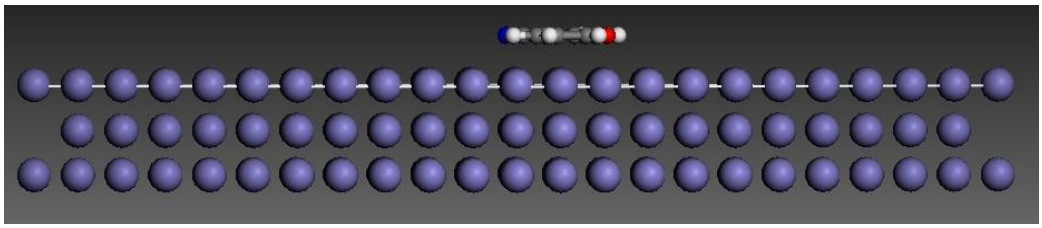
HOMO



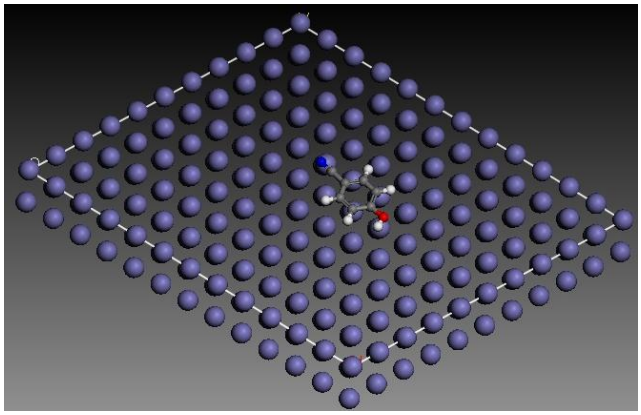
LUMO



ELECTRON DENSITY



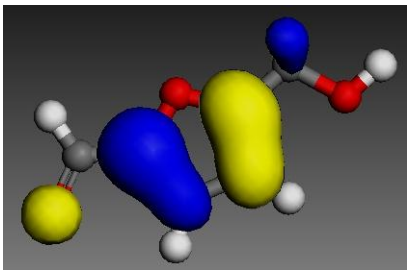
(A)



(B)

Figure 4.58 Electronic properties: (HOMO, LUMO and ELECTRON DENSITY) of Benzeneacetonitrile, 4-hydroxy-.; (BANH)from M.O ethanol extract and representative snap shots from molecular dynamics model of adsorption of BANH molecule on iron surface; side view (A) and top view (B)

(Atomic legend: white= H; gray = C; red = O; blue = N. The blue and yellow isosurfaces depict the electron density difference: The blue regions show electron accumulation while the yellow regions show electron loss).



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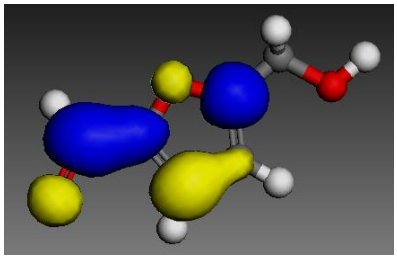
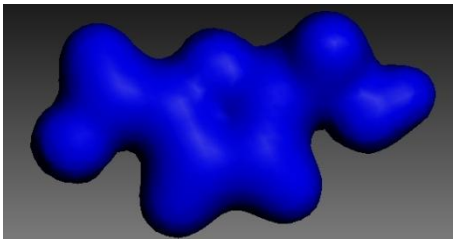


LUMO



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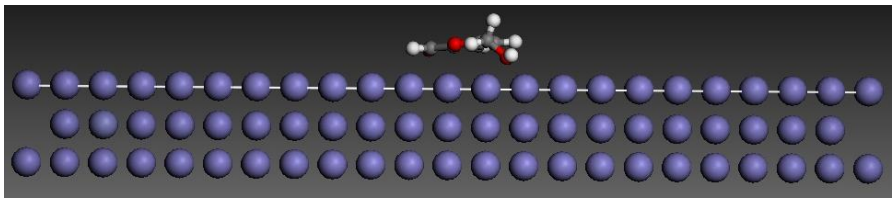
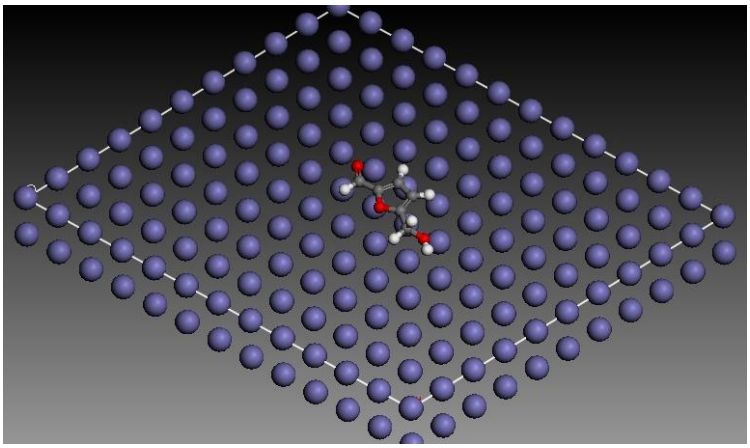


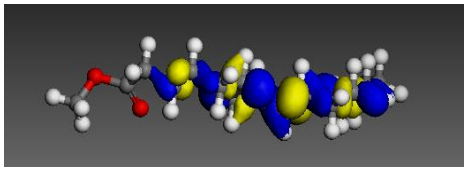
(A)



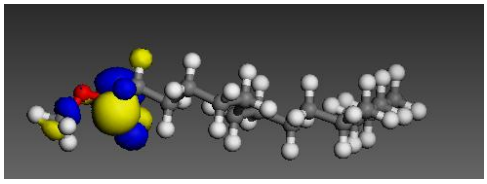
(B)

Figure 4.59 Electronic properties: (HOMO, LUMO, and ELECTRON DENSITY) of 2-Furancarboxaldehyde,5-(hydroxymethyl)-; (FCDH)from M.O ethanol extract and representative snap shots from molecular dynamics model of adsorption of FCDH molecule on iron surface; side view (A) and top view (B)

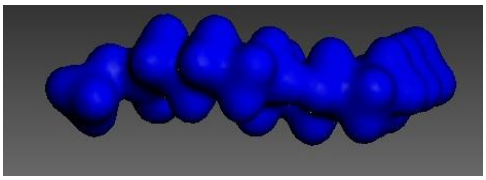
(Atomic legend: white= H; gray = C; red = O; blue = N. The blue and yellow isosurfaces depict the electron density difference: The blue regions show electron accumulation while the yellow regions show electron loss).



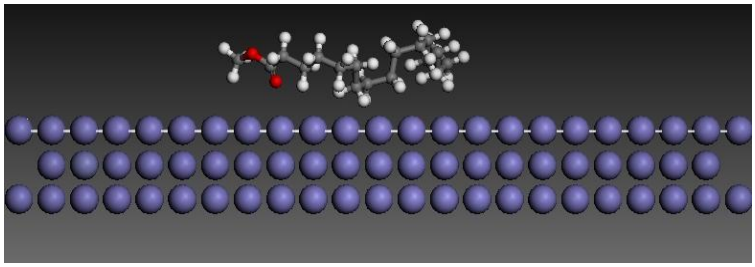
HOMO



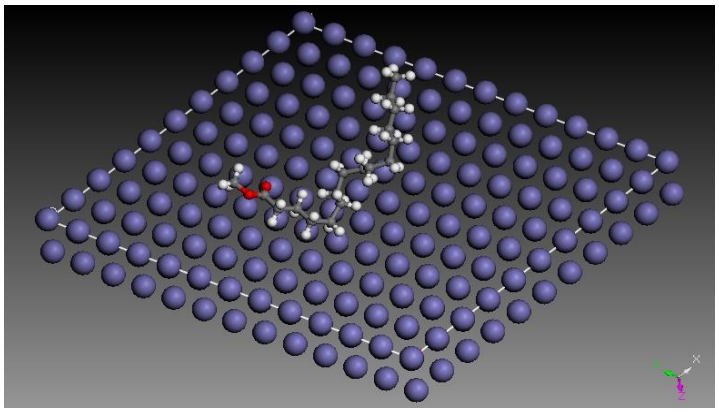
LUMO



ELECTRON DENSITY



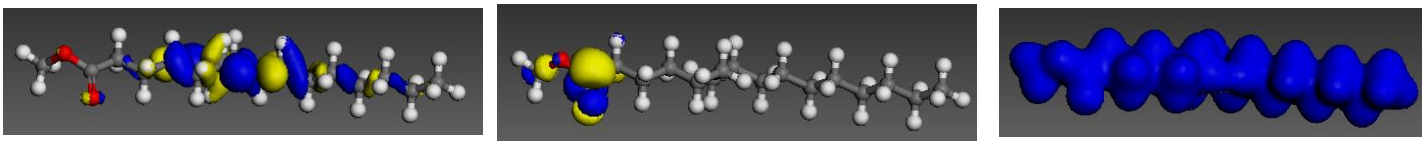
(A)



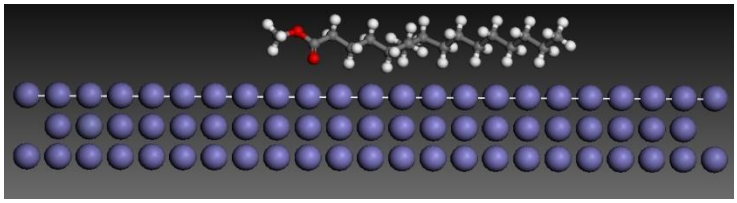
(B)

Figure 4.60 Electronic properties: (HOMO, LUMO, and ELECTRON DENSITY) of n-Hexadecanoic acid (NHDA)from M.O ethanol extract and representative snap shots from molecular dynamics model of adsorption of NHDA molecule on iron surface; side view (A) and top view (B)

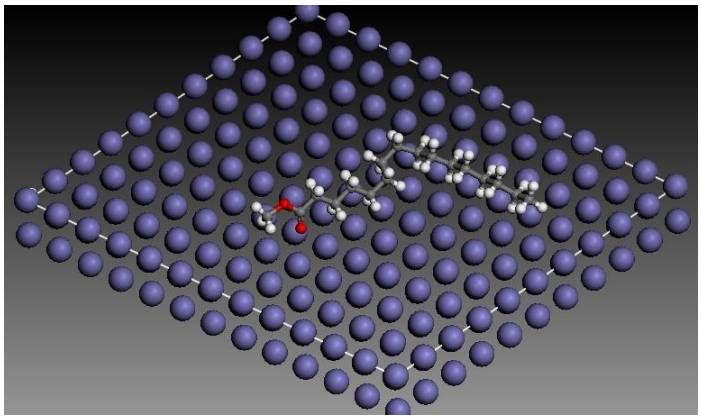
(Atomic legend: white= H; gray = C; red = O; blue = N. The blue and yellow isosurfaces depict the electron density difference: The blue regions show electron accumulation while the yellow regions show electron loss).



HOMO LUMO ELECTRON DENSITY



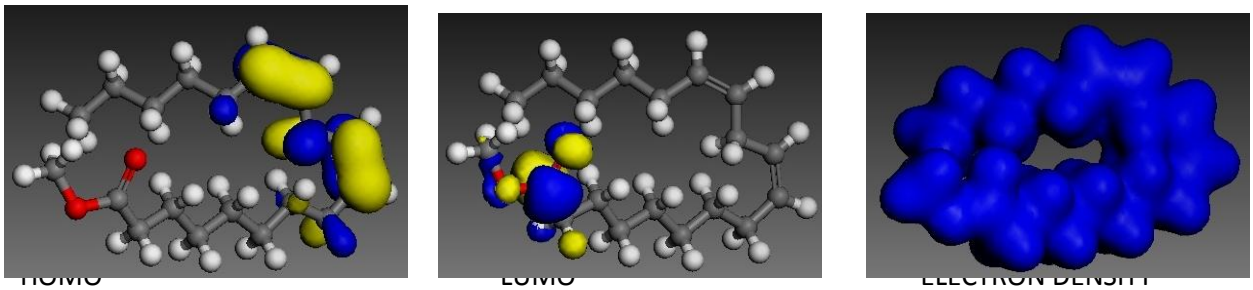
(A)

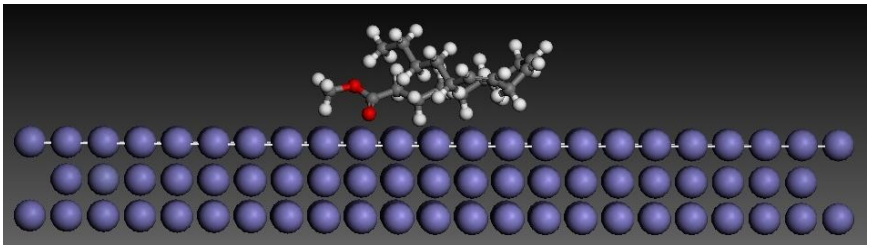


(B)

Figure 4.61 Electronic properties:(HOMO, LUMO, and ELECTRON DENSITY) of Hexadecanoic acid, methyl ester (HAME) from M.O ethanol extract and representative snap shots from molecular dynamics model of adsorption of HAME molecule on iron surface; side view (A) and top view (B)

(Atomic legend: white= H; gray = C; red = O; blue = N. The blue and yellow isosurfaces depict the electron density difference: The blue regions show electron accumulation while the yellow regions show electron loss).





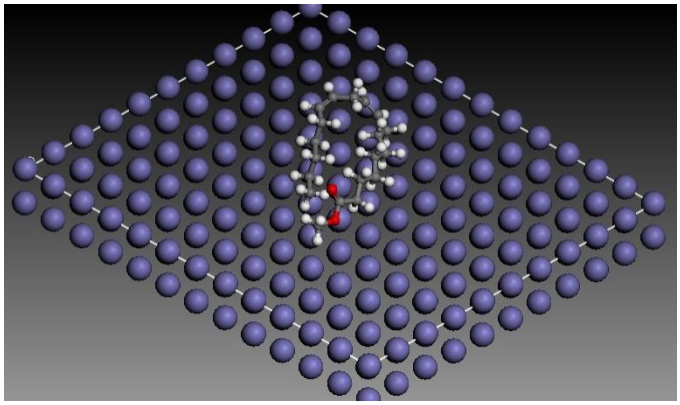
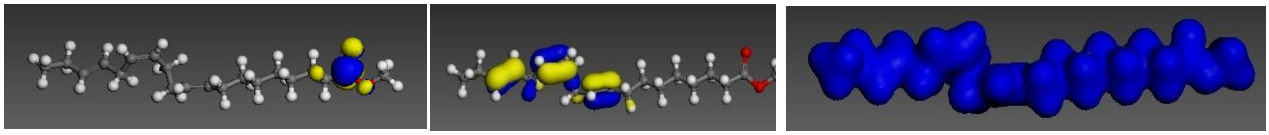
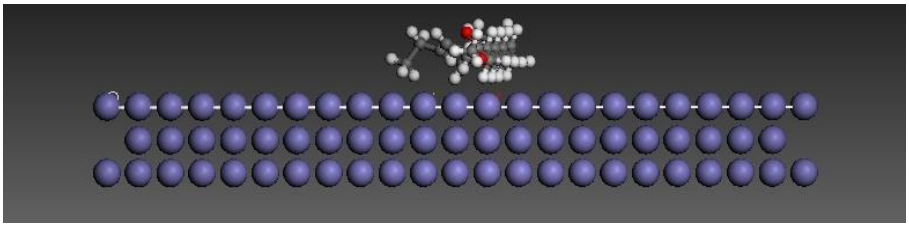


Figure 4.62 Electronic properties: (HOMO, LUMO, and ELECTRON DENSITY) of 9,12-octadecadienoic acid, methyl ester (Z,Z)(ODMA) from M.O ethanol extract and representative snap shots from molecular dynamics model of adsorption of ODMA molecule on iron surface; side view (A) and top view (B)

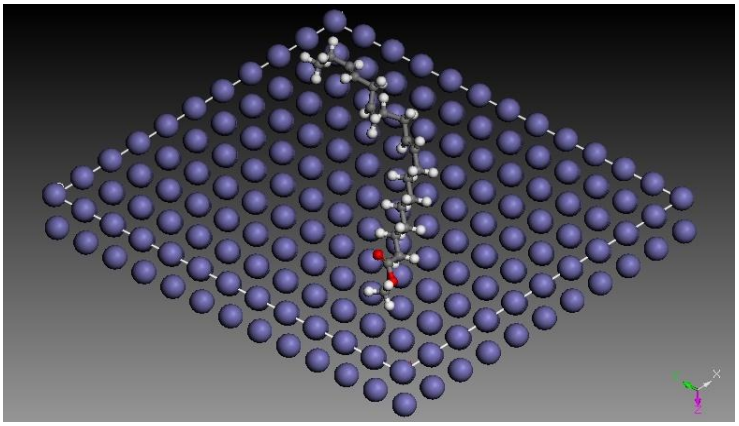
(Atomic legend: white= H; gray = C; red = O; blue = N. The blue and yellow isosurfaces depict the electron density difference: The blue regions show electron accumulation while the yellow regions show electron loss).



HOMO LUMO ELECTRON DENSITY



(A)



(B)

(B)

Figure 4.63 Electronic properties:(HOMO, LUMO, and ELECTRON DENSITY) of 9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-., (OTMA) from M.O ethanol extract and representative snap shots from molecular dynamics model of adsorption of OTMA molecule on iron surface; side view (A) and top view (B)

(Atomic legend: white= H; gray = C; red = O; blue = N. The blue and yellow isosurfaces depict the electron density difference: The blue regions show electron accumulation while the yellow regions show electron loss).

Table 4.54 Calculated quantum chemical properties and interaction energies for the most stable conformation of the selected phytochemical constituents from ethanol extract of Moringa oleifera (M.O)

Property	BANH	FCDH	NHDA	HAME	ODMA	OTMA
E_{HOMO} (eV)	-9.512	-8.828	-9.915	-10.541	-8.398	-8.521
E_{LUMO} (eV)	-0.378	-1.287	-0.445	-0.442	-0.285	-0.177
E_{LUMO}-E_{HOMO} (ΔE)	9.134	7.541	9.47	10.099	8.113	8.404

Mol. Surf. Area (Å^2)	143.211	159.237	401.066	411.162	434.321	470.639
Bind. Energy (Kcal/mol)	-64.86	-69.75	-166.4	170.2	-184.7	176.9

4.5.1 Theoretical Results For Some M.O phytoconstituents.

From the results presented in Figures 4.58-4.63, the electron density (Mulliken charge centers) is saturated all over each of the molecules. Hence, flat lying adsorption orientation should be expected in all selected constituents as observed in the electron density and representative snap shots for the molecular dynamics model of adsorption of the plant extract's biomass on Fe slab presented in Figures 4.58-4.63. From the quantum parameters values in Table 4.53, the obtained values did not show any well defined and cut correlation and none was actually expected since the molecules differ considerably in their chemical structures and their individual inhibition efficiencies are not known (rather the overall IE%). Nonetheless, certain features can still be used to allocate individualcorrosion inhibiting efficacy for the molecules present in the M.O extract.

For instance, from the Table 4.53, it was evident that ODMA hadthe highest HOMO which indicated that it wasthe most easily polarizable or would readily

donate electrons than others, while FCDH had the lowest LUMO which indicated ease of acceptance of electron from the metal to form feedback bond. The trend of E_{HOMO} values decreased in the order ODMA > OTMA > FCDH >

NHDA > BANH > HAME, while the trend of E_{LUMO} decreased in the order OTMA > ODMA > BANH > NHDA > HAME > FCDH. The ΔE values wasin the order; FCDH < ODMA < OTMA < BANH < NHDA < HAME.

a flat lying adsorption orientation on the Fe surface slab. This was expected because of the delocalization of the electron density all around the molecules as could be seen in Figures 4.58 – 4.63 for total electron density.

To quantitatively appraise the interaction between each of the selected molecules and Fe surface, the binding energy was estimated and reported in Table 4.53. A negative binding energy corresponds to a stable adsorption structure (Chidebere et al., 2011).The trend of E_{bind} for M.O extract selected constituent is in the order:BANH > FCDH > NHDA > HAME > OTMA > ODMA. This had a close relationship with the trend of molecular surface coverage or size given before (Table 4.53).

To quantify the interaction between the molecules and the Fe surface, the binding energy (E_{bind}) of each system was calculated using the relationship:

$$E_{bind} = E_{total} - (E_{Fe} + E_{molecule}) \qquad 4.4$$

E_{total}, E_{Fe} and E_{mol} denote the energies of the adsorbed Fe/molecule couple, the Fe slab and the molecule respectively, which were obtained by averaging the energies of the five structures of the lowest energy. A negative value of E_{bind} corresponds to a stable adsorption structure. The obtained E_{bind} values are also presented in Table 4.53 for the different molecules.

The large negative values of the computed binding energiesof the selected constituents of M.O extract, correlated well with the molecular sizes as predicted, and should be responsible for the remarkable inhibition efficiency of the extract. Moreover, the E_{bind} values for some compounds (NHDA, HAME, ODMA and OTMA) are more exothermic than expected for ordinary non covalent interactions, which probably results from significant dispersive interactions arising from the high polarizability of the O atoms, including the pi electron delocalization. This should enhance specific adsorption of the molecules, corresponding to an adsorption mechanism involving blocking of active corrosion sites, in agreement with the experimental findings. Such strong adsorption has been reported for some phytochemical constituents of certain biomass extracts and has been attributed to epitaxial adsorption orientations (Mejaha et al,3=2012; Chidebere *et al*., 2012, Oguzie *et al.,* 2013, Oguzie *et al*., 2014). This phenomenon thus accounts for the obtained high binding energies of the phytochemical constituents of M.O extract, hence the remarkable corrosion inhibiting effect of the extract as observed experimentally.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The gravimetric results showed that mild steel corrodes indefinitely in acidic environment and thus, loses weight with exposure time. Secondly, this behaviour was observed to be more severe in sulphuric acid than in hydrochloric acid.

The potentiodynamic polarization plot for mild steel in the both acid corrodents showed that mild steel dissolves without any evidence of passivation and the current density value was higher in sulphuric acid than in hydrochloric acid confirming the observation from gravimetric test.

The results from activation energy point (temperature / kinetic consideration) of view did not somewhat followed the trend of gravimetric but followed polarization results which was duly attributed to time effect.

However, the introduction of different M.O extracts modified the corrosion behaviour of the metal in the both systems. But the inhibition performance of the different extracts varies according to the extracting solvents and the corrodents. Generally, sulphuric acid extracts performed better in hydrochloric acid environment while ethanol performed better in sulphuric acid environment. Also, polarization results showed that the different extracts exerted higher

inhibition efficiencies in hydrochloric acid than in sulphuric acid. But gravimetric results did not follow this trend. This anomaly was attributed to time and instrumental effects.

Kinetic and temperature considerations showed that the inhibition performance of the different extracts of M.O increases with increase in temperature which was rightly attributed to chemisorptions of molecule in the extracts.

The results obtained from these experiments indicated that ethanol, water and sulphuric extracts of *Moringa oliefera* are good corrosion inhibitors for mild steel in acidic media. The extracts showed high inhibition efficiencies and the inhibition efficiencies were observed to improve with the extract concentration but decreased with prolonged exposure time.

The potentiodynamic polarization results showed that all the extracts acted as mixed type corrosion inhibitors in both acidic media inhibiting both anodic and cathodic corrosion reactions for mild steel.

The GC/MS analytical result performed on the ethanol extract of M.O confirmed that the extracts contained many organic molecules with structures and conformations similar to conventional organic inhibitor which could be responsible for the observed inhibition efficacy exerted by the different extracts of M.O.

The inhibiting potentials of some of the organic compounds from the ethanol extract were theoretically confirmed via DFT based quantum chemical computations. The results from the theoretical modeling showed that the corrosion inhibition of the compounds was based on the adsorption of the compounds on the corroding metal surface and geometric blocking by some molecules due to their flat lying adsorption orientation on the Fe-surface slab provided (by the software). Again, the trend of binding energy and molecular size could be used to assessed the individual performance of the modeled structures.

5.2 RECOMMENDATIONS

Work should be extended to further understudy the effect of these extracts on other forms of corrosion attacks such as localized, microbial corrosion and cracks etc.

Secondly, attempts should be made to further theoretically evaluate the individual inhibitive contributions of other organic molecules identified in the extracts, including the chemisorptions energies of the extract's components (molecules).

Finally, surface morphological imaging techniques can still be adopted to enhance the experimental techniques used in this work and to further evaluate the inhibition efficiency of the extracts.

Electrochemical impedance spectroscopy experimental technique can equally be employed to further establish the trend or kind of adsorption of the molecules in the extract.

5.3 CONTRIBUTION TO KNOWLEDGE

This work provides comprehensive experimental and theoretical evidence of the corrosion inhibitory abilities of Moringa Oleifera..Attention has been shown in the use of organics derived from the relative ease of synthesis and safer handling compared to the heavy metal-based inorganic inhibitors. However, the widespread use of these organic corrosion inhibitors is often limited because it is expensive and quite toxic.

As a result, great interest and focus is been directed towards organic corrosion inhibitors that are eco-friendly, inexpensive, readily available, and renewable. In this regard, lots of research effort has been put into natural products of plant origin such as extracts from roots, barks, leaves, and seeds for corrosion inhibition efficacy in the scientific community. Such plant extracts could thus serve as sources of non-toxic and inexpensive corrosion inhibiting additive in acidic environments. The results obtained from this research work showed that MO extracts effectively mitigated the corrosion rates of mild steel in 0.5 M H_2SO_4 and 1 M HCl solutions, better results were obtained at higher concentrations of MO extracts and at prolonged immersion time.

Weight loss was more in the 0.5 M H_2SO_4 corrodent compared to the 1 M HCl corrodent, showing that 0.5 M H_2SO_4 corrodent was more aggressive on mild steel. Ethanol extract of MO presented highest inhibition efficiency of 97.04% in the 0.5 M H_2SO_4 corrodent while 1 M HCl was 79.22%. Polarization measurements showed that the adsorbed extracts organic matter inhibited the corrosion process via a mixed-inhibition mechanism, affecting both the anodic metal dissolution process and the cathodic hydrogen evolution process. Extract adsorption was further corroborated by the experimental data to fit the Langmuir isotherm.

The experimental findings obtained from this research establishes that MO extract could find practical applications as an inexpensive,available, renewable and non-toxic alternative corrosion inhibitors for mild steel in aggressive acidic environments.

REFERENCES

Abdel – Gaber, A.M., Abd – El – Nabey, B.A., Seadewy, M., (2009),The role of acid anion on the inhibition of the acidic corrosion of steel by lupine extract, C*orrosion Science*, 51, 1038 – 1042.

Abdel – Gaber, A.M., Khanis, E., Abo – Eldahab, H., Adeel,S., (2008), Inhibition of aluminium corrosion in alkaline solutions using natural compounds, *Material Chemistry and Physics,* 109, 297 – 305.

Abdel-Gaber, A.M., Abdel-El-Nabey, B.A., Sidahmed, I.M., El-Zayady A.M., Saadawy, M.,(2005), Inhibitive action of some plant extracts on the corrosion of steel in acidic media*, Corrosion Science,* 65,167-171.

Abdel-Gaber, A.M., Khamis, E., Abo-El Dahab, H., Adeel, S.H., (2006), Inhibition of mild steel corrosion in acidic solutions using natural products, *Materials Chemistry and Physics*, 109,297-305.

Abdel-Gaber, A.M., Abd-EL-Nabey, B.A., Sidahmed, I.M., EL-Zayady, A.M.,Saadawy, M.,(2005), Inhibition action of some plant extracts on the corrosion of mild steel in acidic media, *Corrosion science*, 48, 2765-2779.

Akalezi, C.O., Enenebaku C.K., Oguzie, E.E (2013), Inhibition of acid corrosion of mild steel by biomass extract from the*petersianthus macrocarpus* plant, *J. Mater. Environ. Sci. 4 (2),217-226*

Ashassi-Sorkhabi, H., Eshaghi, M.,(2008), Corrosion inhibition of mild steel in hydrochloric acid by betanic as a green inhibitor, *Journal of Solid State Electrochemistry*, 39,(9) 1497-1501.

Ashassi- Sorkhalbi, H., and Ahasri, E. (2008), Effect of hydrodynamic conditions on the inhibition performance of L-methionine as a green inhibitor. *Electrochemical Acta*, 13943

Fraunhofer, A.J.V., (1974), Concise Corrosion Science, Portcullis press ltd, Red Hill, England. 50-59

Antroprove, L.I., (1977), Theoretical electrochemistry, English translation, Mr. Publishers : Moscow, Pp. 401.

Ashassi-Sorkhabi, H., Eshaghi, M.,(2008), Corrosion inhibition of mild steel in hydrochloric acid by betanic as a green inhibitor, *Journal of Solid State Electrochemistry*, 39,(9), 1497-1501.

Bendahon, E.A., (2006), Study of rosemary oil as a green corrosion inhibitor for carbon steel corrosion in acidic environment, *Applied Surface*, 226, 166-175.

Benett, L.H., Kinger. J., Parker, R.I., Passaglia, E., Reimann, C., Ruff, A.W., Yokowitz, A., Benman, E.B., (1978), Economic effects metallic corrosion in the united state. A three part study for progress: INBS special publication 511 – 1, SD stock NO SN – 003 – 01926, Washington DC, 45-50

Blustein , G., Romognoh, R., Jaen, J. A., Di Sarli, A.R., Del Amo, B., (2006), Zinc basic benzoate as eco-friendly steel corrosion inhibitor pigment for anti corrosive epoxy – coatings, *colloids and surfaces* A. Physic Chem. Eng. Aspects 290, 7 – 18.

Branzo, V., Florentina, G., Florina, B., (2007), Aluminium corrosion in hydrochloric acid solution and the effect of some organic inhibitions, *Material Chemistry and Physics,* 78, 122 – 131.

Brook, P.A (1989). Corrosion Prevention Control: Vol.36, pp 13. Ret.20/12/2012

Burdock, G.A., Carabin, L.G. and Crincoli C.N., (2009), Safety assessment of kola nut extracts as a food ingredient. *Food Chemistry,57,*117-120.

Chauhan, L. R., and Gunasekaran, G., (2007):,Corrosion inhibition of mild steel by plant extract in dilute HCl medium, *Corrosion Science*, 49, 1143-1161.

Committee on corrosion and protection, (1977), Corrosion Eng. Jpn. 26, 7, 401. Ret. 20/12/2012

Corrosion control NAVFAC MO – 307 September 1992. Ret 21/12/2012

Davis, J.R. (1987), Metal handbook ASM international Ohio. Vol. 13, 9th edition, Pp: 104 – 122 and 583 – 609, ,

De Sonza, F.S, Spinelli, A., (2009), Caffeic acid as a green corrosion inhibitor for mild steel, *Corrosion Science,* 51, 642 – 649.

Ebenso, E .E., Eddy, N.O., and Odiongenyi, A.O., (2008), Corrosion inhibitive properties and absorption behavior of ethanol extract of *Piper guinensis* as a green corrosion inhibitor for mild steel in H_2S0_4, *African Journal of Pure and Applied Chemistry*, 2 , 107 – 115

Ect & G., Princeton Applied Research, Application Note corr. – 4 electrochemistry and corrosion overview and techniques. Ret. 21/12/2012

Eddy, N.O., Ibok U. J., Ebenso, E. E., El-Nemr, A. and El-Ashry, E.H., (2009), Quantum chemical study of the inhibition of the corrosion of the mild steel in H_2SO_4 by some antibiotics, *Journal of Molecular Modeling*, 15(9),1085-1092.

Eddy, N.O., Odoemelam. S.A., and Odiongenyi, A.O., (2009), Ethanol extract of Musa species as a green corrosion inhibition for mild steel: Kinetics adsorption and thermodynamic considerations, Electronic Journal of Environment, *Agricultural and Food chemistry*, 8 (5), 243-255.

Eddy, N.O., Odemelam, S. A and Ama, I.N., (2010), Ethanol extract of *Occimum Gratissimum* as a green inhibitor for the corrosion of mild steel in H_2SO_4, *Green Chemistry Letters and Reviews*. 3 (3) 163-172.

Ehteram, A.N., Aisha, H.A.M., (2008), Corrosion behaviour of mild steel in hydrochloric acid solutions int. *J. Electro Chem. Sci.* 3, 806 – 818.

El-Etre, A.Y., (2006): Inhibitive effect of aqueous extract of lawsone on the corrosion of some metals in different media, *Corrosion Science*, 50,285-296.

El-Etre, A.Y., (2006): Khillah extract as inhibitor for acid corrosion of SX 316 steel, *Applied Surface Science*, 47,8521 -8525.

El-Etre, A.Y., (2003), Inhibition of Aluminum Corrosion, *Corrosion Science*, 2485-2495.

El- Etre, A. Y., Abdallah, M., El Tantawy, Z. E., (2005), Corrosion inhibition of some metals using *Lawsonia* extract, *Corrosion Science*. 47, 385-395.

El-Etre, A.Y., (2003), Inhibition of Aluminum Corrosion, *Corrosion Science*. 2485-2495.

El- Etre, A. Y., Abdallah, M., El Tantawy, Z. E., (2005), Corrosion inhibition of some metals using *Lawsonia* extract, *Corrosion Science*. 47, 385-395.

Evans, U, R., (1976), The corrosion and oxidation of metals, *Arnold Education, London*. 5, 12-13.

Evans, U, R., (1976), The corrosion and oxidation of metals, *Arnold Education, London*. Pp. 5, 12-13.

Ferreira, E.S., Giacomelli, C., Giacomelli, F.C., Spinelli,A., (2004),Evaluation of the inhibition effect of 1-ascorbic acid on the corrosion of mild steel, *Material Chemistry and physics,* 83, 129-134.

Fontana M.G., (1986), Corrosion Engineering. Mc-graw Hill book company, New York.pp 20-80

Fontana M.G., (1987), Corrosion Engineering . 3rd edt. Mc-graw hill book company, New York. Pp 1-120

Groark , K.P., (2010), Ritual therapeutic, and protective uses of tobacco (Nicotiana tabacum) among the Tzeltal and Tzotziiinaya of Chiapas Mexico, *Journal of Ethnobiology,* 30 (1), 5 – 30

Gunasekara, K.C., Chanham, C.O., (2004), Effect of Zanthoxylan alatun plant extract on the corrosion of mild steel in aqueous orthophosphoric acid, *Electrochimica Acta*, 54, 3848-3854.

Graeme Wright, (2009), Corrosion protection of metals vii metals -1- corrosion protection. Ret. 21/12/2012.

Hark, H. P., Corbett, R., and Krantz, B., (1998), Inhibition of heavy metals ion corrosion on Aluminum in fresh water cooling system using propylene glycol anti-freeze, *NACC International, Houston, Texas*. 98220

Harrop, D., (1988), Chemical inhibitor for corrosion control proceeding, Univ. of Manchester, pp. 1 – 20, 21-22.

Harvey, J.F., Paul, S, D., (2005), Evacuation of corrosion rate from polarization curves not exhibiting a tafel region, *Corrosion Science,* 47, 3034 – 3052.

Hatch J. E., (1984) Aluminium in – properties and physics metallurgy. pp 242 – 264. Ret. 12/12/2012

Harek, Y., and Larabi, L., (2004), Corrosion inhibition of mild steel in 1 Mol dm^{-3} HCl by oxalic N-phynylhydrazide, N– phenylthiosemicarbazide, *Kem. Ind*. 53, 55 0- 61.

Hurlong, W., Rui-Bin, Jian, X., (2004), Inhibitive effects of some mercapto triazole derivatives on the corrosion of mild steel in 1 M HCl medium. *Corrosion Science*. 46, 2455-2466

Hosseni, M. G., Khalilpur, H., Ershad,S., and Saghatforoush, L. (2009), Protection of mild steel corrosion with new thio-derivative salens in 0.5 M H2SO4 solution, *Journal of AppliedElectrochemistry*. 40,(2) 215-223.

Ihebiodike, M.M., Micheal, C.N., Kelechukwu, B.O., Lebe, A.N., Maduabuchi, A.C., Francis, C.E. Oguzie E. E., (2012) Experimental and theoretical assessment of the inhibiting action of *aspilia Africana* extract on corrosion of aluminiuim alloy HA3003 in hydrochloric acid, *J. Mater Sci.*, 47, 2559–2572

Khaled, K.F., (2010), Studies of iron corrosion inhibition using chemical and electrochemical and computer stimulation techniques, *Electrochemical Act.* 55, 6523-6532.

Khalifa, M.A., El-Batouti, M., Mahgoub, F. Bako, A.A. (2003), corrosion inhibition of steel in crude oil storage tanks, *Material and Corrosion*, 54, 251- 258.

Lebrinin, M., Bentiss, F., Vezin, H., Lagrene E., M., (2006), The inhibition of mild steel corrosion in acidic solution by 2,5-bis 94-pyridyl)-1,3,4- thiadiazole: structure-activity correlation, Corrosion Science, 48,1279-129.

Lecante A., Robert, F., Blandinieres, C.R.,(2010), Anti corrosive properties of .S. Tintoria and G. ouregon alkaloid extracts on low carbon steel, *Current Applied Physics*, 11, 1-38.

Liwei- hua, H.Q., Zhang, S., Chang-ling, P., and Hou, B., (2007), Some new triazole derivatives as inhibitors for mild steel corrosion in acidic medium, *Journal of Applied Electrochemistry*, 38, 289-295

Xiang-Hong, L., Shyu-Duan, D., and Fu H., (2010), Inhibition by Jasmimum mudiflorum Lindl. Leaves extract of the corrosion of cold rolled steel in hydrochloric acid solution, *Journal of Applied Electrochemistry*, 40,(9), 1641-1649.

Ma, L., and Migahed, M.A., (2006), Electrochemical investigation of the corrosion behavior of the mild steel in 2M HCL solution in presence of 1-dodecyl – 4 – methoxy pyridinum bromide, *Material Chemistry and Physics*, 93, 48-53.

Mejeha, M.I., Nwandu, M.C., Okeoma, K.B., Nnanna, L.A., Chidiebere, M.A., Eze, F.C., Oguzie, E.E., Corrosion inhibition and adsorption behavior of leaf extracts of *Aspilia africana* on aluminium alloy AA 3003 in hydrochloric acid, *J. Mater. Sci.*,**2012,**47, 2559

Mohammed, A.A., Khaled, K.F., Sahar, A. Fadi- Allah., (2010), Testing validity of the tafel extrapolation method for monitoring corrosion of cold rolled steel in HCl solutions – experimental and theoretical studies, *Corrosion Science,* 52, 140- 151.

Mohammed, A.A., Mohsen, Q. A. H., (2002), Synergistic effect of I-ions on the corrosion inhibition of Al in 1.0 M phosphoric acid solutions by purine, *Material Chemistry and Physic,* 32, 130-141.

Morad, M.S., (2008), Inhibition of iron corrosion in acid solutions by cefatrexyl: Behaviuor near and at the corrosion potential, *Corrosion Science*, 50, 436-448.

Morelti, G., Guids, F, and Gron, G. (2004), Toyptamine as a Green iron corrosion inhibitor in 0.5 M dearected sulphuric acid, *Corrosion Science*, 46 387-403.

Mounium, L., Found, B., Michel., (2005), Inhibiting effect of some oxadiazole derivatives on the corrosion of mild steel in perchloric acide, *Applied Surface Science*, 252, 950-958.

Muller, E.D. (2002), effect of saccharides reducing sugars-fructose and mannose on the corrosion of aluminum and zinc in alkaline media, *Journal of the Electrochemical society,* 155, (7), 350-359.

Nan, R., and Micheal, P. T., (2001), "AELP analysis of genetic polymorphism and evolutionary relationship among cultivated and wild Nicotiana species", Electrochem. Acta. 16, 559-571.

Nesfor perez (2004), *Electrochemistry and corrosion science*, Book kluwer academic publishers, Canada. Pp 230-250

Nnabuike, O.E., Ebenso, E. E., (2010), Quantum chemical studies on the inhibition potentials of some penicillin compounds for the corrosion of mild steel in 0.1 M HCl, *J. Mol. Model,* 16, 1291-1306.

Njoku, D.I., Chidebera, M.A., Oguzie, K.L., Ogukwe, C.A., Oguzie, E.E (2013)., Corrosion inhibition of mild steel in hydrochloric acid solution by leaf extract of Nicotiana tabacum, Advancs in Materials and Corrosion, 1(2013),54-60.

Obi –Egbedi, N.O., Obot. I.B.,Umoren, S.A., (2010), Sponddias mombin. L. as a green corrosion inhibitor for aluminium in sulphuric acid: corrosion between inhibitive effect and electronic properties of extracts major constituents using density functional theory, *Arabia Journal of Chemistry,* 10, 30-38.

Odebunni , E.O., Oluwaniyu, O.O., Awolola G.V., and Adediji, A., (2001), Proximate and nutrient composition of Kola nitida, bitter kola and aligato peper , *Africa-Journal of Biotech,* 8, 305-310.

Oguzie, E.E., (2006b), Studies on the inhibitive effect of *Occimum viridis* extract on the acid corrosion of mild steel, Materials Chemistry and Physics, 99, 441-446.

Oguzie, E.E., (2006d), Adsorption and corrosion inhibitive properties of *Azadirachta indica* in acid solutions, Pigment and Resin Technology, 35, 6, 334-1079

Oguzie, E.E. (2004b), Influence of halide ions on the inhibitive effect of Congo red dye on the corrosion of mild steel in sulphuric acid solution, *Materials Chemistry and Physics,* 87, 212-217.

Oguzie, E. E., (2008a), Corrosion inhibitive effect and adsorption behavior of *Hibiscus Sabdariffa* extract on the acid corrosion of mild steel, *Material chemistry and physics*, 99, 441-446.

Oguzie E.E., (2008b), Evaluation of the inhibitive effect of some plant extracts on the acid corrosion of mild steel, Corrosion Science, 50, 2993-2998.

Oguzie, E.E., (2007 b), Corrosion inhibition of aluminium in acidic and alkaline media by Sansevieria trifasciata extract, *Corrosion Science,* 49, 1527-1539.

Oguzie E.E., Enenebeaku, C.K., Akalezi, C.O., Okoro, S.C., AYUUK, A.A., Ejike, E.N., (2010): Adsorption and corrosion – inhibiting effect of Dacryodis edulis extrzct on low – carbon- steel corrosion in acidic media , *Journal of Colloid and Interface Science* ,349, 283-292

Oguzie, E.E., Iyeh, K.L. and Onuchukwu, A.I., (2006c): Inhibition of mild steel corrosion in acidic media by aqeous extracts from *Garcinia kola* seed, *Bulletin of Electrochemistry,* 22, (2), 63-68.

Oguzie, E.E., Onuoha, G.N., and Ejike, E.N., (2007a); Effect of *Gongronema latifolium* extract on aluminium corrosion, *Pigment & Resin Technology*, 36 (1), 44-49.

Oguzie, E.E. Okolue, B.N., Ebenso, E.E, Onuoha, G.N., Onuchukwu, A.I., (2004 a): Evaluation of the inhibitory effect of methylene blue dye on the corrosion of aluminium in hydrochloric acid, material science and physics 84, 394-401.

Oguzie, E.E., and Onuchukwu, A.I., (2006a), Corrosion inhibition and adsorption behavior of Ocimium basilicum extract on aluminium, *Pigment & Resin Technology* 35 (2), 63-70.

Oguzie, E.E., Onuoha G.N ., Onuchukwu A.I.,(2005) , inhibitory mechanism of mild steel corrosion in 2M sulphuric acid by methylene blue dye, *Material Chemistry and Physics,* 89, 305- 311.

Oguzie,E.E., Njoku, D.I., Chidebera, M.A., Oguzie, C.E., and Onuoha, G.N, Oguzie, K.L and Ibisi, N. (2014), Characterization and experimental and computional assessment of kola nitida extract for corrosion inhibition efficacy, Ind. Eng.Chem ,Res., 53, 5886-894

Okafor, P.C., Ikpi, M.E., Uwah, I.E., Ebenso, E.E. Ekpe, U.J., Umoren, S.A., (2008), Inhibitory action of *phyllanthus* extract on the corrosion of mild steel in acidic media, *Corrosion Science,* 50, 2310-2317.

Okafor, P.C., Osabor, V.I., Ebenso, E.E., (2007), Eco-friendly corrosion inhibitors: inhibitive action of ethanol extracts of *Garcinia kola* for the corrosion of mild steel in H_2SO_4 solutions, *Pigment and Resin Technology*, 36, 299-305.

Okuda, T., Baes, A.U., Nishjima, W., and Okada M., (2001), Isolation and characterization of coagulant extracted from *Moringa oleifera* seed by salt solution *Water Research*, 35, 405-410.

Olen, L., Riggs, C., Cocke E., (1981), Anodic protection. Theory and practice in the prevention of corrosion. Retrieved 20/12/2012

Olivares, O., Likhanova, N.V., Go'mez, B., Navarrete, J., Llanos-Serrano, M.E., Arce, E., Hallen, J.M., (2006), Electrochemical and XPS studies of decylamides of a –amino acids adsorption on carbon steel in acidic environment, *Applied surface Science,* 252, 2894-2909.

Olivares O., Likhanova, N.V., Go'mez, B., Navarrete, J., Llanos-Serrano, M.E., Arce, E., Hallen, J.M., (2006), Electrochemical and XPS studies of decylamides of a –amino acids adsorption on carbon steel in acidic environment, *Applied surface Science,* 252, 2894-2909.

Olivares –Xometl, O., Likhanova, N.V., Domi'nguez-Aguilar, M.A. Hallen, J.M., Zamudio, L.S., Arce, E., (2006), Surface analysis of inhibitor films formed by imidazoles and amides on mild steel in an acidic environment, *Applied Surface Science*, 252, 2139-2152.

Oliver, B., (1959): Medicinal plants in Nigeria, Nigerian College of Arts, Science and Technology, Ibadan, P.138.

Onuchukwu , A.I., (2004a), The trend of chemical- induced corrosion failure the mechanism and control practices, Journal of Corrosion Science and Technology, 2, 135 – 139.

Ostovari, A., Hoseinieh, S.R., Hashemi, S.J., (2009), corrosion inhibition of mild steel in I.M HCl solution by henna extract: A comparative study of the

inhibition by Henna leaves and its constituents, Corrosion Science, 51, 1935-1949.

Pandian, B.R., and Methnor, G.S., (2008), Natural products as corrosion inhibitor for metals in corrosive media - a review, *Material Letters,* 65, 113-118.

Peter, C. O., E. Ebenso, Udo, J. E., (2006), Azadiriacta indica extracts as corrosion inhibitor for mild steel in acid medium, *Int. J. Electrochem*. Sci.,5,978-993.

Popova,A., Christov, M., (2006), Evaluation of impedance measurements on the mild steel corrosion in acid media in the presence of heterocyclic compounds, *Corrosion Science*, 48,3208-3221.

Popova, A., Christov, M., Raicheva, S., Sokolova, E., (2004), Adsorption and inhibitive properties of benzimidazole derivatives in acid mild steel corrosion, *Corrosion Science*, 46, 1333-1350.

Pourbeix, M. (1978) Atlas of electro chemical equilibria in aqueous solutions, NACE Cebelcor, Huston. Pp 1-8

Quraishi, M.A., A. S., Vinod, K. S., Dileep, K. Y., Ashishi, K.S., (2010): Green approach to corrosion inhibition and sulphuric acid solutions by the extract of Murraya koenigii leaves, Material Chemistry and Physics, 122, 114- 122.

Quraishi , M.A., and Jaya R., (2002): Inhibition of mild steel corrosion by some marcrocyclic compounds in hot and concentration hydrochloric acid, *Materials Chemistry and physics,* 73, 118

Quraishi, M.A., Rafiquee, M.Z.A., Saxena Nidhi, and Kran Sadaf, (2008), Inhibition of mild steel corrosion in presence of fatty acid imidazoline in hydrochronic acid, protection of Metals, 44, (1), 91-98.

Quraishi M.A., and Jaya Rawat, (2002), Inhibition of mild steel corrosion by some marcrocyclic compounds in hot and concentration hydrochloric acid, *Materials Chemistry and physics,* 73, 118

Ralston, K.D., Chrisanti, S., Young, T.L., and Buchehit, R.G., (2008), Corrosion Inhibition of Aluminum Alloy 2024-73 by Aqueous Vanadium Species, *Journal of the Electrochemical society,* 155(7), 350-359.

Raja, P. B., and Sethuraman, M. G., (2008), Inhibitive effect of black pepper extract on the sulphuric acid corrosion of mild steel, *Materials Letter,* 62, 2977-2979.

Raja Pandian Bothi and Sethuraman Mathur Gopalakrisnan, (2008), Inhibitive effect of black pepper extract on the sulphuric acid corrosion of mild steel, *Materials Letter,* 62, 2977-2979.

Ralston, K.D. Chrisanti, S., Young, T.L., and Buchehit, R.G. (2008), Corrosion Inhibition of Aluminum Alloy 2024-73 by Aqueous Vanadium Species, *Journal of the Electrochemical soci*

ety, 155, (7), 350-359.

Rao, C.V., Rao, G.M.M., Kartik, R., Sudhakar, M., Methrotra, S., Geol, R.K., (2003), Ulcer protective effect of Euphorbia hirta, *J. Trop. Med. Plants,* 4, (2), 199-205

Rastogi, R.P., Mehrotra, B.N., (2005): Compendium of Indian Medicinal plants. *Publications and Information Directorate, CSIR, New Delhi*, 5,547.

Sastri, V.S., (2011), Green corrosion inhibitor: Theory and practice, first edition, John Wiley and Son Inc. Canada, pp. 1-27.

Sastri, V.S., (2010), Green corrosion theory and practice, Wiley series in corrosion Wiston ,pp. 1-120

Sastri V.S. (1998), corrosion inhibitors, John Willey & sons ltd Chichester, U.K, Pp. 5 – 10

Sastri, V.S., Packwood, R.H., Brown, J.R., (1987) Physic al metallurgy laboratories cannet Ottawa, Canada PMRL, Pp. 87 – 48

Satapathy, H., Gunasekaran, K., Kumur A.G., Rodrigues P.V., (2009), Corrosion inhibitor by Justicia gendarussa plant extract in hydrochloric acid solution, *Corrosion Science,* 51, 2848-2856.

Saviour, S.U., Ying Li., Wang, F.H., (2010), Effect of polyacrylic acid on the corrosion behavior of aluminium in sulphuric acid solution, *J. Solid State Electrochem*, 14, 2293-230.

Shimzu, K. Funeaux, R.C., Thompson, G.E, Gotoh, A. and Kobayashi, K., (1991), Nature of easy paths for the diffusion of oxygen in thermal oxide films on aluminium, Oxidation of Aluminium. 35 (5/8), 427 – 439.

Sharma, S.K., Chaudhary, A., Singh, R.V. (2008), Gray chemistry verses green Chemistry: Challenges and Opportunities, *RASAYAN Journal of Chemistry,* 1, 68-92.

Stuart, M., (1979), The Encyclopedia of Herbs and Herbalism. Orbis publishing, London. Stupnis ek-Lisac, E., Gazivoda, A., Madz arac, M., (2002): Evaluation of non-toxic corrosion inhibitors for copper in sulphuric acid, *Electrochemica Acta*, 47, 4189-4194.

Talati, J.D., Desai, M.N., Shah, N.K., (2005), meta-Submitted aniline –v salicylideness as corrosion inhibitors of zinc in sulphuric acid, *Materials Chemistry and Physics,* 93, 54-64.

Douglas, A. S., Donalald, M. W., James, E. H., Stanly, R. C., (2004), Fundamentals of analytical chemistry, Eight edition, Thomson Asia Pte Ltd., Singerpore. Pp. 230-280.

Douglas, A. S., Holler, C. W., (2011), Introduction to analytical chemistry, Eight Edition, Thomson Asia Ltd., Singapore, Pp. 180-290.

Unlig. (1921),Corrosion and corrosion control. 2nd Ed. John willey and sons inc, Pp.1-400

Vrsalovic, L., Oguzie, E., Kliskic, S.G., (2011), Corrosion inhibition of cuniofe Alloy with phenolic acids, Chemical Engineering Communications, 198: 11, 1380 –1393.

Yang, W., Yan, C., Hang, F.S., (2000), The study of the interaction of nicotine and ovine serum albumen using uv-visible spectroscopy, Chinese Chemical etters, 11 (3), 247-250.