



School of Earth Sciences and Engineering
Department of Chemical, Materials and Metallurgical Engineering

**CORROSION INHIBITION MECHANISM AND PERFORMANCE OF
SCLEROCARYA BIRREA (MARULA) LEAF EXTRACT IN ACIDIC AND
SEAWATER ENVIRONMENTS**

By

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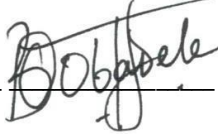
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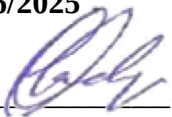
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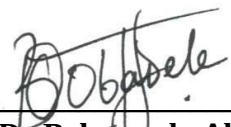
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List of Symbols and Abbreviations

β_a : Anodic Tafel constant

β_c : Cathodic Tafel constant

θ : Surface coverage

η : Global hardness

ρ : Density

σ : Global softness

μ : Dipole moment

χ : Electronegativity

AAS: Atomic Absorption Spectroscopy

AFM: Atomic Force Microscopy

ANOVA: Analysis of variance

CDL: Double-layer capacitance

CR: Corrosion rate

DFT: Density Functional Theory

E.A: Electron Affinity

E_{corr}: corrosion potential

E_{ocp}: open circuit potential

E_{HOMO}: Energy of the Highest Occupied Molecular Orbital

E_{LUMO}: Energy of the Lowest Unoccupied Molecular Orbital

FI: Food industry

FITR: Fourier Transform Infrared Spectroscopy

G: Gram

GC-MS: Gas chromatography mass spectrometry

HSS: High speed steel

H₂SO₄: Sulphuric acid

I: Ionization potential

I.E: inhibition efficiency

I_{corr}: corrosion current density
Mc: Monte Carlo simulations
Md: Molecular dynamics
MLE: marula leaf extract
mm: Millimeter
Mpy: mils of penetration per year
 ΔN : number of electrons transferred
NaCl: Sodium Chloride
OCP: Open Circuit Potential
PDP: Potentiodynamic Polarization
QM: Quantum mechanics
R_{ct}: Charge transfer resistance
R_p: Polarization resistance
SiC: Silicon Carbide
SS: Stainless steel
UV-Vis: Ultraviolet–Visible Spectroscopy
WE: working electrode
 ΔW : weight difference
W₁: weight before corrosion experiment (initial weight)
W₂: weight after corrosion (final weight)
XRD: X-Ray Diffraction

List of Publications

- 1) Shathani, P., Ogunmuyiwa, E. N., Oladijo, O. P., & Obadele, B. A. (2025). Thermodynamics and adsorption behaviour of *Sclerocarya birrea* leaf extract as a potential green corrosion inhibitor for mild steel in a simulated seawater (3.5 % NaCl) environment. *Chemical Thermodynamics and Thermal Analysis*, 19, 100197. <https://doi.org/10.1016/j.ctta.2025.100197>
- 2) Shathani, P., Ogunmuyiwa, E. N., Oladijo, O. P., & Obadele, B. A. Phytochemical characterization of *Marula* (*Sclerocarya birrea*) ethanolic leaf extract: A Precursor for Green Corrosion Inhibitor Development. **Journal name:** *Sciences of Phytochemistry* **Status:** Under review
- 3) Shathani, P., Ogunmuyiwa, E. N., Oladijo, O. P., & Obadele, B. A. Plant leaf extracts as green corrosion inhibitors of steel in acidic and seawater environments: a review. **Journal name:** *Environmental Science and Pollution Research* **Status:** Required Reviews Completed
- 4) Shathani, P., Ogunmuyiwa, E. N., Oladijo, O. P., & Obadele, B. A. Eco-friendly corrosion inhibition of API X42 5L steel in acidic media using *Sclerocarya birrea* leaf extract: Experimental and computational insights. **Journal name:** *Next Materials* **Status:** Transfer to Next Research Journal still pending
- 5) DFT and Monte Carlo simulations for the prediction of corrosion inhibition performance of selected *Sclerocarya birrea* derivatives on Al (111) surface in acidic media. **To be submitted to a Journal**

Abstract

Natural materials, especially derived from medicinal plant extracts, which are renewable, biodegradable, and highly effective, have been the core subject of research lately due to the growing demand for sustainable and environmentally benign corrosion inhibitors. This dissertation explores the corrosion inhibition potential of *Sclerocarya birrea* (Anacardiaceae .Rich) Hochst. subsp. caffra (marula) leaf extract for mild steel, API X42 pipeline steel and Aluminium (AA 1100) alloy in 3.5 % NaCl and 1 M H₂SO₄ corrosive environments. These materials are often utilized in petrochemical, water transportation and construction industries where these corrosive environments are prevalent. Initially, we used FTIR, UV-Vis, and GC-MS techniques alongside preliminary phytochemical screening to identify all the phytochemical compounds, bioactive compounds, and functional groups that will aid in suppressing corrosion. The mechanisms and effectiveness of the *Sclerocarya birrea* ethanolic extract inhibitor were assessed by a multifaceted approach expending weight loss analysis, thermodynamics and adsorption studies, electrochemical impedance spectroscopy (EIS) analysis, open circuit potential (OCP) , potentiodynamic polarisation (PDP), dense functional theory (DFT) , Monte Carlo (MC) simulations, and surface analysis such as X-ray diffraction (XRD) and Raman spectroscopic analysis. These techniques offer a thorough comprehension of the chemical interactions, adsorption processes, and inhibition efficiency that underline the leaf extract's ability to impede corrosion.

When comparing the uninhibited samples to the inhibited ones, the weight loss results for the metals revealed significant corrosion for blank exposed samples in both corrosive media. As the inhibitor's concentration increased, the inhibition efficiencies also increased, suggesting that the inhibitor's effectiveness was dose dependent. *Sclerocarya birrea* inhibitor served as a mixed-type inhibitor, lowering both anodic and cathodic processes on the metal surface, according to electrochemical investigations such as EIS and PDP. With increasing inhibitor concentration, EIS measurements indicated a decline in double-layer capacitance (Cdl) and an increase in charge transfer resistance (Rct) , demonstrating the inhibitor's ability to generate a protective barrier. Stable potential values during prolonged exposure periods demonstrated that a stable protective film has been formed on the metal surface, as confirmed by OCP measurements. Thermodynamic parameters determined by adsorption isotherms indicated that physisorption is the dominant

adsorption mechanism of the inhibitors on the metal surfaces. The best fit in both 3.5 % NaCl and 1 M H₂SO₄ corrosive solutions is given by both the Langmuir and Temkin adsorption isotherm models, which suggests a monolayer adsorption mechanism. With values compatible with physisorption interactions rather than chemisorption, the computed Gibbs free (ΔG) energy of adsorption validates the inherent spontaneity of the adsorption process.

The molecular interactions between the active ingredients in the inhibitor and metal surfaces were further explained by computational insights from DFT and Monte Carlo simulations. DFT simulations determined which functional groups in the leaf extract were responsible for adsorption; they revealed that some of these groups had a high capacity to donate electrons, which made it easier for them to interact with the metal surface. By visualizing the arrangement of extract molecules on the metal surface, simulating the adsorption process, and quantifying adsorption energy values that supported the experimental results, Monte Carlo simulations enhanced these findings. Additional layers of verification were offered by structural and spectroscopic examinations from Raman spectroscopy and XRD surface analysis. The inhibitor's significance for surface protection rather than bulk alloy change is confirmed by XRD data obtained, which also confirms that the crystalline structure of inhibited metal samples is substantially intact. Shifts in distinctive peaks linked to the mild steel, API 5L X42 pipeline steel and AA 1100 metal surfaces were revealed by Raman spectroscopy, signifying the development of a thin protective organic layer. The development of a physisorbed layer and the involvement of functional groups from the inhibitor, such as C-H, C=C, OH, and C-O, in the inhibitory process were further complemented by changes in Raman spectrum characteristics.

Overall, the results obtained from this investigative study demonstrated that *Sclerocarya birrea* ethanol extracted leaf extract exhibits outstanding inhibitory efficacy in both acidic (1 M H₂SO₄) and simulated seawater (3.5 % NaCl) environments, proving its potential as a mild steel, API X42 pipeline steel and aluminium (AA 1100) potential inhibitor that is both economical and sustainable. This study adds to the expanding corpus of research on plant-based corrosion inhibitors by shedding light on the structural effects, thermodynamic behavior, and molecular interactions of natural inhibitors on different metals. The findings imply that *Sclerocarya birrea* inhibitor's eco-friendliness and effectiveness in combating corrosion render it a strong contender for substituting synthetic inhibitors, which are frequently linked to human health and the environment threats. The

significance of multidisciplinary approaches in corrosion science is emphasized in this dissertation, which merges computational modelling and experimental approaches to clarify the complex dynamics of corrosion inhibition and advance the creation of sustainable materials that can be adopted for industrial use.

Keywords: Corrosion inhibition, *Sclerocarya birrea*, Mild steel, Aluminium (AA1100), API 5L X42 pipeline steel, 3.5 % NaCl, 1 M H₂SO₄, Inhibition efficiency

Chapter 1 Introduction

1.1 Background of the study

Metals have had a great influence on human civilization and industrialization throughout history, and they still contribute greatly to today's world of metal-based societies (McCafferty, 2010). Different metals are used in various applications, such as in pipelines and storage tanks, residential and commercial structures, automobiles, car and train manufacturing, bridges and trusses, medical appliances, and electric power, among others (Landolt, 2007). Generally, steel is the most preferred metal and is widely used because of its good microstructure, corrosion resistance, and great aesthetic appearance (Bajaj et al., 2020). Aluminum, its alloys, and matrix composites are commonly sought due to excellent properties which include their high strength to ratio weight, good corrosion resistance, recyclability, non-toxic, and superior heat and electricity conductivity (Mavhungu et al., 2017). However, the useful lifetime and efficiency of steel and any other metals are limited as they wear out over time due to corrosion phenomena.

Corrosion has become a man's worst nightmare, and the race to curb corrosion has long begun, but the ultimate stoppage of it has proved impossible. Corrosion is understood to be an electrochemical process comprising anodic oxidation and cathodic reduction in the presence of an electrolyte which deteriorates the material over time (Quadri et al., 2022).

In nature, metals exist mostly in the oxidized state of oxides or sulphide minerals, but they tend to return to their stable state by emitting energy during chemical reactions to the environment (Jones, 2003). All environments are considered corrosive to a certain degree, as degradation do occur due to the presence of acids, fresh or salt water, steam and gases, air and humidity, soils, and hydrogen sulphides, among others (Ahmad, 2006). The metals also have different grain structures and compositions from alloying and when exposed to different environments, the corrosion rate and mechanisms vary as well. Consequently, the degradation process transpires due to irreversible oxidation-reduction (redox) interactions between the metal surface and the environmental oxidizing agent, wherein the redox reactions comprise two partial reactions (Landolt, 2007). These half-cell reactions encompass the partial oxidation reaction, known as the anodic partial reaction, and the partial reduction reaction, referred to as the cathodic partial reaction. It is through these reactions where a metal will lose one or more of its loosely bound electrons in the metallic state to form a solvated cation in the solution, which is then balanced, in order to ensure an exact count of the electrons involved, by a reduction reaction in which

one or more atoms of a molecule or an ion of species in solution gain one or more of these electrons (Berradja, 2019).

According to Afolalu et al. (2017), the overall cost of other global natural disasters is lower than the cost of annual corrosion-related damages, and it has been forecasted that the cost of corrosion will rise dramatically due to lack of materials, increased energy use, and climatic change. The economic factors vary from the replacement of corroded metals, cost of production and corrosion-resistant materials, efficiency loss, shutdown costs, and so on (Regmi, 2021). The annual cost of problems resulting from corrosion globally is estimated to be around \$US 2.5 trillion, or three percent of the world's gross domestic product (Scheuer et al., 2014). According to the literature, around \$US 314 billion was spent on the direct cost of corrosion in China and was reported to be 3.34 % of China's GDP for the year 2015 (Hou et al., 2017). A related study estimated the direct cost of corrosion in the USA to be around \$US 5.427 billion, representing 2.1 % of the GDP at that time (Uhlig & Revie, 1985). This corrosion phenomenon affects other aspects, including safety, quality of product, human life, as well as the environment due to greater consumption of energy and materials (Angst, 2018).

Corrosion can have adverse effects on safety, such as fire and explosions due to sudden failure, collapse of structures, and the release of toxic products that may reach the environment, affecting water quality and human health (Kolya & Kang, 2024). Furthermore, corrosion puts constraints on natural resources since they must be replaced and repaired, which may result in a future metal crisis because the discovery of new resources is surpassed by their depletion (Ahmad, 2006). However, the rate at which the degradation process occurs can be slowed down using inhibitors.

Corrosion inhibitors are chemical agents that, when introduced in minimal amounts, reduce the rate of corrosion (Eyu et al., 2013). They safeguard the metal by adhering to its surface, creating a film layer that diminishes the oxidation reactions associated with corrosion. However, due to high toxicity, high costs, and non-compliance with environmental laws and regulations, some inhibitors (synthetic inhibitors) were banned from use despite their incredible inhibition efficiency (Zhang et al., 2023). Synthetic corrosion inhibitors offer high efficiencies in harsh aggressive mediums and have a better shelf life than organic inhibitors, but their toxicity among other factors is the major drawback in their continued use (Khadom et al., 2022). Chromate as an example of a synthetic corrosion inhibitor have been widely used for surface treatments in aerospace and steel industries but it was found to contain mutagen, carcinogen and teratogen

which expose workers directly in contact with it to high risk of cancer (Winkler et al., 2025). Thus, chromate and tin have been banned for use in metal finishing and coating across Europe and United States of America due to regulatory restrictions (den Braver-Sewradj et al., 2021). Consequently, focus has transitioned to the formulation of eco-friendly inhibitors sourced from natural plant products, encompassing seeds, roots, bark, leaves, and flowers. These green corrosion inhibitors have been proven to have high inhibition efficiency in protecting metal surfaces against corrosion phenomena, depending on the components and nature of the extract (Killaars & Finley, 2001). The organic plant extract comprises Nitrogen (N), Oxygen (O), and Sulfur (S) heteroatoms, along with other multiple bonds, containing secondary metabolites such as flavonoids, tannins, amino acids, and pigments, which exhibit inhibitory properties (A. Sharma et al., 2022). The intimate interaction between the lone electron pair and the heteroatomic metal facilitates the adsorption of these inhibitor molecules onto the metal's surface (Kaya et al., 2023a).

Several studies have been done on different leaf extracts to determine their inhibition performance on steel against corrosion, and most of them exhibited high inhibition efficiency (Dehghani et al., 2024; Zeng et al., 2024). Researchers have examined the corrosion inhibition efficacy of extracts from various plants, including mango, neem, and aloe vera, on different metals (Abdel-Gaber et al., 2022a). The efficacy of plant extracts as corrosion inhibitors is contingent upon the structural composition of the active constituents. Nevertheless, there exists a paucity of study about the application of marula leaf extract as a corrosion inhibitor, especially for various steel and aluminium alloys. This study aims to fill the information gap and elucidate the efficacy of marula leaf extract as a corrosion inhibitor for various steels in diverse conditions. Despite its status as a versatile and widely utilized indigenous tree in sub-Saharan Africa, marula leaf extract has been neglected and remains unexamined as a potential green corrosion inhibitor (Prinsloo & Street, 2013). In addition, Mashau et al. (2022) established that marula leaves are rich in antioxidants and phytochemicals, hence it places the plant extract as a promising potential for corrosion inhibition. Furthermore, from the literature surveyed it has become evident that the general awareness of the cost of corrosion faced by different industries in Botswana is still lacking and is least emphasized.

1.2 Statement of the problem

There has been a more rapid increase in the industrial application of metals like mild steel, aluminium and pipeline steel in more aggressive environments like seawater and acidic

conditions (Hossain et al., 2022a). Prolonged usage of metals in such environments subject them to severe deterioration and release of metallic ions to their immediate environment. In a quest to solve this nightmare, the world suffers a severe annual monetary loss on costs associated with combating corrosion.

The utilization of inhibitors has become prevalent to mitigate corrosion costs and protect metals. However, since they are costly, non-biodegradable, and loaded with hazardous substances, common synthetic corrosion inhibitors like chromates, nitrates, and sulphates have significant drawbacks and are being faced off. Due to these factors, researchers are looking for eco-friendly alternatives, such as using extracts from medicinal plants to substitute synthetic inhibitors. Marula plant has good medical qualities and is inexpensive, environmentally benign, and biodegradable. Historically, extracts from the *Sclerocarya birrea* tree have been utilized to address many ailments and medical issues (Gouwakinnou et al., 2011). One of the most often used extracts is the tree bark, which has been used to treat illnesses such as diarrhea, gangrenous rectitis, dysentery, proctitis, fever, stomach disorders, and ulcers (Eloff, 2001). Another component of the plant often sought after for its therapeutic purpose is the root, which was used to heal eye sores. This phenomenal tree has been found to boost a great variety of phytochemical compounds and bioactive organics which makes it a compelling candidate for corrosion inhibition studies.

However, till date no research has been done in the literature surveyed on the application of marula leaf extract for metal corrosion inhibition in any kind of aggressive media. This study aims to assess the efficacy of marula leaf extract as a sustainable corrosion inhibitor for mild steel, aluminium, and pipeline steel in acidic and seawater environments.

1.3 Aim and Objectives

1.3.1 Aim

The primary objective of this study is to examine the corrosion inhibition mechanism and efficacy of marula (*Sclerocarya birrea*) leaf extracts in mild steel, aluminum (AA 1100), and API 5L X42 pipeline steel in both 1 M H₂SO₄ and 3.5 % NaCl.

1.3.2 Specific Objectives

1. Reviewing the recent progress on corrosion inhibition and current knowledge of leaf extracts as corrosion inhibitors for metals in acidic and seawater environments, focusing on their effectiveness, inhibition mechanisms, and influencing factors.

2. Conduct phytochemical analysis of *Sclerocarya birrea* ethanolic extract using preliminary phytochemical screening, UV-Vis, FTIR and GC-MS to identify all phytochemical compounds and heteroatoms present that may aid in corrosion inhibition.
3. Employ weight loss and electrochemical techniques (EIS, PDP, and OCP) to determine the influence of inhibitor concentration on the corrosion rate and overall inhibition efficiency in both 3.5 % NaCl and 1 M H₂SO₄.
4. Assessment of *Sclerocarya birrea* inhibitor adsorption mechanism on metal surfaces using adsorption isotherms and thermodynamic studies.
5. Perform quantum chemical calculations (Density Functional Theory and Monte Carlo simulations) to anticipate and confirm the adsorption mechanism, reactivity, and stability of inhibitor molecules on metal surfaces.
6. Analyze surface characteristics and morphological changes induced by the inhibitor using Raman spectroscopy and X-Ray Diffraction techniques, as well as comparison of the inhibition mechanism and efficiency of the results obtained.

1.4 Research Questions

1. What is the current research state of plant leaf extracts as a corrosion inhibitor for steel in acidic and seawater environments?
2. Which phytochemical compounds are present in ethanolic extract of *Sclerocarya birrea* leaf which aid its inhibition capabilities in simulated seawater and acidic environment?
3. Does the marula leaf extract have a corrosion-inhibiting effect on mild steel, aluminum (AA1100) alloy, and pipeline steel?
4. What is the impact of elevated inhibitor concentration on the overall inhibition efficiency and corrosion rate of metals?
5. What is the probable inhibition mechanism by which the leaf extract uses to retard the corrosion in both the environments?
6. How does the performance of the leaf extract compare in metals exposed to seawater to those that are exposed to 1 M H₂SO₄?
7. What molecular attributes of the inhibitor molecules enhance their corrosion inhibition performance as demonstrated by DFT and Monte Carlo simulations?
8. How do the surface appearance and structural properties of the metals differ with and without the leaf extract inhibitor?

1.5 Justification of the Study

Current research endeavors predominantly focus on identifying environmentally friendly corrosion inhibitors, particularly those derived from plant extracts, due to their demonstrated efficacy in mitigating corrosion. Marula tree is a widely distributed tree in Botswana, and it is one of the least utilized trees in the country although research has shown its rich medicinal value. The phenomenal marula plant extracts have never been examined or explored for potential use as a corrosion inhibition agent; hence, this investigation is essential to reveal the possible application of the leaf extract in corrosion inhibition. Success of this study will serve as a relief to the economic burden that the country suffers yearly in procurement of expensive synthetic corrosion inhibitors and other direct costs that can be curbed using eco-friendly corrosion inhibitors. Additionally, this will make it easier to investigate the possible use of additional extracts from the same tree, such as its roots, flowers, seeds, and fruit peels, as inhibitors in future research. Organic inhibitors have been used to inhibit various metals in seawater (3.5 % NaCl) and acidic conditions but there is limited literature on experiments conducted for extended periods of more than a month.

1.6 Scope of the study

This study investigated the proposed low-cost, environmentally friendly, non-toxic ethanolic leaf extract of *Sclerocarya birrea* as an effective green corrosion inhibitor for mild steel, aluminium (AA1100), and API 5L X42 pipeline steel in acidic and simulated seawater environments. The study covered the impact of process factors such as temperature and inhibitor concentration on overall inhibitor efficacy and corrosion rate. The adsorption mechanism on metallic surfaces was investigated by adsorption isotherms, quantum chemical computations, electrochemical analyses, and surface characterization. The results of this study are inconclusive but will require other analytical equipment like X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM), Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX) and Atomic Adsorption Spectroscopy (AAS) to assess the detailed mechanism of corrosion inhibition, complex compounds formed and interactions at the metal-media interface.

Chapter 2 Literature Review

2.1 Properties and industrial applications of metals (mild steel, pipeline steel, aluminium)

Metals are naturally occurring elements characterised by their metallic properties, including good thermal and electrical conductivity, malleability, durability, and ductility (John Wiley & Sons, 2002). They are typically solid at room temperature (except mercury) and are known for their ability to lose electrons, forming positive ions. Metals can also be combined to increase their hardness and strength, forming alloys such as steel (Sigircik et al., 2016).

Steel is an alloy primarily made of iron and carbon as well as many other elements such as manganese, chromium, molybdenum, and nickel (Rao, 2011). It is mostly abundant in the earth's crust in the form of Fe_2O_3 and needs less energy to convert it to Fe (Sultana et al., 2014). Additionally, it can be made to exhibit a variety of microstructures, resulting in a wide range of mechanical properties. With such versatility, steel is widely used in various applications and industries, including construction, power plants, aircraft, transportation, and manufacturing, among others. Based on their chemical composition, microstructure, and purpose for use, steel materials are made in different grades, such as mild steel and pipeline steel (Stranghöner et al., 2019). However, due to their differences in composition and availability, some are used in more applications than others. Steel can also be in the form of pipeline steel, which is generally used as a transportation vector mostly in water, oil, gas, and other pipeline industries because it offers the highest safety, an economic solution, higher strength, more corrosion resistance, high toughness, good thermomechanical rolling, and better welding properties (Jie et al., 2022). The pipeline steel has a low carbon content but can be micro-alloyed with manganese (Mn), niobium (N), vanadium (V), molybdenum (Mo), copper (Cu), and nickel (Ni). This is to compensate for the reduction of mechanical properties resulting from reduced carbon content and increase the strength of the steel to a higher grade (Wang et al., 2015). Pipeline steels are often subjected to high stresses due to internal pressure (radial stress, hoop stress, and longitudinal stress) from the fluids or gas they transport, external traffic, and environmental attacks, which can all cause damage (Ghelloudj et al., 2021). Consequently, their electrochemical and mechanical properties deteriorate over time and so is their resistance to environmentally assisted cracking (Nykyforchyn et al., 2021).

Mild steel has outstanding toughness, ductility, a relatively low price, high machinability, and weldability properties, so it is the most common form of steel used in engineering fields (Umeozokwere et al., 2016). It is a low-carbon steel that can be reshaped into various forms because of its malleability and is used to make, among other things, jigs and fixtures, axles, shafts, bolts, pins, and automotive parts (Rao and Nayak, 2019). It can also be used to prevent cracking in severe bends, improve drilling and punching processes, and is also commonly used in construction. However, mild steel is typically much heavier, weaker, and less durable compared to other steels but can still be strengthened through heat treatment. This treatment involves heating and cooling the steel to change its microstructure, thus enhancing its strength (Daramola et al., 2010). This type of steel lacks a protective coating, which means the present iron can easily react with the moisture in the air to produce iron oxide, also known as ‘rust’. Nonetheless, rust or any other form of corrosion can be prevented through galvanization to protect the steel (Chuka et al., 2014).

Aluminium is one of the metals which is extensively used in the industry and domestic applications such as reactions vessels, condenser tubes, storage tanks, construction material in marine, chemical batteries, pipes and machinery because it has low weight, low price and a high energy density (Olawale et al., 2018). Aluminium possesses a crucial characteristic of exceptional corrosion resistance, attributed to the formation of a thin, adherent, and protective surface oxide layer upon exposure to air (Yin et al., 2008). Aluminium and its alloys are reactive materials susceptible to corrosion when exposed to harsh conditions, such as acidic and alkaline solutions. Once the amphoteric oxide film is dissolved, aluminium and its alloys corrode (Kasuga et al., 2017). The degradation of the protective oxide layer on the aluminium surface renders it susceptible to corrosion when exposed to corrosive medium (Nesane et al., 2023). The corrosion of aluminium typically proceeds through pitting corrosion, where small pits form in the oxide layer exposing the underlying aluminium to the environment (Popova & Prošek, 2025).

Even though steel and aluminium play a critical role in engineering fields and used in several industrial applications, their optimal performance can be affected during operation as they are subjected to various forces within a given environment (Alhassan et al., 2020). Gradually, their mechanical qualities degrade due to the chemical or electrochemical reaction between the material and its environment, known as corrosion (Li et al., 2015). The literature further reveals corrosion as irreparable damage to the metal surface because of chemical reactions where there is an exchange of electrons between steel and its environment (Zhang et al., 2022).

Subsequently, the pure metal is converted to its chemically more stable form, such as hydroxides, sulphides, oxides, etc., and the reaction is both spontaneous and electrochemically favoured (Harsimran et al., 2021). That's, the metal becomes oxidized by losing an electron, which will be gained by the environmental substance acting on the metal and becomes reduced. During corrosion mechanisms, electrons are transferred from the anode to the cathode in each conductive solution (Kadhim and Albdiry, 2017). This study further states that the metal at the anode experiences oxidation through the liberation of free electrons, while the cathodic metal is reduced by accepting the electrons. Consequently, the metal with a lower reduction potential function as the cathode, while the metal with a larger reduction potential serves as the anode; thus, corrosion happens at the anode metal. According to Chigondo and Chigondo (2016), the tendency of the steel to corrode can be determined by the microstructure, composition as formed during the alloying process, or temperature for deformation of a single metal surface developed during fabrication (Fernandes and Montenor, 2015). Furthermore, the presence of electrolytes, the reactivity of steel, the existence of air, moisture, pH levels, gases such as sulphur dioxide and carbon dioxide, and contaminants can induce corrosion. This is a superficial phenomenon that manifests in multiple forms, including pitting, stress corrosion cracking, galvanic corrosion, crevice erosion, and intergranular corrosion, among others (Zhang et al., 2022).

Corrosion in mild steel is different compared to other steel because it does not have the strongest corrosion resistance properties. Once exposed to a corrosive environment such as air or soil where there is water, oxygen, sulphide ions and chloride ions, the iron atoms on the surface layer of mild steel will react with these elements, causing oxidation, which is known as rusting (Umeozokwere et al., 2016). Concurrently, pipeline steel is susceptible to corrosion on both its interior and outside surfaces, as the iron dissolves through reactions with moist soil, groundwater, or seawater in the external environment, while internal corrosion is triggered by the water consisting of hydrogen sulphide, carbon dioxide, or sodium chloride ions (Baker et al., 2008). Aluminium inherently resists corrosion due to its oxide layer and is stable within a pH range of 4-9; but it corrodes in the presence of hostile ions (Nambiar et al., 2021). The oxide layer significantly dissolves when the metal encounters strong acidic or alkaline solutions (Oguzie, 2006).

2.2 Forms of Corrosion

Multiple factors can affect the corrosion rate, such as the type of metal, the corrosion mechanism, and the characteristics of the corrosive environment. These have led to

classification of corrosion into different forms and the major types which have been identified include stress corrosion cracking, uniform, galvanic, pitting, crevice, intergranular, erosion and atmospheric corrosion (Cragnolino, 2021; Kamachi Mudali et al., 2019).

2.2.1 Erosion corrosion

Chukwuemeka et al. (2022) assert that this form of corrosion transpires when the metal surface experiences quick deterioration due to mechanical assault from heightened interaction between the corrosive fluid and the metal surface. In addition, this form of corrosion happens through the combination of corrosion and abrasion or attrition. For action of corrosion and abrasion to occur, solid particles found in the liquid must be harder than the metal affected while in combination of corrosion and attrition, the fluid does not consist of any suspended solids or contains particles softer than the metal (Charng and Lansing, 1982). The protective oxide layer is eliminated during these procedures, so exposing the metal surface to corrosion. Figure 2.1 below shows a pipeline severely deteriorated by erosion corrosion.



Figure 0.1: Erosion corroded metallic component (Source: ((Ajoku et al., 2021))

2.2.2 Stress corrosion cracking (SCC)

This is the modification of metals subjected to tensile stress in a certain corrosive environment, which can be fast-tracked by residual internal stress in the metal or externally applied stress (Eliaz, 2019). SCC occurs mostly in alloys than metals, at high temperatures. For SCC to take place when these factors are fulfilled; tensile stresses; the presence of susceptible material; and subjection to corrosive environment (Harsimran et al., 2021). As residual stress is applied to the material, a small pit forms and grows into a crack, exposing a new active metal surface that will corrode more quickly. This leads to increased fracture propagation, which exposes the new highly active metal surfaces in the crack, rapidly accelerating the metal dissolving until a mechanical failure occurs (Hilti, 2015). Figure 2.2 below depicts a metal which has encountered stress corrosion cracking.



Figure 0.2: Image showing stress corrosion cracking (<https://us.sfs.com/learn-more/detect-prevent-hydrogen-assisted-stress-corrosion-cracking>)

2.2.3 Uniform corrosion

In this form of corrosion also known as general corrosion, the attack is evenly distributed in the metal surface, where there is dissolution of metallic component into metal ions which causes general thinning of the metal and gradually fails (Hansson, 2011). Corrosion proceeds at the same rate over the entire metal surface with oxygen acting as the primary cause. According to Harsimran et al. (2021), cast iron and steel are the most common materials affected by this type of corrosion where they give rusty-like appearance once exposed to moist atmosphere. A metal which has suffered from uniform corrosion is displayed in Figure 2.3 below.

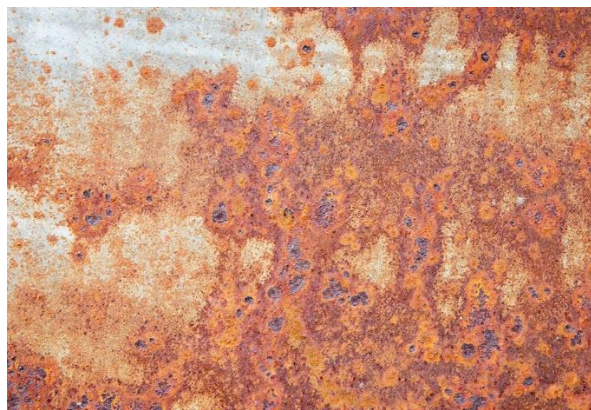


Figure 0.3: Image showing uniform corrosion (<https://steelfabservices.com.au/uniform-corrosion/>)

2.2.4 Pitting corrosion

Pitting corrosion starts in a tiny area of a metal but gets larger and deeper, leaving pits on the surface. Generally, this is extremely localized attack on the passive film which happens to passivated metals and alloys (Harsimran et al., 2021). In addition, the chemical composition of the material, presence of chloride ions, mechanical stress and pH level of the environment can

influence the pitting corrosion. Once the pit is formed, a concentration-cell forms because the base of the pit is less accessible to oxygen than the metal surface. The reduction of oxygen in the pit results in reduced production of hydroxyl ions, enhancing the accumulation of positive charges in the form of Fe^{++} which will then attract negatively charged chloride ions (Charng and Lansing, 1982). Consequently, the created ferrous chloride hydrolyses to form insoluble ferrous hydroxide, which contains excess hydrogen and chloride ions, accelerating the corrosion at the pit's bottom. Metal specimen which has suffered from pitting corrosion is displayed in Figure 2.4 below.



Figure 0.4: Image showing pitting corrosion (<https://steelfabservices.com.au/pitting-corrosion/>)

2.2.5 Crevice corrosion

It refers to the corrosion that happens in confined spaces such as gaps between parts, under gaskets, lap joints, inside cracks and so forth, where immobile solution is trapped and not changed (Hansson, 2011). This can also be defined as the form of corrosion that take place when a slight volume of stationary corrosive fluid is trapped in the interface between two materials in a protected region (Chukwuemeka et al., 2022). The gap or crevice formed creates a microenvironment different from the surrounding environment and this change maybe more anodic, causing the metal to corrode than it would generally in the surrounding environment. A typical example of a metal undergoing crevice corrosion is depicted in Figure 2.5 below.



Figure 0.5: Image showing crevice corrosion (<https://steelfabservices.com.au/crevice-corrosion/>)

2.2.6 Intergranular corrosion

It is a localized corrosion that primarily occurs along the grain boundaries of metals or alloys and is caused by the difference in potential between anodic borders and grains (Birbilis and Hinton, 2011). Furthermore, it is the form that results from the segregation of impurities at the grain borders or the depletion of one of the alloying elements in the grain boundary area (Regmi, 2021). Intergranular corrosion also initiates from a pit but grows rapidly along the susceptible intergranular pathways as shown in Figure 2.6.



Figure 0.6: Image showing intergranular corrosion (<https://steelfabservices.com.au/intergranular-corrosion/>)

2.2.7 Atmospheric corrosion

This is a naturally occurring form of corrosion where the metal is exposed to air and its pollutants and the electrochemical process result from the presence of an electrolyte (Chukwuemeka et al, 2022). For this corrosion to occur, specific parameters must exist, such as the amount of time moisture is in contact with the metal surface, the chemical composition,

the degree of pollution in the atmosphere, and temperature (Ahmad, 2006). Figure 2.7 depict a pipeline which has suffered from atmospheric corrosion.



Figure 0.7: Image showing atmospheric corrosion (Source: Ajoku et al., 2021).

2.2.8 Galvanic corrosion

In this form of corrosion, there is contact between the two different materials through the transmission process where one metal gives up more electrons to the other, also known as the electrochemical process (Chukwuemeka et al., 2022). In this process one metal is protected and becomes cathodic due to slow corrosion rate at the expense of the other which becomes more anodic as it corrodes faster (Zehra et al., 2022). Galvanic corrosion occurs when distinct types of metals, electrolyte, and electrical continuity between the two metals are simultaneously met (Vargel, 2004). Overall, the process involves the dissolution of the anode and the deposition of the metal at the cathode, which enhance corrosion at the anode than it would in isolation. Figure 2.8 below shows galvanic corrosion on the steel bolt and nut.

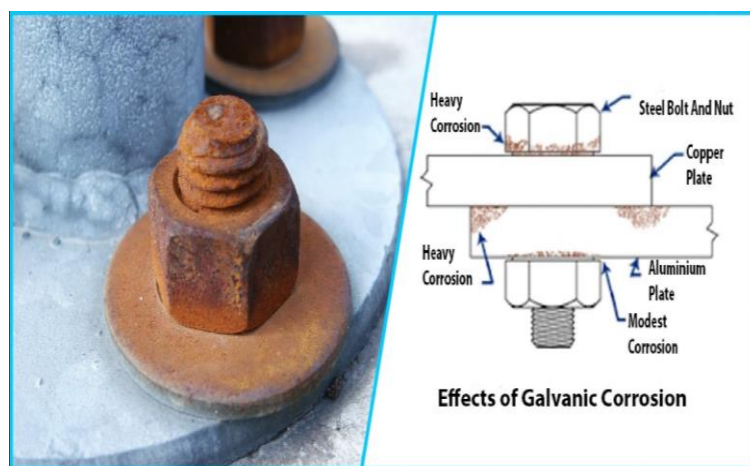


Figure 0.8: Image showing galvanic corrosion (<https://blog.thepipingmart.com/other/what-is-galvanic-corrosion/>)

2.3 Corrosive Environments (Acidic and Seawater) for Pipeline steel, Mild steel and Aluminium

Generally, almost all environments are corrosive to some degree, especially in the presence of air, moisture, salts, gases, alkalis, oxides, acids, organic, and inorganic materials, among others (Fontana, 1987). However, the corrosion mechanism mostly occurs in acidic and seawater environments. Acid solutions are generally utilized for a variety of reasons, including oil well acidizing, acid pickling, acid descaling, and industrial acid cleaning, even though they are aggressive and cause significant metal disintegration (Omah et al., 2020). The acidic agents frequently utilized are phosphoric acid, hydrochloric acid, sulphuric acid, and nitric acid, with hydrochloric acid (1 M) and sulphuric acid being the most used since they provide remarkable performance in the pickling process (Huang et al., 2023). The use of these strong acidic solutions results in corrosion of metal substrates as well as "hydrogen embrittlement" and severe losses of metal materials (Zhu et al., 2022). According to Shibli et al. (2022), the effect of the acidic environment depends on the acid strength, metal resistance, contact time, and temperature.

In marine conditions, metals are corroded due to the presence of chloride ions in oil, gas, water, and other liquids transported via pipeline steel industry (Shyamvarnan et al., 2021). Seawater is highly corrosive and rich in natural electrolytes; hence, the chloride ions can penetrate the coating film to the surface of the metal using the radioisotope technique and cause dissolution of the metal (Cui et al., 2019). As a result, an electrochemical interaction between the chloride ions and the oxide layer on the metal surface would generate metal ions, which subsequently change into hydrogen ions, shattering the protective layer on the metal surface and causing a potential difference between the bare metal and the film (Şahin et al., 2008).

2.4 Cost of Corrosion (direct and indirect costs)

Corrosion is a serious problem, especially in the industrial sphere, as there are direct and indirect costs incurred by the engineering fields. Direct expenses include capital costs (replacement), control costs (constant maintenance and repair), and design costs, which include the use of corrosion inhibitors, extra corrosion-resistant metals, and protective coatings (McCafferty, 2009). This is a requirement for both steel and aluminium since they are utilized in a wide range of industrial applications, and there is a need for guaranteed consistent conditions of safety, economy, and usefulness over the lifespan of infrastructure and equipment (Komary et al., 2023). The cost of corrosion has been shown to outweigh the entire damage caused by all natural disasters combined, including storms, earthquakes, and floods. According

to the World Corrosion Organisation (WCO), the yearly cost of corrosion-related problems worldwide is projected to be \$US 2.4 trillion, or 3 % of global GDP (Scheuer et al., 2014). Koch et al. (2002) found that between 1999 and 2001, the yearly direct costs of corrosion in the United States were \$276 billion.

The costs of corrosion can also be indirect, which involve the shutdown of plants (power and manufacturing plants), loss of product due to leakage caused by corrosion, and contamination of the product from rust particles (Uhlig and Revie, 1985). Besides the economic losses, corrosion can also cause casualties due to structural collapses of infrastructure if there is no maintenance or repair of the equipment. Yang (2020) reported a casualty incident where 215 lives were claimed and 1500 injured in the sewer explosion in April 1992 at Guadalajara, Mexico, which was linked to the degradation in the gas pipeline steel, thus leaking gas into the nearby sewage main. The environmental pollutants can be leaked and introduced into the environment because of the corrosion aftermath (Hussein et al., 2023) . All these risks and costs to the environment could further increase in the future, especially in the oil and gas pipeline steel industry, because new hydrocarbon sources continue to be discovered in more challenging environments, including deeper reservoirs with extreme pressures and temperatures that contain acid gases with higher concentrations (Kostić et al., 2022). Figure 2.10 gives a summary of costs that could be incurred associated with corrosion.

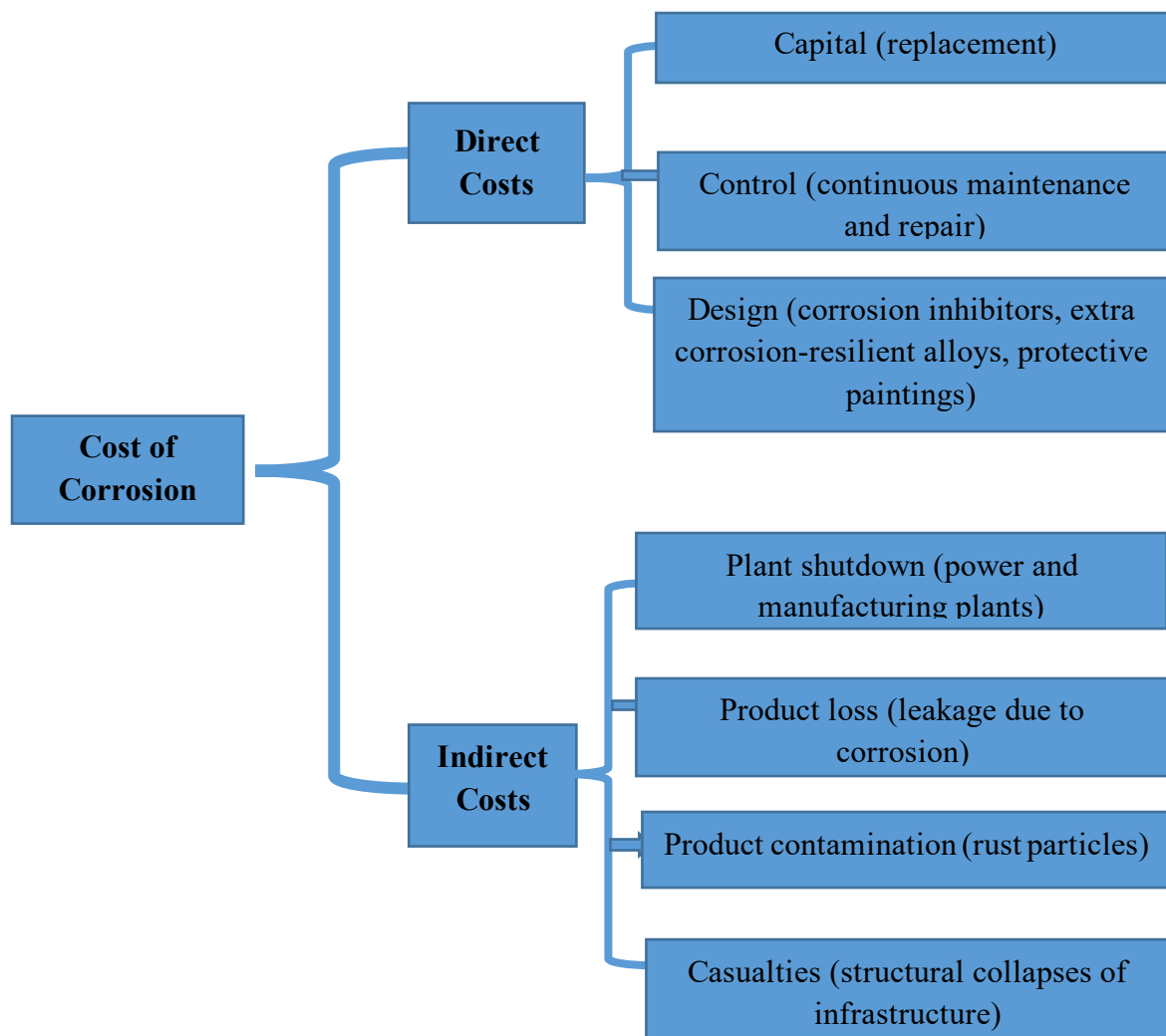


Figure 0.9: Schematic diagram summarising the costs of corrosion (Koch, 2017).

2.5 Corrosion control

To preserve the material and structural integrity, material degradation caused by its interaction with the environment must be reduced. Since corrosion develops naturally when a material is exposed to an aggressive environment over time, corrosion control has traditionally proven to be a difficult operation (Eliaz, 2019). Corrosion control encompasses arrays of techniques that aim to prevent, mitigate, and manage the corrosion processes. The three critical steps required to control any corrosion mechanism are i) understanding the applicable corrosion threat mechanism(s) affecting the asset, ii) selecting and implementing appropriate prevention and iii) mitigation measures, and monitoring conditions to assess whether the control measures are effective or if adjustments are needed (Skovhus et al., 2017). Amidst all the challenges posed by corrosion, there are numerous strategies that the industry has embraced and put into practise

to combat corrosion, including good material design, proper material selection, cathodic or anodic protection, control of the aggressive environment, and by using inhibitors (J. S. Fernandes & Montemor, 2015). One other preventive method widely adopted by industries to combat corrosion is using barrier coatings like paints, powders, waxes and plastics to form a cover layer on the metal surface. Figure 2.10 below illustrates paint coating applied on the metal before utilization.



Figure 0.10: Blasting and painting used as a corrosion control measure (https://www.dookwuise.com/corrosion_control.php#)

Proper material selection for a desired function and environment of operation is one of the strategies that is implored to minimize the effects of corrosion on materials. Many industries have embraced the proper material selection to fit a specific corrosion service as a corrosion prevention strategy since it is recognized to maintain the material. The wrong choice of material for a given corrosive environment can result in structural failure, a limited lifespan, and a loss of structural integrity (Beaumont, 2020). The most important area in corrosion control is a design consideration. Material designers need to have the necessary expertise to ascertain the mechanical characteristics and strength of a specific construction that will increase its corrosion resistance (Kehr, 2021). Because of the uniqueness of its features, the material's improved mechanical and physical qualities make it more attractive for usage in several applications, particularly those where corrosion is an issue.

Furthermore, corrosion can be reduced using electrochemical protection (anodic or cathodic protection). This method applies to metal installed in an electrolyte medium, such as sea water, in which the shielded metal is connected to the cathode of the electric source and a sacrificial metal is attached to the anode (Arya & Dhanya, 2021). The sacrificial metal (which is positively charged) corrodes throughout this process, protecting the covered metal from corrosion. Corrosion can also be slowed down by controlling the immediate environment by simply reducing the chemical contact between the metal and the surrounding gases (Maji & Lavanya,

2024). For example, reducing sulphur, chloride, and oxygen levels in the atmosphere can delay the rate of corrosion (Lou et al., 2021).

Inhibitors have been shown to be the most cost-effective, practical, and easy corrosion control strategy for metals in aquatic situations (Solomon & Umoren, 2015). Inhibitors create a protective barrier on the metal surface and interact with anodic or cathodic reaction sites to limit oxidation or corrosion reactions (Singh et al., 2016). By either raising the activation energy needed for the metal dissolution process or by blocking active anodic sites and creating a passive layer on the metal surface that will impede metal dissolution, these inhibitors help slow down the rates of anodic corrosion (Al-Amiery et al., 2023). Examples of anodic inhibitors include molybdates, orthophosphates, chromates and phosphates. Unlike anodic inhibitors, cathodic corrosion inhibitors work by adsorbing on the metal surface to create a protective layer (Kuznetsov & Redkina, 2022). Examples of cathodic inhibitors are amines, hydrazine and nitrates. Some inhibitors are mixed type implying they can effectively slow down both the anodic and cathodic metal dissolution processes through formation of a protective layer and competing directly for electrons with oxidants. Mixed type inhibitors currently employed in different industries include polyphosphate silicate, benzotriazole and tolytriazole (Kuznetsov, 2018).

2.6 Synthetic and Green Corrosion Inhibitors

Corrosion is inevitable where there is metal involved, but the rate at which it occurs can be reduced or slowed down using anti-corrosion methods, which include the use of inhibitors. According to Eyu et al. (2013), a corrosion inhibitor is described as an inorganic or organic chemical substance that, when added in an adequate amount to an aggressive environment, reduces the rate of corrosion. The classification of corrosion is presented in Figure 2.11. An inhibitor protects the metal surface by either serving as a barrier by adsorbing themselves on the metallic surface (physical adsorption) and producing a coating on the surface or by slowing the anodic, cathodic, and mixed processes (Pacheco et al., 2011). In addition, they enhance the cathodic and anodic polarisation behaviours, elevate the electrical resistance of the metallic surface, and reduce the mobility of ions on the metal surface (Oguize et al., 2004). These substances, which can either be organic or inorganic, have attracted great attention as one of the best strategies for decelerating corrosion rates to have ever been put forward by the engineering community (Veedu et al., 2022).

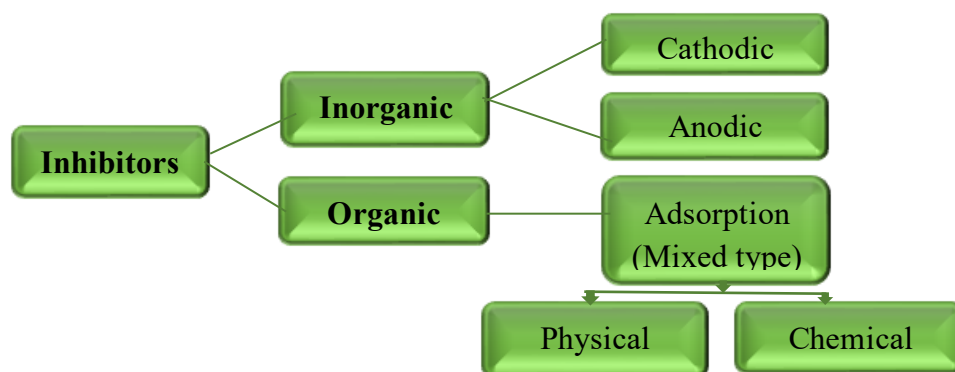


Figure 0.11: Schematic classification of corrosion inhibitors (El Hamdani et al., 2015).

Despite having been demonstrated to be particularly successful in corrosion prevention, inorganic (synthetic) inhibitors such as chromates, nitrates, sulphates, amines, and benzoates were deemed expensive and exhibited non-biodegradable traits. Therefore, their use has diminished, and most have been banned across the world as they showed a carcinogenic and toxic nature to human health and animals; thus, strict environmental regulations and health protocols were against their usage (Lee et al., 2015). These synthetic inhibitors may have permanent or temporary effects, such as damage to the liver and kidneys, either during their synthesis or during their application (Okafor et al., 2011).

On the other hand, organic (green) inhibitors have been used as alternatives to inorganic inhibitors because they are eco-friendly, do not contain any hazardous compounds or heavy metals, and are affordable as they can mostly be attained from green sources such as leaves, fruits, roots, flowers, stems, and seeds of the plants (Tabatabaei majd et al., 2019). Further, these natural substances have a low concentration requirement, high efficiency against corrosion, require a simple procedure to extract, contain polar functions (P, N, S, and O atoms), and have major adsorption centers with conjugated carbon rings that have aromatic rings (Omah et al., 2020). Verma and Khan (2016), reported that heteroatoms aggressively do transfer a lone pair of electrons to generate a coating layer on the metal surface, assisting the attaching of the obstructing particles onto the surface of the metal with unoccupied d orbitals, thereby playing a crucial role in the inhibition of corrosion. Green corrosion inhibitors can be broadly categorized into three classes: cathodic inhibitors, anodic inhibitors, and mixed

inhibitors. Assad and Kumar (2021) established that the cathodic corrosion inhibitors reduce the oxygen atom and the evolution of hydrogen gas at the cathode, thus effectively slowing down the corrosion process. Substances with low solubility, such as calcium and magnesium carbonates, are the ones that block the cathodic sites (Sastri et al., 2007). The study also indicated that anodic corrosion inhibitors work by interacting with the metal surface to form insoluble hydroxide, which impedes the binding site of the metal surface and raises the potential of corrosion, slowing the process and preventing further oxidation. Anodic inhibitors are often effective in the pH range of 6.5–10.5, and such potent oxyanions include, among others, chromates, sodium nitrite, and molybdates (Nwigwe and Nwoye, 2023). Meanwhile, mixed inhibitors are substances that suppress both the anodic and cathodic processes, i.e., inhibitors containing phosphonate, carboxyl, or amino operate as barriers to the anode dissolution and cathodic oxygen reduction (Sastri, 2011).

2.7 Corrosion Inhibition Mechanism of the Leaves

Inhibitors encompass heteroatoms (P, N, S, and O) that adsorb directly on the surface of the metals, forming a passivating layer, and the organic inhibitors are the ones with the most effective adsorption molecules as well as the ions (Okewale and Olaitan, 2017). The adsorbate layer reduces the rate of corrosion on the metal surface by isolating the surface of the metal from the corrosive agent (Mejha et al., 2010). Through different mechanisms, inhibitors can delay the corrosion process, and they are classified based on their mechanism of action, such as scavengers, oxidizers, hydrogen evolution poisons, adsorption-type inhibitors, and vapor phase inhibitors (Begum et al., 2021). Previous research has proven that surfactant corrosion inhibitors, notably from plant extracts, have a high ability to protect metals from corrosion (Salleh et al., 2021). The extracts consist of phytochemical compounds including alkaloids, amino acids, flavonoids, proteins, tannins, polyphenols, and anthraquinones, which have been considered potential corrosion preventative agents (Fang et al., 2019). This was proven by Raja et al. (2013), where the anti-corrosion properties of alkaloids derived from the leaves and bark of the *Ochrosia oppositifolia* plant were examined for mild steel in 1 M HCl medium. Similarly, anti-corrosion behavior for different amino acids with several ions was also examined on mild steel in 40 % H₃PO₄ by Morad et al. (2002). Also, aloe vera leaf extracts were studied in 1 M HCl and constituted rutin, chrysophanol glucoside, anthranol, aloin-barbaloin, and aloin-emodin, which were considered to have an inhibition effect (Obot et al., 2013).

The active functional groups found in these green corrosion inhibitors have unpaired electrons that are ready to interact with the metal specimen in contact, where both physical and chemical adsorption occur (Shibli et al., 2022). For electron-pair adsorption, the protonated molecules of the polymer are attracted to the positively charged molecules of the metal. However, Shibli et al. (2022) further revealed that in the adsorption process, there is competition for electron between the molecules of polymer and the hydrogen ions once they are adsorbed on the metal surface, thus releasing hydrogen gas and polymer molecules, hence neutralizing the process. As the metal gains more electrons and becomes more negative, hydrogen in the environment and oxygen molecules on the metal surface simultaneously build up. Therefore, electrons will be transferred from the d-orbital of Fe to the vacant π orbital, removing the extra negative charge from the polymer and enabling its effective adsorption on the metal (Mobin and Rizvi, 2017).

2.8 Inhibition Performance: Efficiency

Different organic inhibitors have been studied to prove their performance against corrosion in various media. To determine the efficiency of an inhibitor, various methods are employed based on the medium. These methods include weight loss, scanning electron microscopy with energy-dispersive X-ray spectroscopy, electrochemical impedance techniques, Fourier transform infrared, density functional theory, and atomic force microscopy (Fang et al., 2019).

Based on the nature of the extract and its components, green corrosion inhibitors have shown various inhibition performances against the rate of corrosion, and their efficiencies are depicted in Table 2.1.

Table 0.1: Corrosion inhibition performance efficiency for various plant leaf extracts in acidic and alkaline environments.

Leaf inhibitor	Metal	Media	Method of investigation	Maximum inhibition efficiency (%)	References
Cabbage extract	X70 steel	1 M HCL	SEM, XPS, AFM, DFT, MD	95.87	(Sun et al., 2022)
Groundnuts	Mild steel	1 M H ₂ SO ₄	Response Surface Methodology (RMS)	86.30	(Olawale et al., 2018)
<i>Pimenta dioica</i>	Mild steel	0.5 M & 1 M HCl	EIS, PDP	99.00	(Anupama et al., 2015)
<i>Azadirachta indica</i>	Mild steel	2.0 N HNO ₃	WL	80.50	(S. K. Sharma et al., 2010)
<i>Gossipium hirsutum L.</i>	Aluminium	2 M NaOH	WL	97.00 (leaves) 94.00 (seed)	(Abiola et al., 2009)
<i>Ziziphus spina-christi</i>	Mild steel	3.5 % NaCl	SEM/EDS, OCP, EIS, GXRD	91.52	(Shahryari & Gheisari, 2023)
<i>Crataegus oxyacantha</i>	Carbon steel	1 M HCl	WL, SEM/EDS, PDP, UV-Vis	94.00	(B. F. Zehra et al., 2022)
<i>Gingko biloba</i>	J55, N80, P110SS and C110 steels	3.5 % NaCl	HPHT autoclave, SEM, XRD	J55 – 96.00 C110 – 58.00 N80 – 89.00	(A. Singh et al., 2014)

				P110SS – 74.00	
<i>Eucalyptus</i>	Mild steel	3.5 % NaCl	EIS, PDS, GIXRD, SEM/EDS, UV-Vis	90.00	(Tabatabaei majd et al., 2019)
<i>Lippia javanica</i>	Aluminium	1 M HCl	EIS, PDP, UV-Vis, FTIR, Contact angle	91.89	(Nesane et al., 2023)
<i>Nandina domestica</i>	Carbon steel	37 % HCl	EIS, PDP, Tafel	96.00	(Q. Wang et al., 2022)
<i>Thunb Cape</i>	Mild steel	20 % H ₃ PO ₄	EIS, PDP, SEM, Quantum chemical calculations	80.00	(Abdel-Gaber et al., 2022b)
gooseberry					
Green Nettle	Mild steel	3.5 % NaCl	EIS, PDP, DFT, FE-SEM, XPS, FTIR, MD simulations, QM	95.00	(Ramezanzadeh, Bahlakeh, Ramezanzadeh, et al., 2019)
<i>Myrobalan</i>	Mild steel	1 M HCl	EIS, PDP, OCP, MC simulations, MD, UV-Vis, FT-IR, DFT, AFM, SEM	91.00	(Dehghani et al., 2020)
Maple	Q235 steel	0.5 M H ₂ SO ₄	EIS, MD simulations, FTIR, UV-Vis, SEM, XPS,	81.60	(Wang et al., 2023)
Almond	Aluminium	1 M HCl	RSM, WL, SEM	97.90	(Olawale et al., 2018)
(<i>Prunus Amygdalus</i>)					
Sweet Potato	Mild steel	0.5 – 1.5 M H ₃ PO ₄	EIS, PDP, SEM, WL	99.80	(Olamide et al., 2023)
<i>Mangifera indica</i>	Mild steel	3.5 % NaCl	EIS, PDP, Raman, UV-Vis, FE-SEM, MC & MD simulations, FTIR	91.00	(Ramezanzadeh, Bahlakeh, & Ramezanzadeh, 2019)
<i>Terminalia arjuna</i>	Mild steel	0.2 M HCl	EIS, PDP, WL, SEM, FTIR	64.10	(Hossain et al., 2022b)
<i>Derris Indica</i>	Aluminium	1 M NaOH	EIS, PDP	60.20	(Nambiar et al., 2021)
<i>Ziziphus</i>	Mild Steel	3.5 % NaCl	WL, ANOVA test	89.00	(Al-Shamkhani & Ateik, 2018)
<i>Tithonia diversifolia</i>	304 SS	1 M HCl	PDP, FTIR	77.27	(Firdausi & Kurniawan, 2016)
(Hemsl) <i>A. Gray</i>					
<i>Psidium</i>	Mild Steel	1 M H ₃ PO ₄	Tafel, WL, EIS, SEM, FTIR	89.00	(F. D. Fernandes et al., 2021)
<i>Guajava</i>					

<i>Spilanthes acmella</i>	Mild Steel	1.0 M HCl	Tafel, WL, EIS, Linear polarization, AFM, FTIR, SEM, Contact angle	97.20	(Begum et al., 2021)
<i>Justicia Secunda</i>	Aluminium	0.5 M HCl	EIS, PDP, SEM	94.30	(Iroha and Maduelosi, 2021)
<i>African mangosteen</i>	Low Carbon Steel (LCS)	0.5 M H ₂ SO ₄	WL, PDP, EIS, AFM, FT-IR, SEM	96.14	(Rathod et al., 2022)
<i>Phoenix Pusilla</i>	Mild steel	1 M HCl	WL, AAS	85.96	(Satish et al., 2023)

2.9 Marula Tree (*Sclerocarya birrea*) as potential green corrosion inhibitor

Sclerocarya birrea, commonly known as the marula tree, is an indigenous drought-resistant species widely distributed in Africa, but mostly in sub-Saharan Africa (Adel, 2011). Generally, the marula tree grows in riverine woodland, wooded grassland, and bushland with a warm, frost-free climate but may also survive where temperatures drop below freezing point for a very short time, such as during the winter season (Orwa et al., 2009). It is known to be a highly salt-tolerant tree that can grow up to 18 m tall and have a trunk diameter of 120 cm with a grey bark as well as lateral roots that can reach up to 30 m. Marula trees prefer sandy, stony, or sandy loam soils with annual rainfall varying from 200 to 1370 mm (Hal, 2013). This is one of the most utilised indigenous wild fruits, with a potential source of income for primary producers in most countries as most of its parts are edible. Marula is a multipurpose tree due to its nutritional value drawn from the fruit, cosmetic oil from the seed, which has high fat, citric acid, protein, malic acid, phosphorus, and zinc, among others, as well as medicinal value from the bark and leaves (Nerd and Mizrahi, 1993). In addition, the fruit has the highest vitamin C content and can be eaten raw or by producing jams, juice, dry fruit tolls, conserves, or fermented to make alcoholic beverages such as Amarula, traditional beer, or wine. Figure 2.12 shows marula tree prior to flowering, it is one of the plants where the leaves for this investigation was harvested.



Figure 0.12: A marula tree taken around Botswana International University of Science and Technology (BIUST) campus in Palapye, Botswana.

2.9.1 Phytochemical constituents of marula (*Sclerocarya birrea*) leaves

Phytochemicals are bioactive non-nutrient chemical substances present in diverse plant parts such as fruits, peels, barks, roots, leaves, grains, and other plant parts (Lampe & Chang, 2007). These chemical substances have a biologic effect and have recently been used in corrosion control. They participate in the inhibition of metal surfaces in aggressive solutions through chemisorption, physisorption, and retro-donation to block active metal surfaces, thus protecting the metal surface from corrosion (Bhardwaj et al., 2021). Based on the plant metabolism activity phytochemical compounds can be grouped into two groups ; primary constituents which is mainly sugars, amino acids, chlorophyll and proteins and secondary constituents being alkaloids, saponins, tannins, flavonoids, and phenolic compounds (Krishnaiah et al., 2007). Corrosion inhibition in most literature has been associated mostly with secondary constituents of the phytochemical compounds as they are the ones absorbing on the metal surfaces to provide surface coverage to the metal layer (Eddy et al., 2014).

Sclerocarya birrea has been thoroughly explored for its anti-diabetic, anti-inflammatory, analgesic, antiparasitic, antibacterial, and antihypertensive properties (Mariod & Abdelwahab, 2012). This led to the analysis of the phytochemical substances present in the various parts of the tree, particularly the leaf, depending on which portion of the tree is of interest at the time,

as phytochemicals are typically thought to have therapeutic properties that can bring healing (Bai et al., 2011).

The biomedical literature has indicated the existence of polyphenols, tannis, flavonoids, alkaloids, anthocyanis, and significant levels of saponosides in marula barks and leaves (Belemtougri et al., 2001). In addition, tannis (in dominance procyanidins), triterpenoids, coumarins, polyphenols, phytosterols, organic acids (gallic & quinic) amongst flavonoids present quercetin and its derivatives (quercetin 3-O- α -(5''-galloyl), arabinofuranoside, quercetin 3-O- β -D-(6''galloyl), galactopyranoside, quercetin 3-O- β -D-glucopyranoside0, kaemp-ferol and its derivatives (kaempferol 3-O- α -L—rhamnopyranoside have been reported to be in abundance in *Sclerocarya birrea* plant leaves (Ojewole et al., 2010). (Braca et al., 2003; Maharaj et al., 2022) further revealed the presence of gallic acid, (-)-epicatechin 3-O-galloyl ester and (-1) epigallocatechin 3-O-galloyl ester in the leaves of marula. Additionally, marula leaf extracts are reported to possess high antioxidant activity and phenolic compound content (Mashau et al., 2022).

The phytochemical makeup of the same tree might differ from one geographical location to the next due to an array of factors, including geographical location, water limitation, soil and nutrient dynamics (Ogwu et al., 2025) . The rainfall pattern, soil fertility, which both play an important role in metabolism activity and lipid growth of plants, fluctuates from one place to the next, resulting in varied compositions and concentrations of phytochemical elements of the same tree in different regions (Ghasemzadeh et al., 2018). Furthermore, the evolution of secondary chemistry in plants characterized by strong phylogenetic signals of traditional compound classes and weak signals of specialized structural motifs, has been attributed to influence the phytochemical make up of each tree (Uckele et al., 2021).

Finally, the selection of the extraction technique and the type of solvent plays a pivotal role in optimizing the production yield of phytochemicals and antioxidants from your leaf extract (Dhanani et al., 2017; Kamarul Zaman et al., 2020). The solvent to be used is determined by the polarity of the solute of interest, which has a substantial impact on the number of polyphenols extracted (Altemimi et al., 2017). Phytochemical extractability is greatly influenced by the polarity of the extraction medium and the proportion of solute to solvent (Iloki-Assanga et al., 2015).

2.9.2 Marula leaf extracts extraction techniques

Innumerable researchers have employed a range of extraction methods in their efforts to obtain a higher yield of phytochemical compounds from various tree sources. However, when it comes to *Sclerocarya birrea*, most of the published literature has focused more on extracting phytochemicals from the stem, roots, and bark, rather than from the leaves (Belemtougri et al., 2001b; Manzo et al., 2017; Russo et al., 2018a). In one study Russo et al., 2013 defatted 150 g of marula leaves in 5 volumes (v/w) of n-hexane. The defatted leaves were then subjected to maceration using different solvents including, CHCl₃, CHCl₃: MeOH (9:1), and MeOH in amber vials at room temperature for 6 days. Throughout the extraction, the bottles were shaken at regular intervals, and the solvent was replenished every 48 hours. Following maceration, each solvent extract was filtered through cellulose paper (17-25 µm) and concentrated in a rotary evaporator at 37 °C under reduced pressure. Following the completion of the extraction process, all extracts were weighed and stored at 4 °C in the dark until further use. Maceration technique was also utilized by Braca et al., (2003) to extract 386 g of air-dried *S. birrea* leaves after defatting with petroleum ether. The powdered leaves were subjected to exhaustive maceration (6 L) for 48 hours with the same solvents in their ration as used by Russo et al., (2013) to give four decoctions of 8.0, 20.0, 4.3 and 22.5 g respectively.

In a study of antioxidant properties of methanolic extracts of different parts of the *Sclerocarya birrea* Mariod et al., (2008) macerated 25 g of sun-dried powdered leaves in hexane and subjected it to extraction three times with 30 mL of 60 % methanol at a solid to solvent ratio of 1:10 (w/v) at a temperature of 50 °C . The extract was concentrated at 40 °C using a rotary evaporator and stored at 4 °C until use. To study the effects of *sclerocarya birrea* (A.Rich) leaf extracts on calcium signalling in cultured rat skeletal muscles Belemtougri et al., (2001) macerated 6 g of powdered leaves in deionized water at room temperature with continual agitation for more than 24 hours. It was then boiled, allowed to cool, and filtered and concentrated by a rotary evaporator. A crude decoction obtained was then stored in refrigerator until use in the experiments. This method was also adopted by Belemtougri et al., (2006) to macerate 25 g of *sclerocarya birrea* leaves but after freezing the extractant was then lyophilized to give brown powder which was subsequently utilized in the experiments.

There are limited literature reports on maceration or any reported technique on ethanolic extraction of marula leaf extracts and its phytochemical analysis for safeguarding against metal dissolution. In Botswana no previous studies have been conducted on the extraction of

Sclerocarya birrea leaves for the corrosion inhibition studies or phytochemical analysis for the potential use in metal protection.

2.10 Corrosion monitoring techniques

Corrosion monitoring techniques plays a pivotal role in assessing, predicting and managed all risks associated with corrosion processes. They assist us in tracking corrosion progress, identifying possible trouble areas, and applying timely steps to maintain structural integrity, ensuring reliability and safety of industrial systems. In addition, corrosion monitoring techniques, they assist in the better understanding of green corrosion inhibitors like leaf extracts in corrosion control, their inhibition phenomenon and mechanism. There are two main groups of corrosion monitoring techniques being gravimetric / weight loss method and electrochemical measurements. The sensitivity, convenience of setup, data processing, capacity to uncover underlying corrosion mechanisms, and relevance in the field of corrosion prevention and research all play a role in technique selection (Popova & Prošek, 2022).

2.10.1 Gravimetric or weight loss technique

It's a non-electrochemical technique where small pieces of the metal under the investigation are immersed or suspended in a corrosive solution at conditions set by the investigator. It is a readily applicable and cost-effective technique that provides an initial understanding of the inhibitor's impact on inhibition (Azzaoui et al., 2017). Due to its reliability weight loss is the mostly used corrosion inhibition assessment technique (R. Karthik et al., 2015). Surface coverage (Θ), corrosion rates, and inhibition efficiency (%) can all be determined by utilizing the weight loss readings. The specimens from the weight loss experiment can then be subjected to surface analysis to evolve corrosion inhibition mechanisms, surface morphology and to study the extent of corrosion on the surface itself.

2.10.2 Electrochemical measurements

There are low cost and reliable measurements performed to determine a material's electrochemical properties. The rate of decay, passivation, and open circuit potential render materials to behave differently to a charge-transfer response is passed through the material from an electrical disturbance source (Munir et al., 2016). To perform the measurements, a computer-controlled electrochemical analyser is used. An electrochemical cell uses a platinum wire auxiliary electrode (PtE), a saturated calomel reference electrode (SCE), and a working electrode (the metal specimen being investigated) (Kaya et al., 2023a). The most used to study a material corrosion behavior includes electrochemical impedance spectroscopy (EIS),

potentiodynamic polarization (PDP), open circuit potential (OCP), Tafel Plot, noise measurement and chronoamperometry. The EIS has been deemed a potent tool for corrosion kinetics at the solid/solution interface because it is successful in working in a steady-state frequency domain rather than the time domain (Xia et al., 2021; Macdonald, 2006). In addition, it is a non-destructive technique used for monitoring corrosion rate and is suitable for evaluating the electrochemical properties of modified surfaces, including small corrosion rates (Nkomo and Masia, 2021). Meanwhile, in PDP, metal-wide variations are applied and is a destructive process where corrosion resistance is measured. For this technique, a current is passed through an electrolyte to modify the electrode's potential at a predetermined rate (Aslam, 2023). PDP can estimate the corrosion potential, corrosion current density, corrosion rate and passivation potential. On the other hand, OCP is a passive method used to detect surface and material change due to exposure as well as predict the lifetime of the protective passive film and identify corrosion processes that lead to failures (Khan et al., 2020). This approach involves simultaneous anodic and cathodic reactions. OCP is useful for monitoring the corrosion state of an electrode as it can indicate whether the electrode is becoming corroded over time (Xia et al., 2021). However, OCP does not provide information about the corrosion rate but gives qualitative data on the corrosion state (Kendig and Leidheiser, 1976). Overall, all these techniques can be used together to provide a complete understanding of corrosion behaviour. In addition, OCP is normally used to calibrate the results from EIS and PDP.

2.11 Existing knowledge gaps in literature

Over the last decade, numerous plant leaf extracts have been researched and tested as a viable green corrosion inhibitor to standard synthetic inhibitors. Although there is a developing study trend in the area, there is no relevant literature published on the investigation of *Sclerocarya birrea* as a prospective green corrosion inhibitor for metals in harsh conditions.

API 5L X42 Pipeline steel metal used for water transportation over long distances locally has never been studied under seawater and sulphuric acid conditions; hence this study will elucidate its corrosion mechanism and how it responds to marula leaf inhibitor at different concentrations. The results from this study will inform its applicability in different environments with similar corrosive agents.

The underlying mechanism of corrosion inhibition by the *Sclerocarya birrea* leaf extract remains unknown and must be evolved for different steel and aluminium in varying corrosive environments so its performance and applicability can be known. Undertaking the corrosion

studies using this leaf extract will also help in comparison of inhibition performance against other medicinal leaves which have been used to alleviate the corrosion problem which is not provided by the literature currently. There is lack of comprehensive literature on investigations of the extract leaf corrosion inhibition over extended periods, therefore conducting these experiments with *Sclerocarya birrea* over two months will unearth its effectiveness over longer durations. Long-term studies will assist overcome the gap in the long-term stability and durability of the leaf extract, allowing it to be attempted in real-life industrial corrosive conditions.

Chapter 3 Materials and Methods

This chapter outlines the materials, experimental procedures and analytical methods employed to investigate the corrosion inhibition mechanism, potential and performance of *Sclerocarya birrea* (marula) leaf extract in acidic and seawater environments for mild steel, API X42 5L pipeline steel and Aluminium (AA1100) metal specimens. Firstly, the chapter focuses on the collection of marula leaves, its extraction and characterization of the extractant using phytochemical screening, Fourier Transform Infrared spectroscopy, Ultra-Violet Visible Spectroscopy and Gas Chromatography – Mass Spectroscopy techniques. The study then utilized a combination of gravimetric (weight loss) method, Electrochemical tests (Open Circuit Potential, Electrochemical Impedance Spectroscopy and Potentiodynamic Polarization techniques) and surface analysis techniques such as X-ray Diffraction and Raman spectroscopic analysis to evaluate the (extractant) inhibitor's effectiveness and adsorption behavior. Additionally, quantum chemical calculations of Dense Functional Theory and Monte Carlo simulations were performed to gain molecular-level insights into the interaction between the extract's bioactive compounds and the aluminium and steel surfaces.

3.1 Materials

The materials utilized for the experimental work in this have been tabulated in Table 3.1. All these materials including solvents have been used at different stages of analysis.

Table 0.1: List of all materials used for the experiments conducted.

Material	Source	Properties
1. Marula leaves	Collected from marula trees in Biust Campus , Palapye	Mature and green leaves
2. Card boxes	Collected from Choppies and Spar Palapye stores	Brown hard boxes
3. Whatman No.1 filter paper	Tisch Scientific , USA	Standard 185 mm, 100 pack, 1001-185
4. Silicon carbide papers	Akasel, Denmark	P120 to P2400 grits
5. Mild steel	A1 Hardware , Palapye	Flat bar
6. Aluminium – AA1100	Mechanical department, BIUST	Sheet
7.API X42 Pipeline steel	Seven Star Steel Pipeline Group, Palapye	Flat bar

8.Sodium Chloride	Rochelle Chemicals, South Africa	Analytical grade
9.Sulphuric acid	Rochelle Chemicals, South Africa	Analytical grade, 98%
10.Hydrochloric acid	Rochelle Chemicals , South Africa	Analytical grade
11. Ammonia	Rochelle Chemicals, South Africa	Analytical grade
12. Sodium Hydroxide	Rochelle Chemicals, South Africa	Analytical grade
13. Chloroform	Rochelle Chemicals, South Africa	Analytical grade
14. Acetone	Rochelle Chemicals, South Africa	Analytical grade
15. Iron (III) Chloride, FeCl ₃	Rochelle Chemicals, South Africa	Analytical grade
16. Polymer resin	AMT composites, South Africa	Crystal clear 200 PART A & B, clear urethane casting resin
17. Aluminium foil tape	A1 hardware Palapye	Shiny, sticky and reflective
18. Copper wires	A1 Hardware , Palapye	3 m long
19. Nylon string	A1 Hardware , Palapye	5 m yellow in color
20. wooden metal suspenders	A1 Hardware , Palapye	Flat, made from roof rafters
21. High Speed Steel drill bits	A1 Hardware , Palapye	3.5 mm carbon coated drill bits
22.Diamond polishing suspension	Akasel , DiaMaxx , Denmark	Mono 3 µm to 9 µm

3.2 Extraction of *Sclerocarya birrea* (marula) leaf.

Marula leaves were collected around BIUST campus, sorted to remove distorted, faulty, and not-so-green leaves. Prior to washing the weight of the leaves was obtained, shade-dried naturally at ambient temperature for 10 days. The card boxes which the leaves were dried were

changed every two days. After ten days of shade drying the leaves were subjected to size reduction using hammer mill & chopper (Staalmeester, JF 2D model). Sample obtained from the hammer mill were subjected to further size reduction by pestle and mortar to obtain a fine powder. Accurately 200 g of the powdered leaves was weighed using a four-digit analytical balance, transferred to a 2000 mL volumetric flask and soaked in 1000 mL of ethanol for 72 hours. This was triplicated hence 600 g macerated with equivalent of 3000 mL for the three days. To obtain a homogeneous extract, the resultant solution was filtered overnight (24 hours) with Whatman No.1 filter paper. Thereafter, the filtrates were concentrated with a rotary evaporator at 40 °C at 110 rpm for 70 minutes, and the thick slurry attained and refrigerated at 4 °C for 24 hrs. Corrosion test solutions were then prepared by dissolving specified amount of the marula leaf extract in 300 mL of 1 M H₂SO₄ and 300 mL of 3.5 % NaCl and used for corrosion study by weight loss and electrochemical techniques.

3.3 Marula leaf extractant phytochemical compounds characterization

3.3.1 Qualitative phytochemical screening of marula ethanolic extract

Phytochemical screening was carried out using conventional protocols as outlined by (Evans and Trease 2009, Gul et al. (2017) and Rao et al. (2016)). The following qualitative tests were performed.

- i) Saponins: To test saponins presence, 1 mL of marula extract was diluted with distilled water to 20 mL and shaken in a graduated cylinder for 15 minutes. A one-centimeter layer of foam shows the presence of saponins.
- ii) Phenols: 0.5 mL the marula ethanolic extract was mixed with 1 mL of water in a test tube, followed by 1 to 2 drops of Iron III chloride (FeCl₃) were added. A blue, green, red, or purple colour indicates a favorable result.
- iii) Glycosides: 0.5 mL of marula leaf extract was mixed with 1 mL of water in a test tube, and a few drops of aqueous NaOH were added. A yellow coloration shows the presence of glycosides.
- iv) Flavonoids: Three drops of strong hydrochloric acid (HCl) were added to a tiny amount of plant-based ethanol extract. The immediate appearance of a red colour suggests the presence of flavonoids
- v) Alkaloids: 2 mL of extract was added to a test tube, followed by 0.2 mL of weak HCl and 1 mL of Meyer's reagent. A yellowish coloration indicates the presence of an alkaloid.

- vi) Tannins: 5 mL of marula extract was added to a test tube, followed by 2 mL of a 5 % FeCl_3 solution. A greenish-black precipitate suggests the presence of tannins.
- vii) Terpenoids: In a test tube with 2 mL of chloroform, 0.5 mL of extract was added. This is followed by the addition of 3 mL concentrated H_2SO_4 , forming a layer. The reddish-brown coloration of the interface shows terpenoids.
- viii) Anthraquinones: In a conical flask, 10 mL of benzene was poured to 6 g of marula leaf powder, which was steeped for 10 minutes before being filtered. A further 10 mL of 10 % ammonia solution was added to the filtrate and forcefully shaken for 30 seconds, with pink, violet, or red indicating the presence of anthraquinones in the ammonia phase.

3.3.2 Fourier Transform Infrared spectroscopy (FTIR) analysis.

Sclerocarya birrea powdered leaves and its ethanolic extract, were subjected to FTIR analysis using the Vortex 70 V vacuum spectrometer from Bruker (China). The powdered sample and ethanolic extract were fed into the apparatus separately, and spectral data were taken in transmittance mode at ambient temperature (27 °C) spanning the range of 4000 to 400 cm^{-1} (Govindhan et al., 2021; Jozanikohan & Abarghoeei, 2022). All the samples were analyzed in triplicates with KBr as our blank. The collected spectral data was then compared to the reference to identify the functional groups present in the sample.

3.3.3 Ultra-Violet Visible Spectroscopy (UV-Vis) analysis

Marula ethanolic extract was subjected to UV-vis analysis to identify functional groups chromophores. The spectral data was obtained in the wavelength range of 200 to 800 nm using a dual beam Thermo scientific UV-visible spectrophotometer (Evolution 201), having ethanol as reference. After the plot of the UV-vis spectrum the functional groups present were then deduced from various peaks in the spectra. Figure 3.1 below shows the Thermo Scientific Evolution 201 UV-Vis spectrophotometer used for ethanolic extract analysis.



Figure 0.1: Thermo Scientific Evolution 201 UV-Vis spectrophotometer.

3.3.4 Gas Chromatography – Mass Spectroscopy (GC-MS) analysis

For the extraction phase, 10 g of powdered marula leaves were steeped in 30 mL of ethanol for 24 hours at room temperature. After 24 hrs period has elapsed the extractant was filtered using ashless sodium sulphate paper before bubbling the resulting solution in nitrogen (Maina et al., 2016). The Agilent Technologies 7890 B Gc system (Chemetrix, USA) shown in Figure 3.2 was used for this analysis. Plant ethanolic extract was assessed by injecting a 2.0 μl sample into the helium mobile phase, which flowed at a rate of 1.0 $\mu\text{l}/\text{min}$ and was heated to 290 $^{\circ}\text{C}$. The experimental steps were examined within the 40–600 m/z range at intervals of 0.5 seconds. The total run time was 50 minutes with an initial solvent delay of 5 minutes . The chromatogram data were analyzed and cross-referenced with the Wiley Spectral library search engines.



Figure 0.2: Agilent 7890 B Technology Gas Chromatography-Mass Spectroscopy.

3.4 Preparation of the solutions and metal specimens

3.4.1 Simulated seawater (3.5 % NaCl)

10.5 g of analytical grade (58.68 g) sodium chloride was weighed on analytical balance and then transferred into a 500 mL volumetric flask. Subsequently, 100 mL was measured using a graduated cylinder and the mix was swirled for few minutes then topped up with an extra 200 mL of distilled water before transferring the solution to the 500 mL bottle where the immersion test was to be conducted in. The calculations for the exact amount of sodium chloride used (10.5 g) is in the appendix section.

3.4.2 1 M H_2SO_4 solution

29 ml of analytical grade (98 %) sulphuric acid was measured using a measuring cylinder and transferred to a 500 mL volumetric flask. It was diluted with 300 mL of distilled water to produce 1 Molar solution. The calculations for the volume of solvent used is provided in the appendix section.

3.4.3 Inhibitor concentrations

For each of the concentration levels that is (5, 10, 15 & 20 g/L), 3 mL of the extractant was pipetted out of the extractant and diluted with a certain amount of the ethanol to reach the required concentration level. For example, to prepare 5 g/L, 3 mL of the extractant was diluted

with 120 mL of ethanol and transferred to the prepared corrosive solutions. The resulting solution was mixed for around 5 minutes for homogeneity before the specimens were immersed for the weight loss experiment and electrochemical tests.

The dilution formula ($C_1V_1 = C_2V_2$) equation 3.1 was utilized to compute the required concentrations. It was used to prepare the required dilute solution. The resulting calculations are provided in the appendix.

$$C_1V_1 = C_2V_2 \dots \dots \dots (3.1)$$

3.4.4 Metal specimens

i) metal specimens' preparation for weight loss corrosion test

Using an abrasive cutting machine (Labotom-15, Struers, Denmark), square dimensioned coupons of 20 mm × 20 mm × 1.5 mm were obtained. The API 5L X42 pipeline and mild steel specimens were cut using this machine with a 350 mm cut-off wheel at 2350 revolutions per minute (rpm) using Clarke cutting discs. Aluminium was cut into the same square dimensions using a hacksaw. For both steels and aluminium samples, the preparations were in accordance with the American Society for Testing and Materials (ASTM) standards, particularly ASTM G1-03(2022) and ASTM E3-11. The chemical compositions of the metal specimens are presented in Table 3.2 to Table 3.4. To ensure smooth drilling, all the samples were center punched in the upper corners using the center puncture and drilled uniform holes of 3.5 mm using standing floor drilling machine. The drill holes are to facilitate suspension of the specimens in the test solutions. The surface of the metals was then mechanically polished with diamond grinding and polishing using Silicon Carbide (SiC) emery paper of P120 to P2400 grits respectively. Diamond polishing suspension (3 µm to 9 µm) was utilized to finish the metal surfaces as per ASTM G31-21. The specimens were cleaned with distilled water and acetone, then dried at room temperature, and stored in a desiccator 24 hours before use. The precise weight of the specimens before immersion was recorded as the initial weight, (W_1) using analytical balance. The samples prepared for weight loss tests prior to grinding and polishing are displayed in Figure 3.3.

Table 0.2: The chemical composition of mild steel.

Element	C	P	S	Mo	Si	Mn	Cr	Ni	Fe
Weight (%)	0.184	0.0109	0.0121	0.0127	0.186	0.378	0.166	0.0550	balance

Table 0.3: The chemical composition of API 5L X42 Pipeline steel

Element	C	Mn	P	S	Si	Cu	Ni	C	Mn	V	Nb	Ti	Al	B	N	Fe
Weight (%)	0.065	1.2	0.006	0.002	0.217	0.011	0.009	0.029	0.040	0.010	0.008	0.018	0.034	0.002	0.0043	98.53

Table 0.4: The chemical composition of Aluminium (AA 1100) alloy.

Element	Zn	Mn	Cu	Si + Fe	Al
Weight (%)	0.01	0.05	0.05 – 0.2	0.95	Balance



Figure 0.3: Weight loss metal specimens after drilling and grinding before polishing.

ii) Metal specimens' preparation for electrochemical tests

Metal specimens measuring 1 cm x 1 cm were used to perform electrochemical potentiodynamic polarisation, open circuit potential, and impedance studies. The specimens were connected to a copper wire, and an aluminum foil sticker was utilized to stick the wire to the surface of the metal. The samples were then cold mounted using a transparent epoxy adhesive and let to dry. These were then polished with a grinder polisher and Silicon Carbide (SiC) abrasive paper of P120 size down to P2400, repeatedly rinsed with distilled water and air dried at room temperature before use as according to with ASTM G59-97 electrochemical standards (Ghica et al., 2019; Horton, 2019). Figure 3.4 below shows the cold mounted samples to be used for electrochemical tests.



Figure 0.4: Cold mounted polished metal specimens ready to be used for electrochemical experiments.

3.5 Corrosion inhibition monitoring

3.5.1 weight loss (non-electrochemical technique)

The weight of the cut samples was obtained using accurate weight balance (Mettler Toledo, four-digit scale) post corrosion exposure. Weighed coupons (in duplicates) were thoroughly immersed; by using nylon threads, corrosion mediums were created in 500 mL container bottles containing 3.5 % NaCl and 1 M H₂SO₄ with and without different inhibitor doses and exposed for 70 days. Each sample was removed from the solutions at an interval of 7 days, cleaned with deionized water, rinsed with acetone, and dried with paper towels. The weights will be gathered and used to estimate the changes that occurred throughout the experiment. The loss in weight was then computed and the results averaged. The experiment was carried out for 70 days with weight loss recorded every 7 days and at different concentrations of the inhibitor of 0 g/L (control), 5 g/L, 10 g/L, 15 g/L, and 20 g/L of stock solutions of marula leaf extract. The weight loss set up and color changes observed over different days are shown in Figure 3.5.

Using the data obtained from the above, the following parameters were estimated using the equations 3.2 to 3.3.

i) weight loss

$$\Delta W = W_1 - W_2 \dots\dots\dots (3.2)$$

where, ΔW is the weight loss measured by taking the difference between the averaged initial specimen weight (W_1) and the final weight (W_2), following exposure to the corrosive test solutions both in the presence and absence of inhibitor.

ii) The corrosion rate which was calculated using the approach developed by Noor (2007).

$$CR = \frac{\Delta W K}{A.T.\rho} \dots\dots\dots (3.3)$$

where, CR is the corrosion rate (mm/py), ΔW is the weight loss in g, K is a constant valued at 87 500, A is the surface area of the steel specimens in cm², T is the immersion duration in hours and ρ is the density is metal density in g cm⁻³.

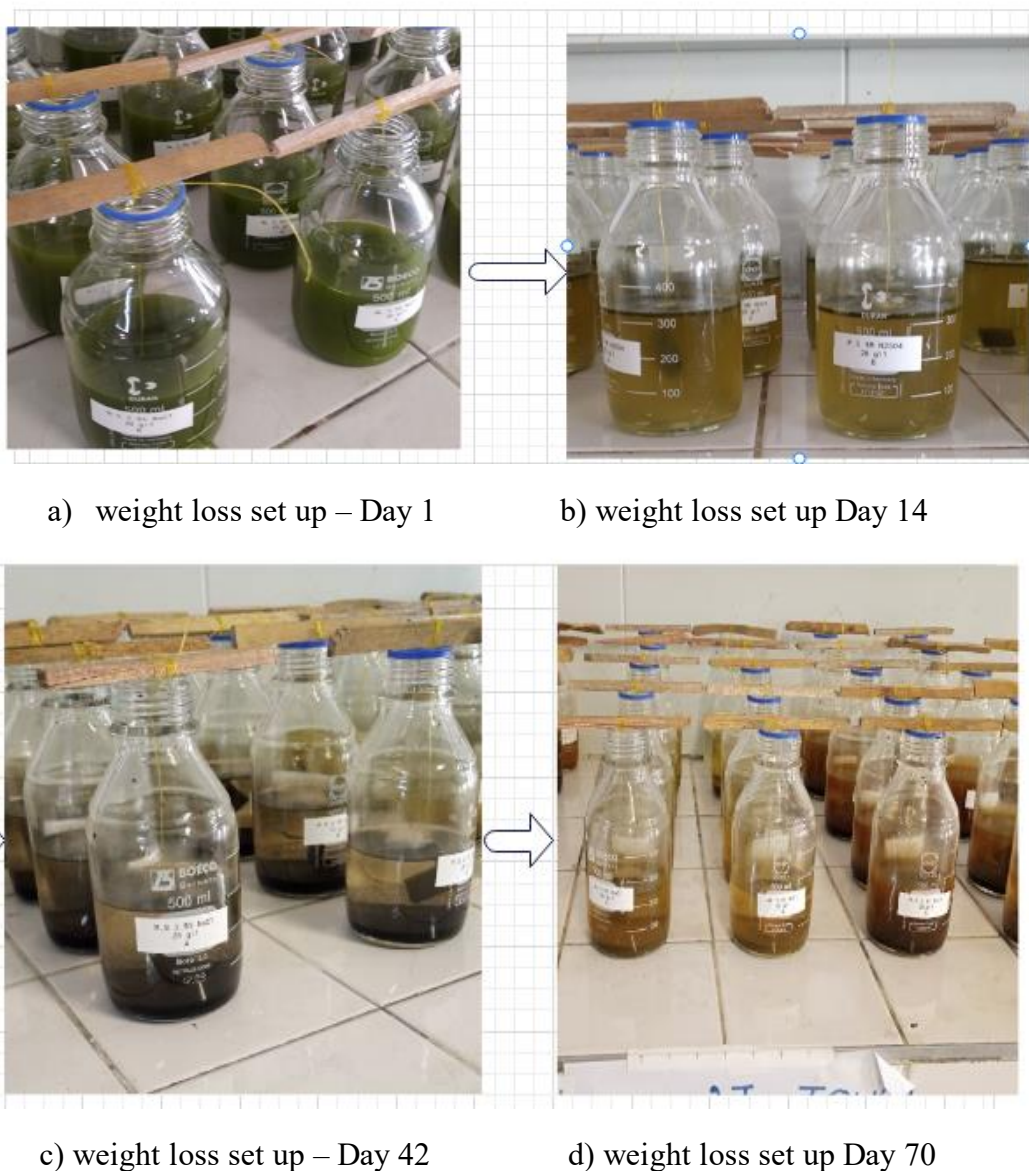


Figure 0.5: A picture of the setup for the weight loss experiment used for data collection after a) 1, b) 14, c) 42, and d) 70 days.

3.5.2 Electrochemical methods

The electrochemical studies were all performed at room temperatures. Electrochemical impedance spectroscopy (EIS), Open Circuit Polarization (OCP), and Potentiodynamic Polarization studies were carried out using the Potentiostat Gamry 3000 and Gamry software v7.07 or equivalent. The cell consisted of platinum wire auxiliary electrode (PtE), and a Silver/Silver Chloride (Ag/AgCl) reference electrode. Each metal specimen with its computed area was used as a working electrode (WE). Before starting the experiment, the steady state open circuit potential (E_{ocp}) was determined by immersing the electrode in the corrosive solutions of 3.5 % NaCl and 1 M H_2SO_4 for 3600 seconds, with disturbance capacity of 10 mV. The electrochemical set up is displayed in Figure 3.6.

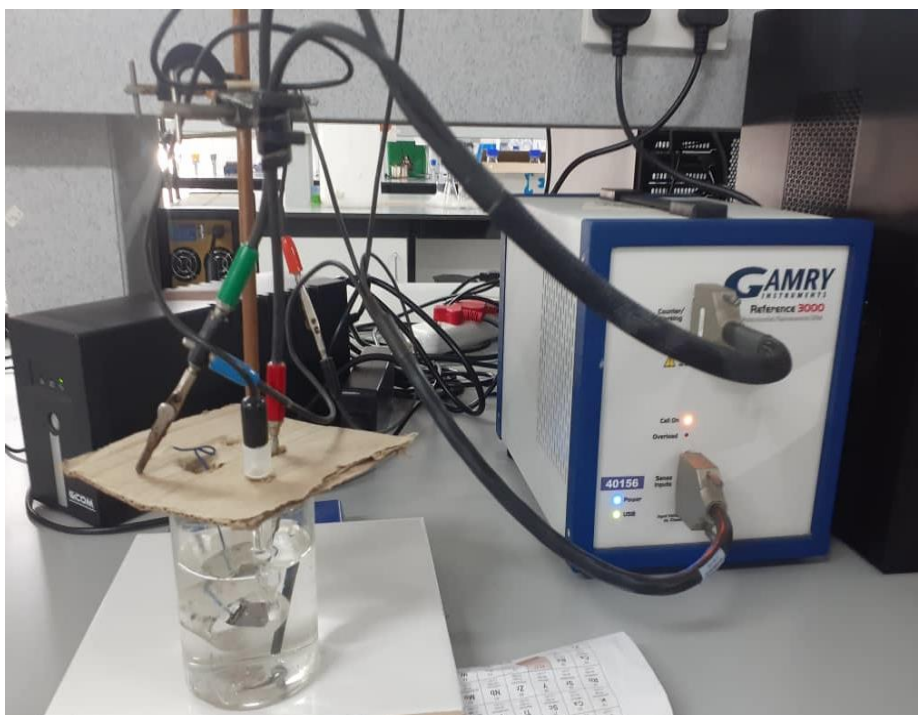


Figure 0.6: Electrochemical test set up on the Gamry Potentiostat Reference 3000.

3.5.2.1 Open Circuit Potential (OCP) method

The OCP of this investigation experiment utilized a Gamry Reference 3000 potentiostat to assess the electrochemical stability of the system over a period of 3600 seconds. The experimental setup consisted of immersing metal specimens (mild steel, pipeline steel, and AA1100) in 3.5 % NaCl and 1 M H₂SO₄ solutions, both with and without the inhibitor. A three-electrode arrangement was used, utilizing the metal as the working electrode, a silver-chloride electrode as the reference, and a platinum electrode as the counter electrode. The OCP was observed continuously, providing ample time for stabilization to take place, thereby ensuring dependable and representative baseline potential values. The data was meticulously recorded with Gamry's Framework software, guaranteeing high precision and compliance with ASTM G59-97 electrochemical standards (Ghica et al., 2019; Horton, 2019).

3.5.2.2 The Potentiodynamic Polarization (PDP) method

This corrosion experiment's electrochemical cell included a working electrode, a reference electrode, a counter electrode, a test solution of seawater (3.5 % NaCl), and 1 M H₂SO₄. The reference electrode monitored and controlled the system's voltage (V), whilst the counter electrode measured and controlled the current flowing through the established circuit. The corrosion potential (E_{ocp}) for the specified electrochemical cell was measured at a certain pH using a multimeter. The corrosion potential was allowed to stabilize before the experiment began, to guarantee that the system being researched had reached a stable state.

As the electrochemical reaction occurred, the metal's open circuit potential changed, and the potentiodynamic polarisation (PDP) scan was initiated. The various electrodes were attached to a potentiostat, which was subsequently linked to a computer-controlled system. Corrosion monitoring was carried out in real time, with readings obtained from the Computer Graphics User Interface (GUI), which displayed a plot of voltage vs time and current vs time. Following that, the Tafel plot was created by setting a potential that ranged from 0.25 V below the E_{ocp} to 0.25 V above it. The plots are then used to determine the corrosion potential (E_{corr}) and current density (I_{corr}).

Using data obtained in the potentiodynamic polarization method the following parameters were then estimated using equation 3.4 to 3.5.

i) Inhibitory efficiency (IE)

$$I.E(\%) = \left(\frac{I_{corr(o)} - I_{corr(i)}}{I_{corr(o)}} \right) \times 100 \dots\dots\dots (3.4)$$

where, $I_{corr}(i)$, and $I_{corr}(o)$ represent the corrosion current densities in the presence and absence of an inhibitor, respectively.

ii) The degree of surface coverage (θ)

$$\theta = \left(\frac{I(o) - I(i)}{I(o)} \right) \dots\dots\dots (3.5)$$

In this context, θ represents the surface coverage, $I(i)$ is the current density in the presence of the inhibitor, and $I(o)$ is the current density without the inhibitor.

3.5.2.3 The electrochemical impedance spectroscopy (EIS) method

The EIS study was performed in a three-electrode PDP with a minor potential variation of 5 to 50 mV of AC voltage throughout a frequency range of $10^5 - 10^{-2}$ Hz. For this study effort, EIS was utilized to calculate resistance and current flow values in the presence and absence of the *Sclerocarya birrea* leaf inhibitor. The EIS analysis values were presented in the Nyquist plot, with the real part of the impedance (Z_{real}) on the x-axis and the imaginary part ($-Z_{imaginary}$) on the y-axis.

The data obtained was then used to estimate inhibition efficiency and double layer capacitance by using equation 3.6 to 3.7.

i) Inhibitory efficiency (I.E.)

$$I.E(\%) = \left(\frac{R_{ct}(inh) - R_{ct}(blank)}{R_{ct}(inh)} \right) \times 100 \dots\dots\dots (3.6)$$

where, $R_{ct}(inh)$ is the charge transfer resistance in the presence of the inhibitor, while $R_{ct}(blank)$ is the charge transfer resistance in the absence of the inhibitor.

ii) The double layer capacitance ($Cd1$) was calculated using the following equation (Xue et al., 2012).

$$Cd1 = (1)/(2\pi x f_{max} R_{ct}) \dots\dots\dots (3.7)$$

where, $Cd1$ is the double capacitance, f_{max} is the frequency at Z 's highest value, and R_{ct} is the charge transfer resistance.

3.6 Thermodynamics and absorption kinetics

3.6.1 Weight loss coupled with temperature variation

To elucidate the thermodynamic and kinetics of the corrosion inhibition exhibited by the *Sclerocarya birrea* leaf extract, the specimens were subject to weight loss corrosion monitoring in Thermo Fisher Scientific, Isotemp GD28 (USA) water bath. The water bath was filled with tap water to a level of about 5 cm from the top and temperature in Kelvins varied from 303, 313 and 323 K, while the inhibitor concentrations were varied from 0, 10 and 20 g/L and the weight loss was acquired after 2, 4 and 6 hrs of immersion. To keep the temperature constant for the period of immersion the water bath was kept closed with its lid.

The experiments were repeated two (2) times for repeatability and reliability of the obtained data. From the data obtained absorption isotherms, surface coverage , kinetics, and effects of temperature on the corrosion rate and inhibition efficiency were estimated and analyzed. Figure 3.7 shows the Thermo Fisher Scientific , Isotemp water bath utilized for these experiments



Figure 0.7: Fisher Scientific, Isotemp GPD 28 water bath.

3.6.2 Determination of thermodynamic and activation parameters

The activation energy (E_a), enthalpy of heat (ΔH°), and entropy of activation (ΔS°) were estimated for mild steel, API 5L X42 pipeline steel, and aluminium (AA1100) in corrosive conditions with 3.5 % NaCl and 1 M H_2SO_4 respectively.

3.6.2.1 Activation energy (E_a)

It was estimated using the Arrhenius equation (3.8) (Kohout, 2021; Mahmmud et al., 2024).

$$\text{Log } CR = \text{Log } A - \left(\frac{E_a}{2.303RT} \right) \dots \dots \dots (3.8)$$

where A is the Arrhenius plot's pre-exponential factor, CR is the corrosion rate, T is absolute temperature in Kelvins, and R is the Universal Gas Constant . The slope of the curve drawn between $\text{Log } CR$ and $1/T$ indicates the value of the activation energy (E_a) at 303, 313 and 323 K, respectively.

3.6.2.2 Enthalpy of activation (ΔH°) and entropy of activation (ΔS°)

The transition state equation (3.9) was used to compute the enthalpy of heat (ΔH°) and entropy of activation (ΔS°) (Toghan et al., 2023).

$$\text{Log } \left(\frac{CR}{T} \right) = \left[\left(\text{Log } \left(\frac{R}{N_h} \right) + \left(\frac{\Delta S^\circ}{2.303R} \right) \right) \right] - \left[\left(\frac{\Delta H^\circ}{2.303R} \right) \right] \dots \dots \dots (3.9)$$

where CR is the corrosion rate, N is the Avogadro's number, T is the absolute temperature in Kelvins, R is the Universal Gas Constant, and h is the Planck's constant.

A plot of $\text{Log} (CR/T)$ vs $(1/T)$ yields a straight line with a slope and intercept of $[\text{Log} (R/Nh) + (\Delta S^\circ/2.303R)]$, which may be used to compute the enthalpy of heat (ΔH°) and entropy of activation (ΔS°).

3.6.3 Adsorption Isotherms

3.6.3.1 Langmuir adsorption isotherm

Equation 3.10 represents the mathematical expression for Langmuir's adsorption isotherm, (Lorhuna et al., 2024; Oo & Nikolaychuk., 2024).

$$\text{Log} \frac{\Theta}{1-\Theta} = \text{Log} (K_{ads}) + \text{Log} (C_{inh}) \dots \dots \dots (3.10)$$

where C_{inh} represents the inhibitor concentration (g/L), K_{ads} (g/L) is the adsorption equilibrium constant, and Θ is the degree of surface coverage (I.E % /100). If the adsorption follows the Langmuir isotherm, a straight line can be drawn between $(C_{inh}/)$ and C_{inh} , or between $\text{Log} (C_{inh}/)$ and $\text{Log} C_{inh}$.

3.6.3.2 Freundlich adsorption isotherm

Equations 3.11 express the adsorption isotherm numerically (Abdullah & Othman, 2024).

$$\text{Log} \Theta = \text{Log} (K_{ads}) + n \text{Log} (C_{inh}) \dots \dots \dots (3.11)$$

where $\Theta < n < 1$, Θ is the degree of surface coverage, C_{inh} is the concentration of the inhibitor, and K_{ads} is the equilibrium constant in the adsorption processes. In this isotherm, a linear relationship exists between the logarithm of surface coverage (Θ) and inhibitor concentration (C_{inh}).

3.6.3.3 Temkin adsorption isotherm

This adsorption isotherm is mathematically represented by equation 3.12 (Obaike Adejo et al., 2024; Srinivasa Rao & Siddhartha, 2017). The Temkin adsorption isotherm provides some insights into the nature of interactions that occur in the adsorbed layer of *Sclerocarya birrea* at the metal surface.

$$\Theta = -\left(\frac{1}{2a}\right) \ln C_{inh} - \left(\frac{1}{2a}\right) \ln K_{ads} \dots \dots \dots (3.12)$$

where a represents the molecular interaction factor in the adsorbed layer, K_{ads} is the equilibrium constant, C_{inh} is the inhibitor concentration, and Θ is the degree of surface covering.

3.6.3.4 El-awady adsorption isotherm

The El-awady adsorption isotherm can be described numerically by equation 3.13 (Abdelshafi et al., 2022).

$$\text{Log } \frac{\Theta}{1-\Theta} = \text{Log } K' + Y \text{Log } C_{inh} \dots \dots \dots (3.13)$$

where Θ is the degree of surface coverage, K_{ads} is the equilibrium constant, $K_{ads} = K'^{(1/y)}$, C_{inh} is the inhibitor concentration, and (x) is the number of water molecules replaced by one organic adsorbate molecule ($x = 1/y$).

3.6.4 Determination of the Gibbs free energy (ΔG_{ads})

From the K_{ads} values attained from adsorption isotherms the Gibbs free energy was computed from equation 3.14 (Akinbulumo et al., 2020):

$$\Delta G_{ads} = -2.303RT \text{Log } (K_{ads} \times C_{H_2O}) \dots \dots \dots (3.14)$$

where C_{H_2O} is the concentration of liquid water (55.34 M at 25 °C), R is the Universal Gas Constant, and T is the absolute temperature in Kelvins.

3.7 Computational analysis - Quantum chemical analysis

3.7.1 Density Functional Theory (DFT)

Quantum chemical calculations were used to predict the molecular structure, electron distribution, and electron transfer of the organic inhibitors Ethanol,2-(octadecyloxy) (T1), Hexadecanoic acid, ethyl ester (T2), Octadecanoic acid, ethyl ester (T3), and Octadecanoic acid (T4)) to the Al and Fe surfaces. Figure 3.8 shows the architecture of T1, T2, T3, and T4. Geometry optimization was first performed utilizing the B3LYP/6-31G(d) DFT approach to accelerate structural geometry calculation. Optimization was not performed in the solution phase because it had a small effect on structure and energy (Hadisaputra et al., 2021; Huong et al., 2020; Wirayani et al., 2018). Geometric and quantum chemical parameters were calculated using Gaussian 09 (Frisch et al., 2016).

Using the obtained data quantum chemical characteristics were computed, including E_{HOMO} , E_{LUMO} , Gap energy ΔE , ionization potential (I), electron affinity (A), electronegativity (χ), hardness (η), and number of electron transfers (ΔN) using equations 3.15 to 3.19.

i) Ionization potential (I)

$$I = -E_{\text{HOMO}} \dots \dots \dots (3.15)$$

ii) Electron Affinity (A)

$$A = -E_{\text{LUMO}} \dots \dots \dots (3.16)$$

ii) Electronegativity (χ) and iv) hardness (η) of each organic inhibitor were estimated using equations 3.33 and 3.34 (Yang & Parr, 1985):

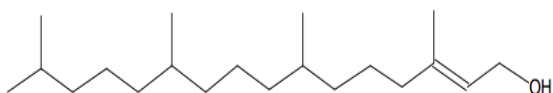
$$\chi = \frac{(I+A)}{2} \dots \dots \dots (3.17)$$

$$\eta = \frac{(I-A)}{2} \dots \dots \dots (3.18)$$

v) Number of electrons transferred (ΔN) from each organic inhibitor to each metal surface was estimated by equation 3.35 according to Pearson's theory (Pearson, 1988, 1990).

$$\Delta N = \frac{\chi^M - \chi^{\text{Inh}}}{2(\eta^M + \eta^{\text{Inh}})} \dots \dots \dots (3.19)$$

where χ^M and χ^{Inh} are the absolute electronegativity values of the metal (Al or Fe) and the organic inhibitor, respectively. η^M and η^{Inh} represent the absolute hardness values of the metal and organic inhibitors, respectively. Theoretical investigations of $\chi^M = 3.23$ eV and $\eta^M = 2.77$ eV were used to quantify the amount of electrons transferred (Pearson (1988); Sastri & Perumareddi (1997)).



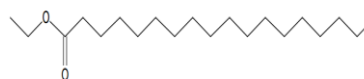
a) 3,7,11,15-Tetramethyl-2-hexadecen-1-ol (T1)



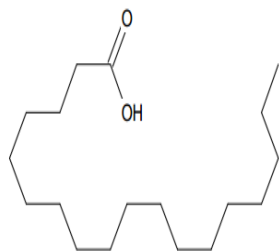
b) Ethanol, 2-(octadecyloxy) (T2)



c) Hexadecanoic acid, ethyl ester (T3)



d) octadecanoic acid, ethyl ester (T4)



e) Octadecanoic acid (T5)

Figure 0.8 (a – e) : Chemical structures of the four derivatives of *Sclerocarya birrea* ethanolic leaf extract.

3.7.2 Monte Carlo (MC) simulations

Monte Carlo simulations were performed using Material Studio 7.0 software (Hadisaputra et al., 2020a). The simulation was implemented using COMPASS Force Field to optimize all inhibitor compounds (Hadisaputra et al., 2021). Inhibitor molecules were simulated on the surface of Al (111) and Fe (110) metal with a supercell (20×20) and a vacuum thickness of 15 nm created on the metal plane. Simulations were carried out with target atoms on the Al (111) and Fe (110) metal surfaces using one (1) inhibitor molecule and 100 H₂O molecules.

3.8 Surface and morphological analysis

3.8.1 X-Ray Diffraction (XRD)

Before and after the experiment, XRD analysis was performed to determine the crystallographic structure and chemical composition of each specimen to identify corrosion products and assess inhibitor absorption on the metal surface. The surface alterations during the corrosion experiment were compared to the specimen's surface analysis prior to exposure. The measurements were performed using X-Ray Diffractometer (Drawell W-XRD-Y300, China) operating with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 Kv and 40 mA. Data was collected over 2θ range of 20° to 80° with a step size of 0.02° and scan rate of $10^\circ / \text{min}$. The obtained data was plotted using Origin software to produce diffractograms and phase identification was obtained by using the reference data from the International Centre for Diffraction Data (ICDD) database.

3.8.2 Raman Spectroscopy

Raman spectroscopy was used to analyse metal specimens before and after corrosion trials. Following exposure, the coupons were carefully taken from the electrolyte, gently rinsed with distilled water, dried at room temperature, and analysed by Raman spectroscopy. The

measurement was performed using a 100 X magnification objective with a grind of 600 l/mm. The 521/ cm Si peak was used for calibration. This analysis focused on all samples in the spectral range of 120 to 1820 cm^{-1} . Each spectrum was subjected to baseline subtraction and normalization pre-treatments.

Chapter 4 Results and discussion

4.1 *Sclerocarya birrea* (*S.birrea*) phytochemical analysis and compositional characterization
The ethanolic *S. birrea* leaf extract was subjected to phytochemical screening, FTIR, UV-Vis and GC-MS analysis to obtain the phytochemical compounds, organic compounds and functional groups present that aid in inhibition of metal specimens in corrosive media. Furthermore, phytochemical screening performed on the extract yielded results as presented in Table 4.1.

4.1.1 Preliminary phytochemical screening of *Sclerocarya birrea* results

Phytochemical screening of ethanolic extract of *Sclerocarya birrea* leaf extract has shown significant presence of phytochemical compounds as presented in Table 4.1. The leaves showed highest presence of flavonoids and phenols as observed from strongest colour changes observed. *Sclerocarya birrea* leaves also proved to be rich in alkaloids, terpenoids and glycosides which agrees with the findings reported by Matenanga et al. (2024) which indicated the presence of phytochemicals in ethanolic extracts of ripe *Sclerocarya birrea* fruit pulp. There were no tannis, saponins, or anthraquinones detected in the leaves' ethanolic extract. In a separate investigation, Russo et al. (2018) reported tannis on the barks and leaves of *S.birrea* methanolic extracts. The rich phytochemical profile of this indigenous tree from the results observed allows for it to be used for corrosion inhibition investigations.

Table 0.1: Phytochemical screening of *Sclerocarya birrea* ethanolic extract.

Constituents	Observation	Results
Flavonoids	Strong red coloration	++
Phenols	Deep blue coloration	++
Tannis	No colour change	-
Saponins	No colour change	-
Alkaloids	Yellowish coloration	+
Anthraquinones	Faint brown coloration	-
Terpenoids	Reddish brown coloration	+
Glycosides	Yellow coloration	+

+ Present; ++ strongly present; - absent

4.1.2 Fourier Transform Infrared spectroscopy (FTIR) analysis

The spectra analysis from FTIR revealed distinctive peak values for several functional groups identified in the ethanolic *S.birrea* leaf extract (Figure 4.1). The functional groups were observed in various bands and are primarily linked to phytochemical chemicals found in the leaves of this noble tree, including tannis, saponins, alkaloids, anthraquinones, and flavonoids.

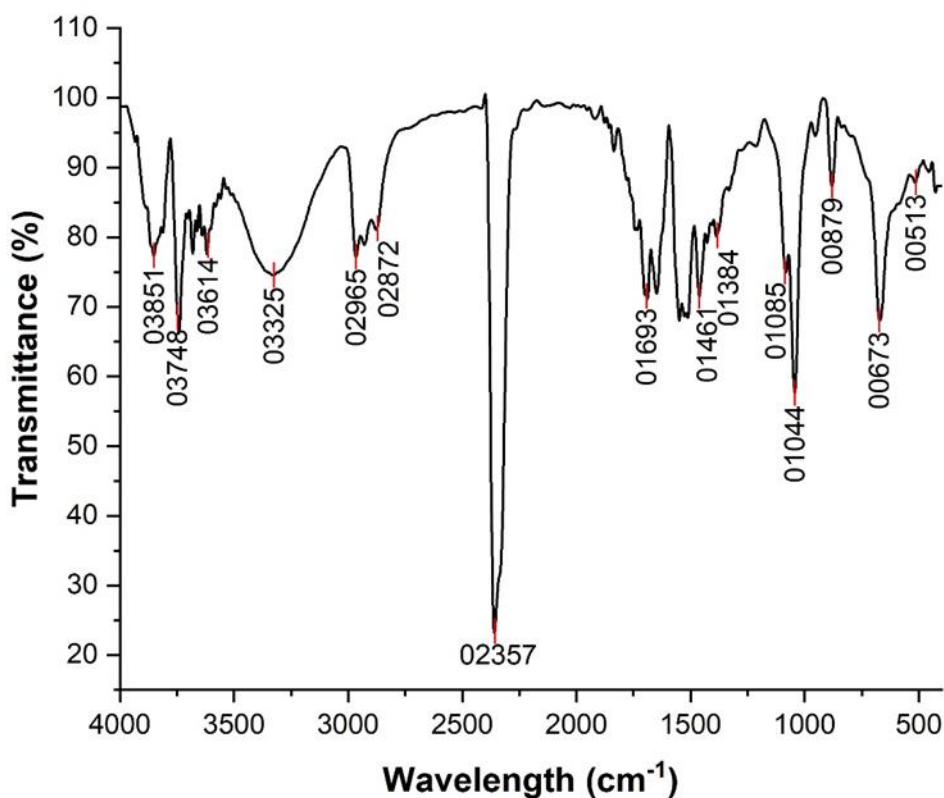


Figure 0.1: FTIR Spectrum for ethanolic extract of *Sclerocarya birrea*.

Despite the clear evidence of the bands in the spectra, Table 4.2 displays the exact distinct peaks from *S.birrea* leaf extract to portray the bonds and their functional groups. These peaks correspond to vibrational modes associated with specific functional groups, which reveal information about the extract's molecular structure. The largest peaks identified were 3851, 3748, 1693, 1044, and 673 cm^{-1} , indicating O-H stretching vibrations and the presence of alcohols or phenols.

The apparent existence of aliphatic C-H stretching vibrations at 2965 and 1461 cm^{-1} suggests that alkane structures occur in the *S.birrea* leaf extract. Peak 2357 cm^{-1} is consistent with triple bond stretching (C), which suggests the existence of alkynes or amines. The presence of carbonyl groups, possibly from aldehydes, ketones, or esters, is indicated by the carbonyl stretching vibration at 1693 cm^{-1} . Furthermore, detection of an alkene signal at 1384 cm^{-1} indicates C=C double bonds. The signal at 3325 cm^{-1} represents C-N stretching vibrations, indicating that the extract contains amines or amides. The significant peak at 1044 cm^{-1} corresponds to benzene ring out-of-plane bending vibrations, which indicate the presence of aromatic compounds. Notably, peaks at 879 cm^{-1} (C-Cl stretching), 673 cm^{-1} (C-Br stretching),

and 5130 cm^{-1} (C-I stretching) indicate the presence of halogenated compounds in the *S. birrea* leaf extract, possibly chloroalkanes, chlorobenzenes, alkyl iodides, bromoalkanes, or bromobenzene. In addition, alcohol, phenols, alkynes, carbonyls, alkenes, amines or amides, and aromatic compounds have been discovered as components that contribute to the extract's complexity.

The O-H stretching vibrations identified in the FTIR spectrum indicate the presence of phenolic compounds, which are well-known for their corrosion-prevention properties. These compounds have the potential to accumulate on the metal surface, generate a supine coating, preventing redox reaction from occurring and shielding the metal, therefore impeding corrosion processes. (Lakshmi, 2016; Loto, 2017a). Furthermore, heteroatoms such as nitrogen, oxygen and sulfur are present in phenols and they can protonate in solutions, donating unshared electron pairs, unsaturated bonds (such as double or triple bonds), and planar conjugated systems with all forms of aromatic cycles in their structures, all which attribute to its effectiveness as corrosion deterrents (Loto, 2017b). Alkynes, alkenes, and halogenated chemicals existence indicates the potential presence of organic molecules with unsaturated or reactive sites. Understanding these functional groups facilitates the exploration of novel corrosion inhibition methods. For example, double bonds in alkenes may aid in adsorption on metal surfaces, minimizing corrosive reactions. Alkenes in small sizes frequently adsorb and desorb on metallic surfaces to prevent corrosive substances from reaching the metal surfaces (Chen et al., 2016).

Alcohols, carboxylic acids, and amines functional groups, can also generate passive coatings on metal surfaces, suppressing the redox reactions that contribute to corrosion (Assad & Kumar, 2021a; Loto, 2017b). Carboxylic acids serve to retard corrosion by binding to partly dissipated metal ions, preventing additional disintegration and corrosion (Al Otaibi & Hammud, 2021; Miralrio & Vázquez, 2020). Through electron exchange, aliphatic amines act as electron donors during redox processes, stabilizing metal cations and preventing the formation of reactive species that cause corrosion (Huang et al., 2022). Meanwhile, hydroxyl groups also combat corrosion by adhering to the substrate and forming a thin film coat, impeding corrosion by altering the environment's electrochemical properties (Assad & Kumar, 2021a).

Table 0.2: FTIR peak values and functional groups of ethanolic extract of *Sclerocarya birrea*.

No.	Bond	Functional Group	Peak value
1.	O-H	Alcohol	3851
2.	COOH	Carboxylic acid	3748
3.	O-H	Alcohol	3614
4.	N-H	Primary amine	3325
5.	C-H	alkane	2965
6.	C-H	aldehydes or ketones	2872
7.	C≡C	Amine	2357
8.	C=O	Ketone	1693
9.	C-H	Alkane	1461
10.	C=C	Alkene	1384
11.	C-O	Ester	1085
12.	C-H	Out-of-plane bend in aromatic compounds.	1044
13.	C-Cl	alkyl chlorides	879
14.	C-Br	Alkyl bromides	673
15.	C-I	Alkyl iodides	513
16.	C-O	Ether	496

4.1.3 Ultra-violet (UV-Vis) spectroscopy analysis

UV-Vis analysis was utilized to determine the phytoconstituent profile of *S. birrea* leaf extract. Molecules identified had chromophores, aromatic rings, electron lone pairs, σ bonds, and π bonds, all of which play a vital role in corrosion inhibition (Karpagasundari & Kulothungan, 2014). With regards to the strong peaks and appropriate baseline established, the qualitative UV-Vis profile of ethanolic *S. birrea* leaf extract has been acquired at wavelengths between 200

and 800 nm (Figure 4.2). Peaks at 209, 229, 324, 353, 390, 438, 482, 535, 553, 614, 644 and 679 nm were attained from the profile with the absorption of 1.309, 1.465, 1.78, 0.887, 0.653, 0.231 and 2.34 respectively.

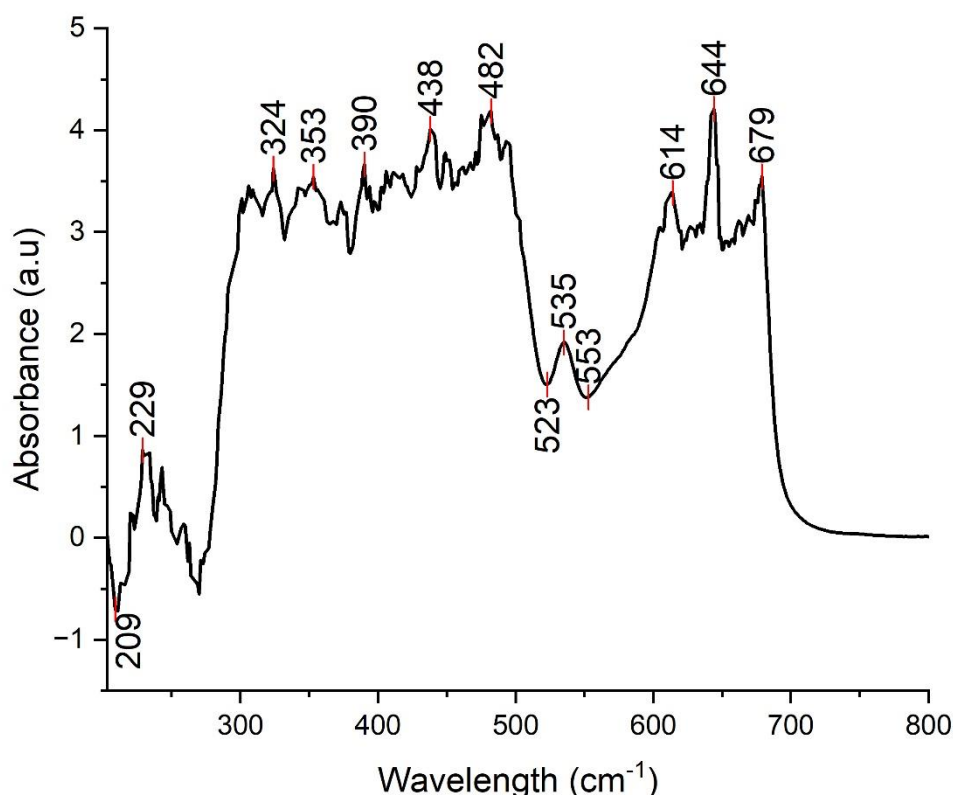


Figure 0.2: UV-vis adsorption spectrum of ethanolic extract of *Sclerocarya birrea*.

However, since the spectrum was unable to represent all the detected wavelengths and precise absorbance, these were listed in Table 4.3. The presence of heteroatoms and unsaturated groups like S, N, and O is evident from the overlap of peaks in the 200–400 nm range. The absorption peak at 229 nm is ubiquitous in most plant extracts, which is attributed to the π – electrons (Yesudass et al., 2016). This indicates the high content of organic chromophores in ethanolic leaf extract of *S. birrea*. Peaks between 239 and 679 nm in the spectrum profile suggests the presence of phenolic compounds and alkaloids (Karpagasundari & Kulothungan, 2014b).

Table 0.3: UV-Vis of ethanolic extract of *Sclerocarya birrea*.

Sample No.	Wavelength (nm)	Absorbance (a.u)
1.	209	0.001399654
2.	229	0.311306404
3.	239	0.180704354
4.	270	0.063772838

5.	307	0.835008062
6.	324	0.876372136
7.	353	0.864873572
8.	381	0.721332439
9.	390	0.883084852
10.	402	0.753459239
11.	425	0.833893528
12.	438	0.952784449
13.	482	0.994375441
14.	523	0.452774494
15.	535	0.531942979
16.	552	0.432929827
17.	614	0.830348781
18.	621	0.720826868
19.	644	0.995859163
20.	679	0.860618401

4.1.4 Gas chromatography-mass spectrometry (GC-MS) analysis

The *S. birrea* ethanolic extract was subjected to GC-MS analysis over a duration of 60 minutes, including a 5-minute initial delay (Eddy et al., 2011). Several phytochemicals were discovered as shown in Figure 4.3. Through comparison of the mass spectrum of the constituents with the main library such as National Institute of Standards and Technology (NIST) libraries and Wiley 9.0, all these compounds were properly characterized and identified.

The active phytoconstituents, along with their respective retention times (RT), molecular weight, structure and percentage peak area were presented in Table 4.4 below. The discovered components and their corresponding peak percentages include Dodecane (35 %) , Benzenaminium, Ethanol, 2-(octadecyloxy) (12 %) , 3,7,11,15-Tetramethyl-2-hexadecen-1-ol (47 %), Lupan-3-ol , acetate (9 %), 1-(+)-Ascorbic acid 2,6-dihexadecanoate (38 %), Phytol (62 %) , Pagicerine (7 %), 1-(hydroxymethyl)-1,2-ethanediylester (2 %), among others. From the 17 compounds found, 12 of them have been described as corrosion inhibitory compounds. The 3,7,11,15-Tetramethyl-2-hexadecen-1-ol was discovered by AT et al. (2023), in *Clerodendrum infortunatum* (CIW) and portrayed high inhibitory effectiveness against mild steel corrosion in 0.5 N HCl by forming multiple molecular coats on the metal surface that followed Temkin adsorption isotherm. Through anodic preponderance and donor-acceptor interactions caused by the transfer of a single pair of electrons from the oxygen atom to the empty “d” orbital, this compound provided mixed inhibition protection. Another study by Adindu (2023) also detected this chemical component as a major constituent in the ethanolic extract of *Pennisetum purpureum* which was used in safeguarding mild steel degradation in harsh acidic

environments. Through adsorption on the metal surface, the study demonstrated that 5, hydroxy pentadecanoic acid and 3,7,11,15-Tetramethyl-2-hexadecen-1-ol reduced both anodic and cathodic corrosion.

Octadecanoic acid, commonly known as stearic acid was also among the twelve (12) corrosion inhibitory compounds detected. It is one of the most abundant fatty acids and exists as a glycerol ester in most animals and plant fats. From the findings of *S. birrea* ethanolic leaf extract, this compound was discovered at retention time of 51.79 s and at 52.25 s ethyl ester was found which have been reported to be great contributor to corrosion inhibition. Octadecanoic acid (9.12 %) was reported in high concentrations in *Ficus Benjamin* (FB) gum extract, which was employed for aluminum degradation inhibition in 0.1 M HCl environment (Eddy et al. 2014). The gum extract inhibited corrosion through synergistic adsorption of its numerous components resulting in the formation of multiple layers on the substrate. Chemisorption was the most popular mechanism of adsorption, fitting best with the Frumkin and Dubinin-Radosevic adsorption models. Meanwhile, Liu et al. (2006) used stearic acid (9.01 %), which was also detected in *S. birrea*, to block an oxide-free iron surface and demonstrated monolayers of the compound built iron surface to hinder corrosive substances from gaining access to the metal.

Hexadecanoic acid, ethyl ester identified at a retention time of 52.250 s in *S. birrea* leaf extract have also been attributed to great corrosion inhibition results in various studies. It was found as one of four major chemicals in the *Solanum Erianthum* extract, which was applied as an inhibitor for 6063 Aluminum alloy in various sea water settings, and the results revealed that it generated a passivation layer of tannates on the aluminium substrate (Bodude et al., 2018). Furthermore, strong hydrogen bonds and metal complexes are conceived to be formed by the various groups that surround the molecule, ultimately preventing the anodes or micro-anodes forming on the metal.

At a retention period of 46.35 seconds, 1-(+)-Ascorbic acid 2, 6-dihexadecanoate was also detected in *S. birrea* ethanolic leaf extract. This compound has been proven to effectively inhibit mild steel rebars degradation in chloride cement mortar with a solid working model from donating electrons to free radicals, neutralizing and reducing oxidative damage to cells and tissues (Argiz et al., 2022). Ascorbic acid demonstrated high inhibition efficiencies over an eight-month period in the *S. birrea* ethanolic leaf extract study. In a similar investigation, it served as an organic corrosion inhibitor to prevent deterioration of reinforcements immersed

in a simulated concrete pore solution with mortars in contact with chlorides, according to Brix et al. (2022). A high inhibition efficacy of 88.96 % was achieved at an ideal dosage of 0.1 g/L, with the inhibitor proving to be anodic type inhibitor and the dominance adsorption mode being chemisorption. Furthermore, Irwan et al. (2019) demonstrated a high efficiency of 85.4 % with ascorbic at 50 ppm attained after 15 days against metal dissolution low content carbon steel in a marine environment; the compound suppressive action was due to metal surface adherence to build a protective layer. Other compounds found in the *S. birrea* ethanolic leaf extract that may play a pivotal role in achieving high inhibitory efficiency include phytol and pagicerine. Phytol, a branched chain of unsaturated alcohol found in all plants as chlorophyll, is a cyclic alcohol of diterpene that is widely found in various significant plant oils such as *Lantana radula* and *cleome serrate* (Taj et al., 2021). Meanwhile, Pagicerine, recognized as a rare vobasine type indole alkaloid was initially reported from *Pagiantha ceriferu* and *Rauvolfia yannanensis* (Reina et al., 2014).

The phytochemical compounds identified in the ethanolic leaf extract of *Sclerocarya birrea* were presented as mass spectrum, to distinguish them based on their specific molecular ion peaks and structural characteristics, as depicted in Table 4.4.

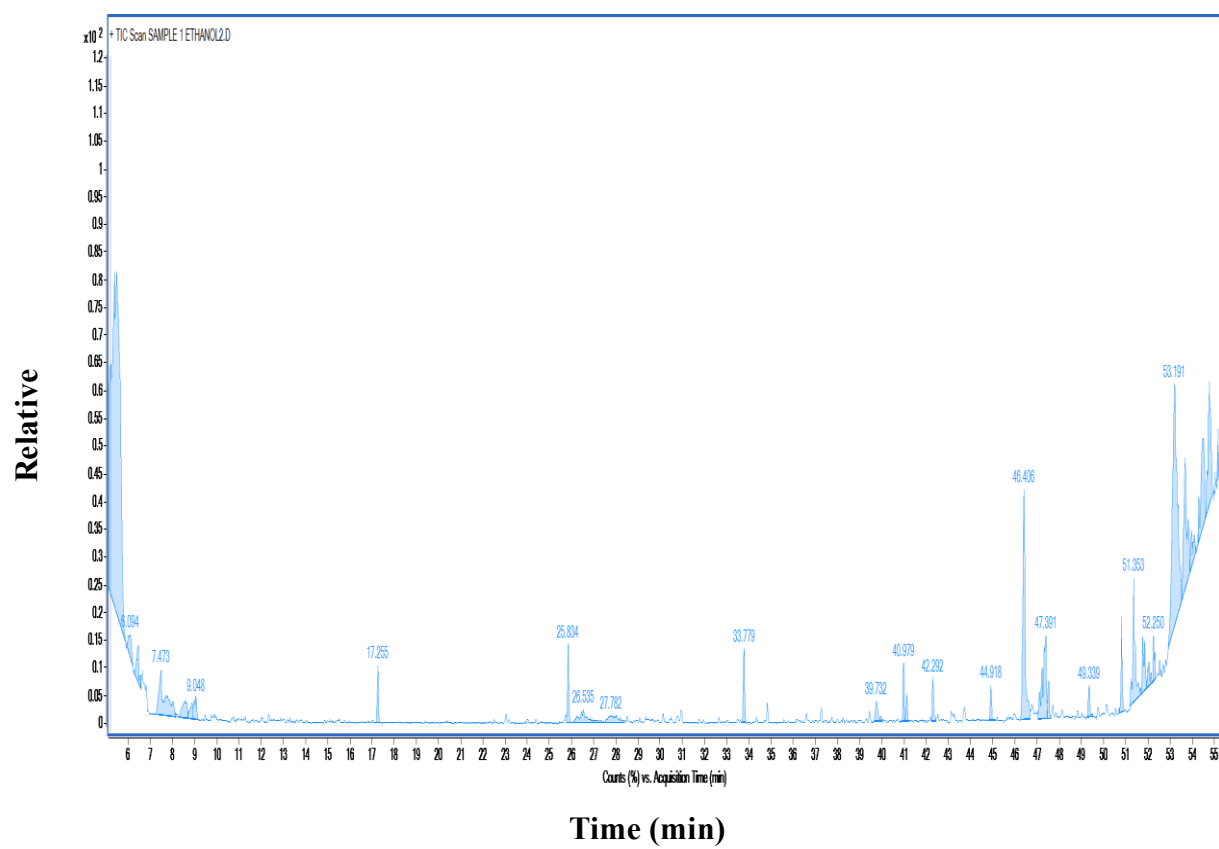
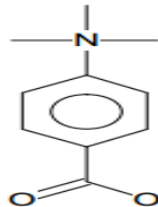
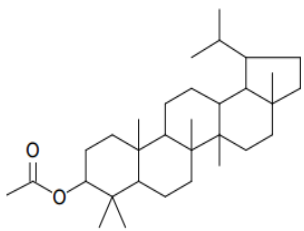
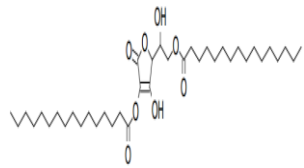
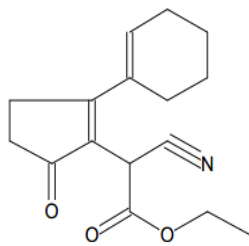


Figure 0.3: GC-MS chromatogram of *Sclerocarya birrea* ethanolic leaf extract.

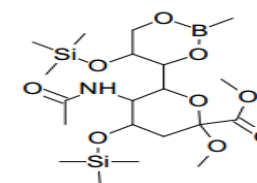
Table 0.4: GC-MS phytochemical analysis of *Sclerocarya birrea* ethanolic leaf extract.

No.	Retention Time (min)	Probability (%)	Name of Compound	Molecular Formula	Molecular weight	Molecular Structure
1.	25.856	48.7	Dodecane	C ₁₂ H ₂₆	170	
2.	33.735	22.0	Nonadecane	C ₁₉ H ₄₀	198	
3.	39.797	5.1	Benzenaminium, 4-carboxy-N,N,N-trimethyl-, hydroxide, inner salt	C ₁₀ H ₁₃ NO ₂	179	
4.	41.001	4.9	Ethanol, 2-(octadecyloxy)	C ₂₀ H ₄₂ O ₂	314	
5.	42.292	57.6	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	C ₂₀ H ₄₀ O	296	

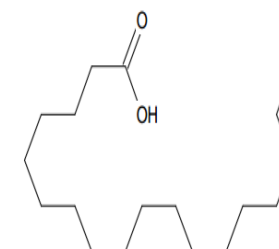
6.	43.736	10.3	Lupan-3-ol, acetate	$C_{32}H_{54}O_2$	470	
7.	46.385	18.6	l-(+)-Ascorbic acid 2,6-dihexadecanoate	$C_{38}H_{68}O_8$	652	
8.	47.369	35.3	Hexadecanoic acid, ethyl ester	$C_{18}H_{36}O_2$	284	
9.	49.339	32.4	1-Cyclopenten-3-one, 1-(1-cyclohexen-1-yl)-2-[(carboxyethyl)(cyano)methyl]	$C_{16}H_{19}NO_3$	206	
10.	50.805	76.7	Phytol	$C_{20}H_{40}O$	296	



11.	51.396	14.6	β -N-Acetylneuraminic acid, methyl ester-2-methyl-7,9-methyl-boronate-3,8-di(trimethylsilyl)	$C_{20}H_{40}BNO_9Si_2$	321
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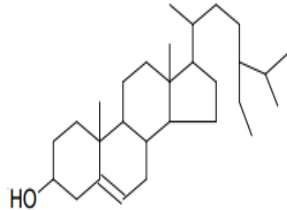
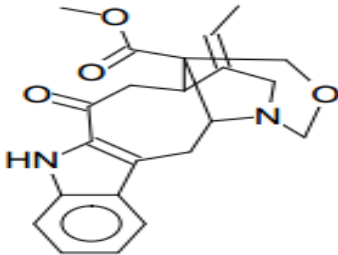
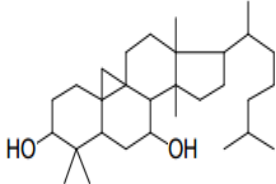
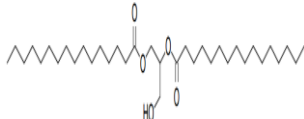


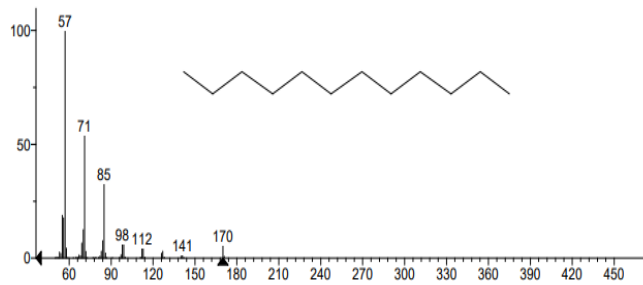
12.	51.790	15.7	Octadecanoic acid	$C_{18}H_{36}O_2$	284
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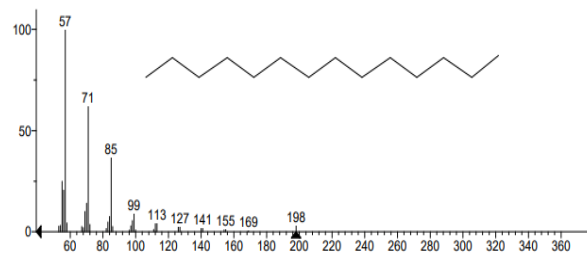
13.	52.250	14.4	Octadecanoic acid, ethyl ester	$C_{20}H_{40}O_2$	312
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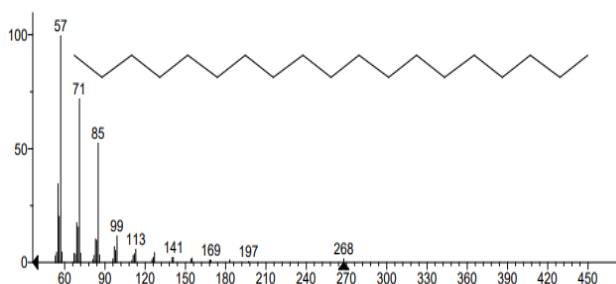
14.	53.235	18.5	γ -Sitosterol	$C_{29}H_{50}O$	414	
15.	53.672	18.9	Pagicerine	$C_{22}H_{24}N_2O_4$	352	
16.	54.482	28.0	9,19-Cyclolanostane-3,7-diol	$C_{30}H_{52}O_2$	444	
17.	55.248	31.1	Hexadecanoic acid, 1-(hydroxymethyl)-1,2-ethanediyl ester	$C_{35}H_{68}O_5$	568	



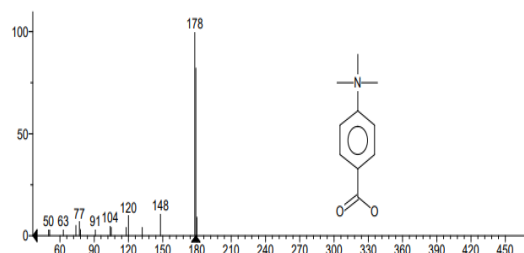
a) Dodecane



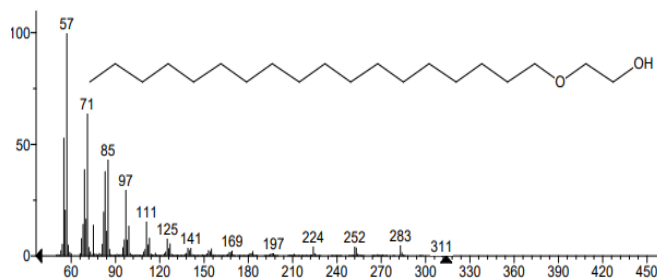
b) Tetradecane



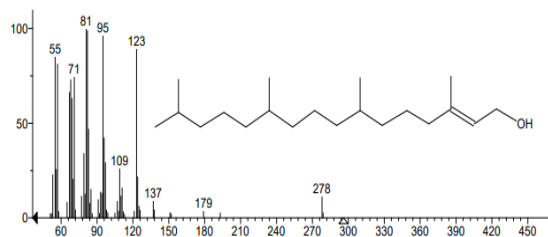
c) Nonadecane



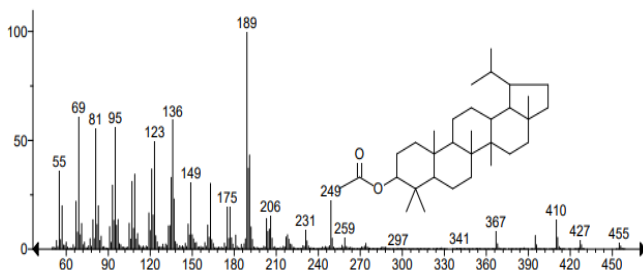
d) Benzenaminium, 4-carboxy-N, N,N-trimethyl-, hydroxide, inner salt



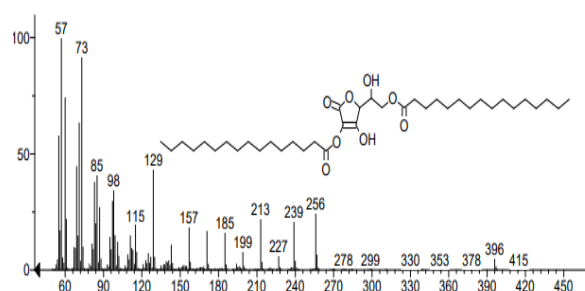
e) Ethanol, 2-(octadecyloxy)



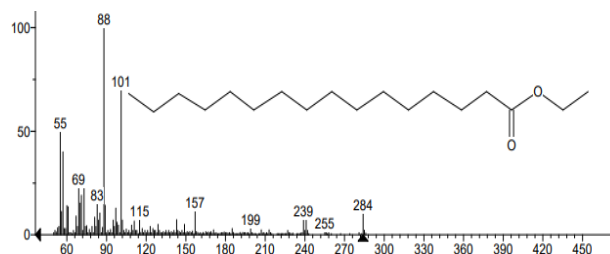
f) 3,7,11,15-Tetramethyl-2-hexadecen-1-ol



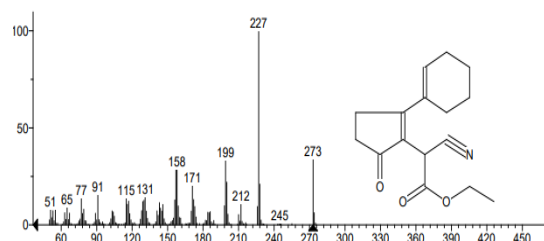
g) Lupan-3-ol, acetate



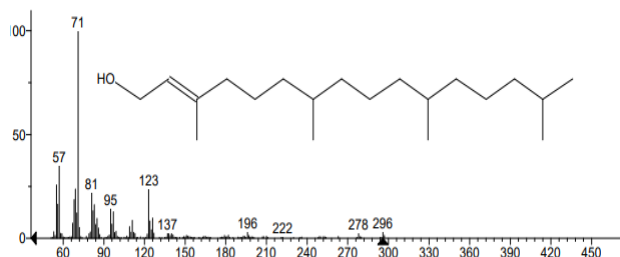
h) 1-(+)-Ascorbic acid 2,6-dihexadecanoate



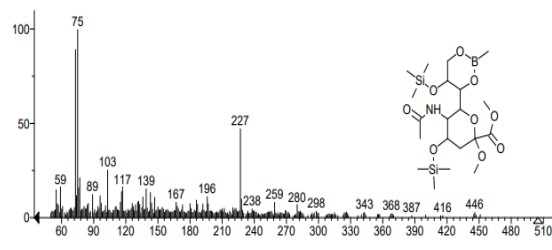
i) Hexadecanoic acid, ethyl ester



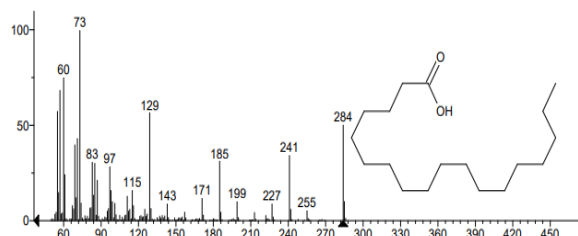
j) 1-Cyclopenten-3-one, 1-(1-cyclohexen-1-yl)-2-[(carboxyethyl)(cyano)methyl]-



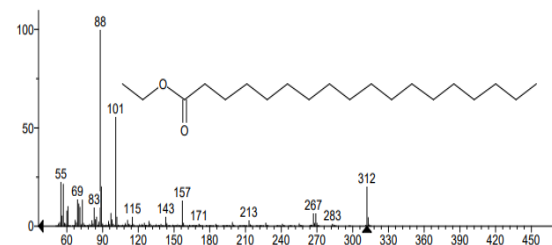
k) Phytol methyl-boronate-3,8-di(trimethylsilyl)-



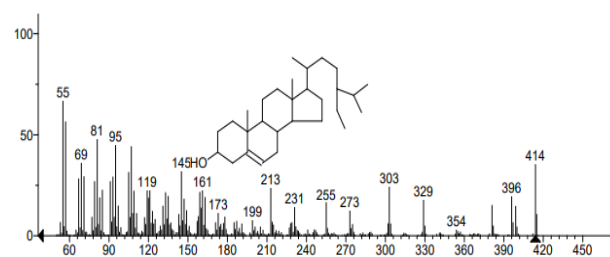
l) β-N-Acetylneuraminic acid, methyl ester-2-methyl-7,9-



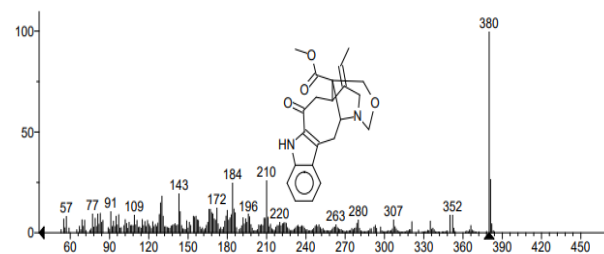
m) Octadecanoic acid



n) Octadecanoic acid, ethyl ester



o) γ-Sitosterol



p) Pagicerine

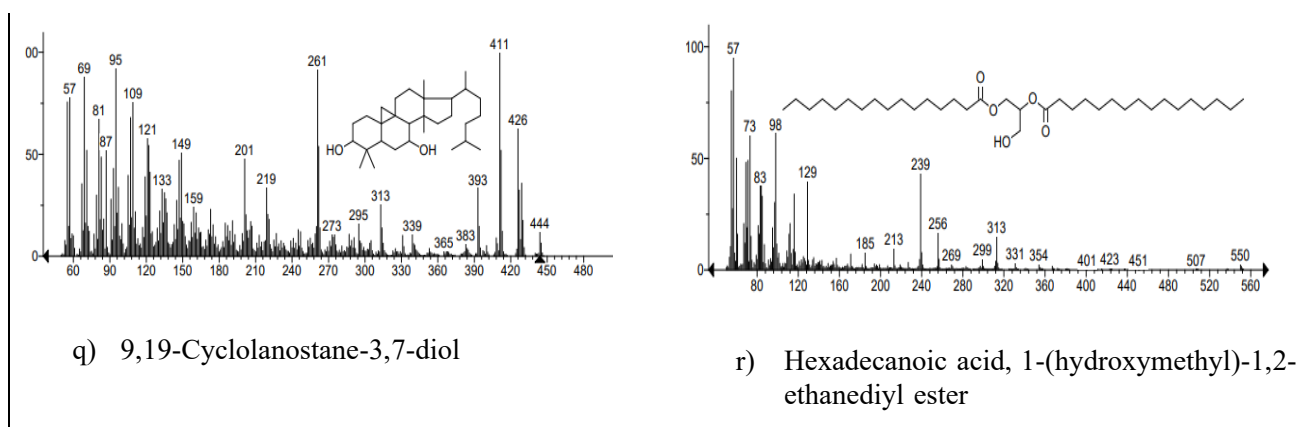


Figure 0.4: Mass spectra of the identified phytochemical compounds in the ethanolic extract of the *Sclerocarya birrea*.

Like most medicinal plants, *Sclerocarya birrea* has a rich bioactive and phytochemical profile with therapeutic purposes due to related biological activities and nature of the compounds extracted, which are summarized in Table 4.5. It shows the evaluated diverse range of biological effects, including antioxidant properties, antimicrobial activity against various pathogens, anti-inflammatory potential, and possible anticancer properties among others.

Table 0.5: Biological activity and nature of the compounds detected in *Sclerocarya birrea* ethanolic leaf extract.

No.	Name of compound	Nature of the compound	Biological Activity	References
1.	Dodecane	Alkane	Anti-bacterial	(Khanal et al., 2022)
2.	Nonadecane	Alkane	No activity	-
3.	Benzenaminium, 4-carboxy-N,N,N-trimethyl-, hydroxide, inner salt	unknown	No activity	-
4.	Ethanol, 2-(octadecyloxy)	Alcohol	Anti-microbial	(Karthik et al., 2023)
5.	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	Apha tocophenol	Antioxidant, anti-inflammatory	(Elufioye et al., 2017)
6.	Lupan-3-ol, acetate	Triterpenoid	Antiprotozoal, antimicrobial, anti-inflammatory,	(Vijayashalini et al., 2017)

			antitumour, chemoprotective	
7.	l-(+)-Ascorbic acid 2,6-dihexadecanoate	Vitamin C	Antioxidant, enzyme cofact(Kumar & Sati, 2021)modulator	(P. Kumar & Sati, 2021)
8.	Hexadecanoic acid, ethyl ester	Fatty acid ester	Nematicide, pesticide, Lubricant, antiandrogenic, flavour, hemolytic 5-Alpha reductase inhibitor	(Siswadi & Saragih, 2021)
9.	1-Cyclopenten-3-one, 1-(1-cyclohexen-1-yl)-2-[(carboxyethyl)(cyano) methyl]	Polyphenol/phenethylamine alkaloid	No activity	-
10.	Phytol	Diterpenoid / Diterpene Alcohol	Anti-microbial, anti-cancer, anti-inflammatory, hypocholesterolemic, nematicide, anti-coronary	(M. T. Islam et al., 2018)
11.	β -N-Acetylneuraminic acid, methyl ester-2-methyl-7,9-methylboronate-3,8-di(trimethylsilyl)	Sialic acid	Antibacterial, detoxification, boosting immune system	(Wu et al., 2020)
12.	Octadecanoic acid	Stearic acid	No activity	-
13.	Octadecanoic acid, ethyl ester	Stearic acid ester	Antioxidant, anti-inflammatory	(Siswadi & Saragih, 2021)

14.	γ -Sitosterol	Triterpene	Antihyperglycemic, anticancer	(Sirikhansaeng et al., 2017)
15.	Pagicerine	Alkaloid (Indole alkaloids)	Anti-inflammatory, antinociceptive, antitumoral, antioxidant, antimicrobial	(Rosales et al., 2020)
16.	9,19-Cyclolanostane-3,7-diol	triterpene	Antioxidant, hepatoprotective, anti-inflammatory, antimicrobial	(Ali et al., 2007)
17.	Hexadecanoic acid, 1-(hydroxymethyl)-1,2-ethanediyl ester	ester	Antioxidant	(Arora & Kumar, 2017)

Generally, phytochemical and bioactive compounds of the ethanolic leaf extract of *Sclerocarya birrea* were identified and characterized using UV-Vis, GC-MS, preliminary phytochemical screening and FTIR techniques. The UV-Vis analysis detected characteristic peaks resembling chromophores between 200 and 800 nm wavelength range. Meanwhile, the presence of alkanes, alkenes, phenols, esters, amines, aromatic rings, carboxylic acids etc. were confirmed using FTIR. Additionally, 17 phytochemical compounds were also discovered through GC-MS, including major phytochemical constituents such as phytol, pagicerine, octadecanoic acid, γ -Sitosterol and Hexadecanoic acid, ethyl ester which exhibited the highest peaks in the chromatograph. Overall, *Sclerocarya birrea* leaf extract proved to be a rich source of an array of phytochemical compounds, functional groups, and different bioactive compounds. Due to this rich profile, *Sclerocarya birrea* may be used as a potential corrosion inhibitor, taking into consideration various factors which may affect the extract's performance such as media, type of material used and operating conditions.

4.2 Corrosion inhibition by weight loss

4.2.1 Corrosion inhibition behavior of *Sclerocarya birrea* ethanolic leaf extract on mild steel, pipeline steel and aluminium at room temperature employing the mass loss technique in simulated seawater and 1 M H₂SO₄ environments.

Every seven days, as the weights were being documented, the results for the metal specimens (mild steel, API X42 pipeline steel, and aluminum (AA1100) immersed in 3.5 % NaCl and 1 M H₂SO₄ were recorded. The observed physical changes were captured by a camera attached to the phone, in between weight loss measurement to infer the mechanisms of inhibition, adsorption, and corrosion on the surfaces of the metals. The weight loss experiment was carried out in duplicates to guarantee that the results are repeatable and reproducible.

4.2.1.1 The effect of inhibitor concentration on metal corrosion rates in a 3.5 % NaCl environment.

The corrosion rates of metals inhibited with a leaf extract increased dramatically with time probably due to desorption of the inhibitor molecules from the metal surface over prolonged exposure periods. Initially, when the *Sclerocarya birrea* inhibitor is introduced in an aggressive medium it produces a safeguard coating on exposed surface, slowing the metal dissolution process. However, as time passes, the inhibitor molecules may gradually detach or desorb from the metal surface, reducing protective covering and allowing corrosive substances to encounter the metal, thus increasing corrosion rate. The leaf extract without any stabilization added to it, like all other organic materials, deteriorates with time and its efficiency is significantly decreased (Clodoveo et al., 2021). Figures 4.5 a, b, and c present corrosion rates of mild steel, API 5L X42 pipeline steel, and aluminium (AA1100) in 3.5 % NaCl and 1 M H₂SO₄ corrosive environments, both with and without the *Sclerocarya birrea* inhibitor.

Mild steel and API 5L X42 pipeline steel specimens immersed in control (blank) demonstrated most severe corrosion rates, with maximum of 0.24 mm/yr for mild steel, and 0.31 mm/yr for pipeline steel, respectively (Figure 4.5 a & b). The corrosion rate decreased over time but remained higher than inhibited specimens. Overall, corrosion rate decreased with increased inhibitor concentration, followed by this order control (0 g/L) > 5 g/L > 10 g/L > 15 g/L > 20 g/L. Highly concentrated extracts include more molecules, resulting in a more effective film layer on the substrate (Njoku et al., 2024). When concentration of the leaf extract is high, more inhibitor molecules cling onto the metal surface, establishing a more robust and denser layer of protection that inhibits corrosive substances from reaching the metal. At high concentrations, the inhibitor molecules' greater coverage and interaction with the metal surface contribute to a

more efficient corrosion inhibition process, hence reducing the corrosion rate in the 3.5 % NaCl environment (Ahmed et al., 2021). In saline settings, optimal concentration should be identified for better results, as the link between an inhibitor's activity and corrosion is proportional to its concentration.

Meanwhile, the corrosion rate for aluminum was 0.012 mm/yr after 7 days and 0.014 mm/yr after 14 days. Following these recordings, aluminum revealed negative corrosion rate values (Figure 4.5 c). This is possibly due to the matrix of oxide film layer of the aluminum film and adsorbed inhibitor molecules to reduce corrosion rates by forming a robust and steady protective barrier on the metal. Findings from FTIR, UV-vis, and GC-MS revealed that *Sclerocarya birrea* leaf extract includes heteroatoms, aromatic rings, flavonoids, and oxygen-carrying functional groups, all of which can be adsorbed on aluminum surfaces. Due to their greater electron density, heteroatoms serve as active sites for chemical adsorption or physisorption (Kumari & Lavanya, 2022). When the inhibitor interacts with the oxide layer, it improves the oxide film's protective properties, boosting corrosion resistance. This synergistic influence between the inhibitor and the oxide layer can result in a notable decrease in the extent of corrosion, and in some cases, negative corrosion rates, indicating that the metal is being protected rather than eroded (Jakeria et al., 2021). This event highlights the feasibility of combining inhibitors with aluminum's natural oxide layer to create a very efficient corrosion protection system capable of actively preventing corrosion processes.

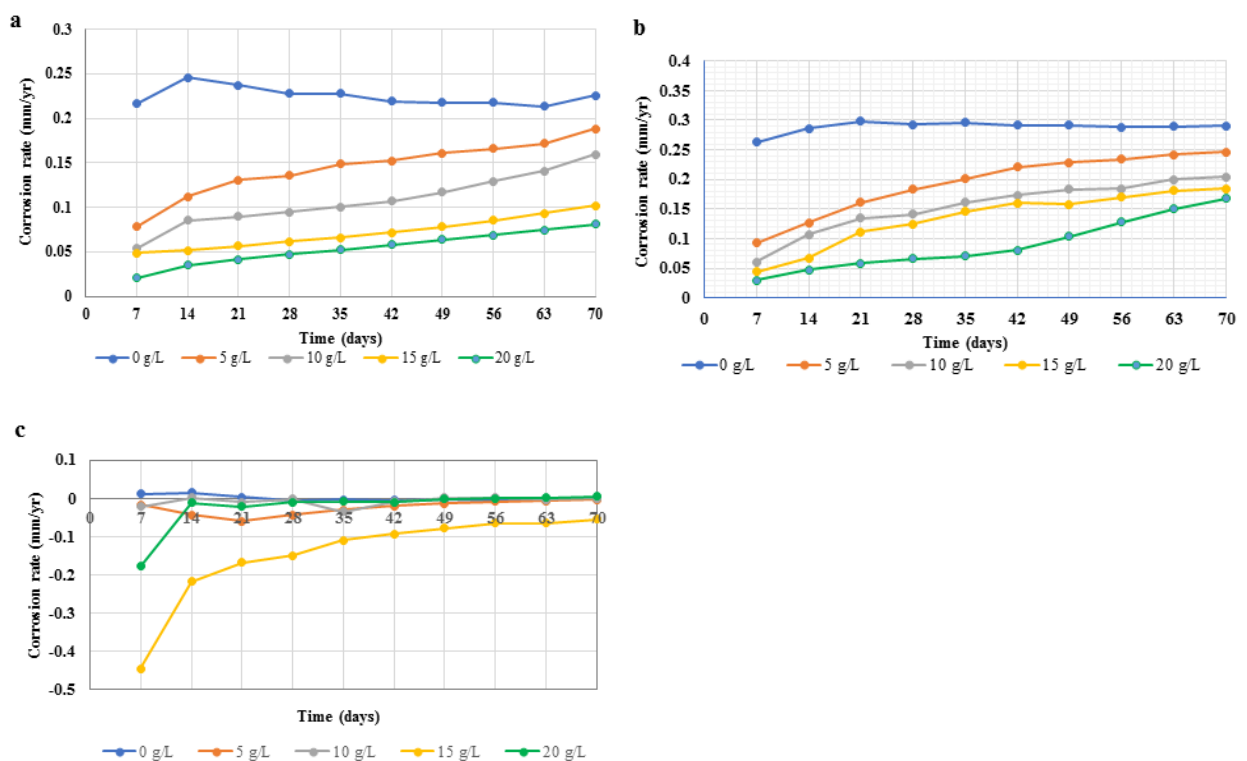


Figure 0.5: Corrosion rate vs exposure duration for a) mild steel, b) API 5L X42 pipeline steel, c) AA1100 immersed in 3.5 % NaCl solution with and without different doses of *Sclerocarya birrea* inhibitor for 70 days.

4.2.1.2 The effect of leaf inhibitor concentration on inhibition efficiency in a 3.5 % NaCl environment.

The overall efficiency of the leaf extract in retarding corrosion is one of the primary variables utilized to identify green corrosion inhibitors (Zakeri et al., 2022). For this experiment, the leaf inhibitor efficacy was high for the first 7 days before gradually decreasing until day 70. Figures 4.6 a, b, and c depict the inhibition efficiencies of API 5L X42 pipeline steel, mild steel and aluminium (AA1100) against immersion duration.

According to the results shown in Figure 4.6 (a) and (b), the inhibitor's efficacy was high on day 7 and subsequently reduced until day 70. Inhibition efficacy fluctuated with time owing to various reasons. Initially, the inhibitor chemicals contained in the leaf produced a layer of protection for the metal substrate, preventing corrosion. However, long-term exposure to a harsh condition may cause this shielding layer to (Ezugha & Aralu, 2023; González-Parra & Di Turo, 2024). Furthermore, the stability compounds that impede corrosion, their surface adherence capabilities, and environmental conditions all influence lifespan as well as performance of the protective coating (Ramazan et al., 2023). Additionally, inhibitor molecules and corrosive environment mutual interaction can change over time, reducing the overall efficacy of the inhibitor. This inhibitory efficiency decrease over time is a common finding in corrosion inhibition research, stressing the importance of considering the temporal stability and performance of inhibitors when assessing their utility in practical applications over lengthy periods.

Aluminium's inhibitory efficiency could not be calculated using the same formula as the other two metals since the metal gained weight after day 21 (Figure 4.6 c). The corrosion rate was reduced to nearly zero by combining the oxide coating and the absorbed molecules of the extract, signifying 100 % efficiency.

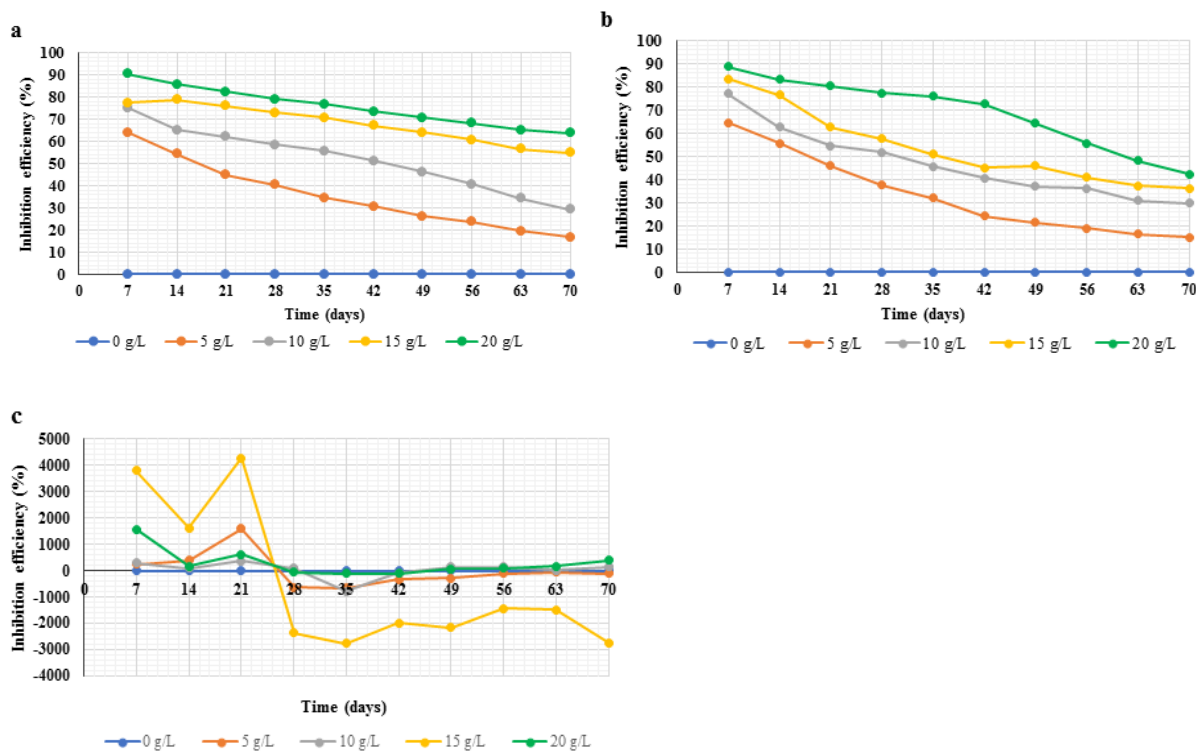


Figure 0.6: The inhibition efficiency vs exposure duration for a) mild steel, b) API 5L X42 pipeline steel and c) AA1100 immersed in 3.5 % NaCl solution with and without varying *Sclerocarya birrea* inhibitor dosages.

4.2.1.3 The effect of inhibitor concentration on metal corrosion rates in 1 M H_2SO_4 environment

Due to considerable harshness of the corrosive media in comparison to the simulated seawater environment, specimens subjected to 1 M H_2SO_4 corroded at high rates. Acidic environments are more detrimental to metal surfaces than saline environments. Acids considerably attack metal surfaces aggressively and stimulate faster electrochemical processes, making them far more toxic (Wicaksono et al., 2023).

Among the three metals, aluminium (AA1100) corroded the least, followed by mild steel and API 5L X42 pipeline steel as observed in Figure 4.7. Aluminum (AA1100), which is more resistant to corrosion in general, exhibits decreased rates of corrosion even in harsh sulfuric acid (Nathiya & Raj, 2017). The processes underlying these varying corrosion tendencies are related to the inhibitor's protective effects on steel, which reduce the corrosive impact of sulfuric acid, whereas aluminum naturally generates a protective oxide layer that resists corrosion. Mild steel and API 5L X42 pipeline steel do not generate an oxide layer; their protection is solely dependent on the adherence of organic compounds on their surfaces (Palumbo et al., 2019). Furthermore, the diffusion rate of ferrous sulphate corrosion products affects the overall degradation of steel in sulfuric acid (Panossian et al., 2012).

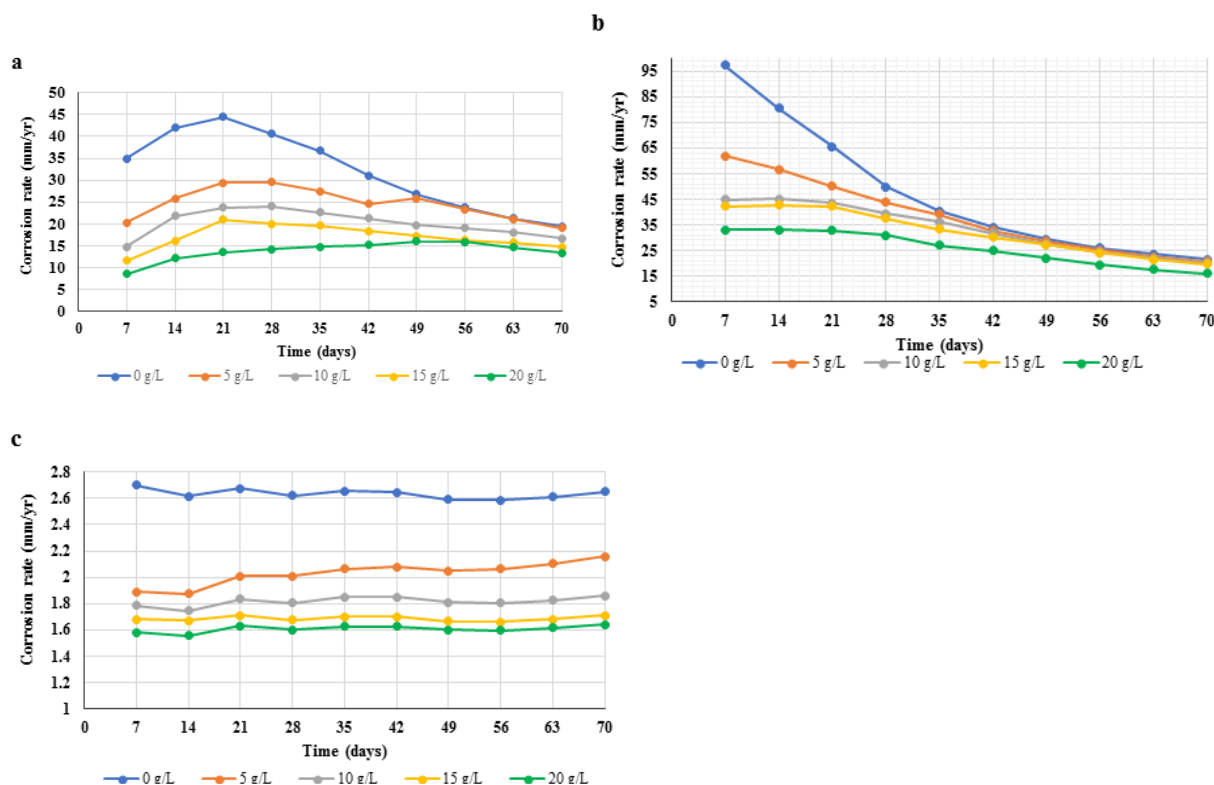


Figure 0.7: Corrosion rate vs exposure duration for a) mild steel, b) API 5L X42 pipeline steel, c) AA1100 immersed in 1 M H₂SO₄ solution in the absence and presence of varying concentrations of *Sclerocarya birrea* inhibitor after 70 days of exposure.

4.2.1.4 The effect of leaf inhibitor concentration on inhibition efficiency 1 M H₂SO₄ environment.

Figures 4.8 a, b, and c show the findings for specimens exposed to 1 M H₂SO₄ for all three metals. A similar trend is visible for specimens treated to 3.5 % NaCl, where the efficacy of the leaf inhibitor is high at day 7 and then declines as the exposure is prolonged.

All the metals shown in Figure 4.8 a, b, and c have high inhibitory efficiency owing to the surface attachment of the extract's active compounds, hence aiding in corrosion resistance. However, as the duration of exposure is prolonged, factors such as temperature variations and the type of the inhibitor may alter inhibitory performance, resulting in a decline in efficiency over time (Bijapur et al., 2023). Furthermore, a decline in inhibitory effectiveness over the observed duration can be influenced by a range of variables, including changes in inhibitor concentration, the adsorption-desorption equilibrium in the metal substrate as well as inhibitor's stability under these circumstances (Chakravarthy & Mohana, 2014).

The inhibitory efficiency of mild steel became practically constant after day 35, but AA1100 accomplished this only after 28 days. This phenomenon is known as inhibitor equilibrium; once

the inhibitor has stabilized on the metal substrate the inhibition efficiency remains constant. This behavior is induced by the dynamic contact between the inhibitor and contact surface, which results in observed fluctuations of inhibitory efficacy over time (Chandrabhan et al., 2022).

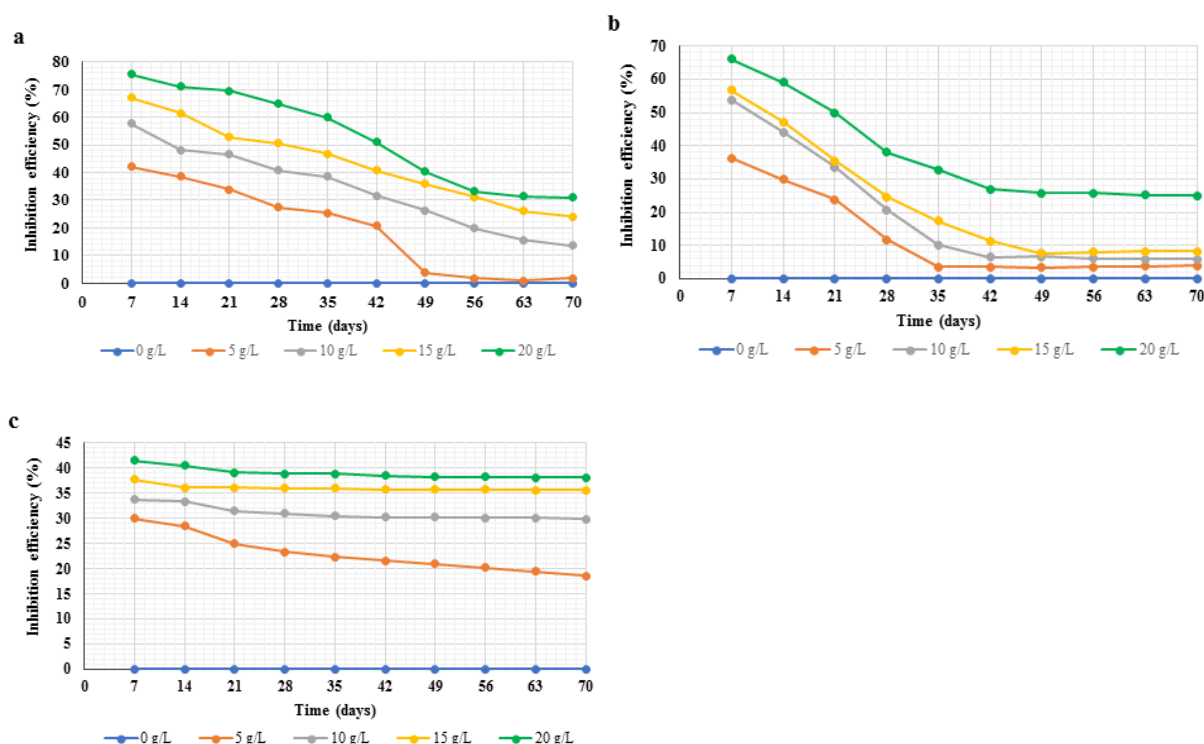


Figure 0.8: The inhibition efficiency vs exposure duration for a) mild steel, b) API 5L X42 pipeline steel and c) AA1100 submerged in 1 M H₂SO₄ solution with and without different dosages of *Sclerocarya birrea* inhibitor.

4.2.2 General physical observations from room temperature weight loss experiments

The observed trend of enhanced effectiveness of inhibition as the dosage of the inhibitor increases across all the three metals immersed in 3.5 % NaCl and 1 M H₂SO₄ attributable to *Sclerocarya birrea* molecules adsorption on the surfaces, thus blocking active sites that may favor the corrosion process. Organic molecule inhibition has been regarded as a regular substitution process in which an inhibitor molecule in liquid state replaces a certain number of molecules absorbed on the metallic substrate (Okafor et al., 2010). In mild steel and API 5L X42 pipeline steel a metal-inhibitor complex can be formed when the exposed substrate's Fe²⁺ ions amalgamate with the inhibiting molecules (El-katori et al., 2020). The resultant complex formed on the metal surface depending on its solubility can either prevent or accelerate additional metal degradation. As displayed in Figure 4.9 organic molecules were physically

attached to the suspended metal surface, jam-packed around the specimen and completely covering it. The GC-MS data demonstrated that the *Sclerocarya birrea* ethanolic extract has a high concentration of heteroatoms and phytochemical substances, which safeguard the metal through coat formation on its surface. The quantity of adsorbed inhibitor molecules on the metal surface rose with a rise in the dosage of the inhibitor but deposited back into the solution after extended metal exposure. Observations showed that the physisorption of *Sclerocarya birrea* inhibitory compounds on metallic surfaces significantly reduces metal degradation.

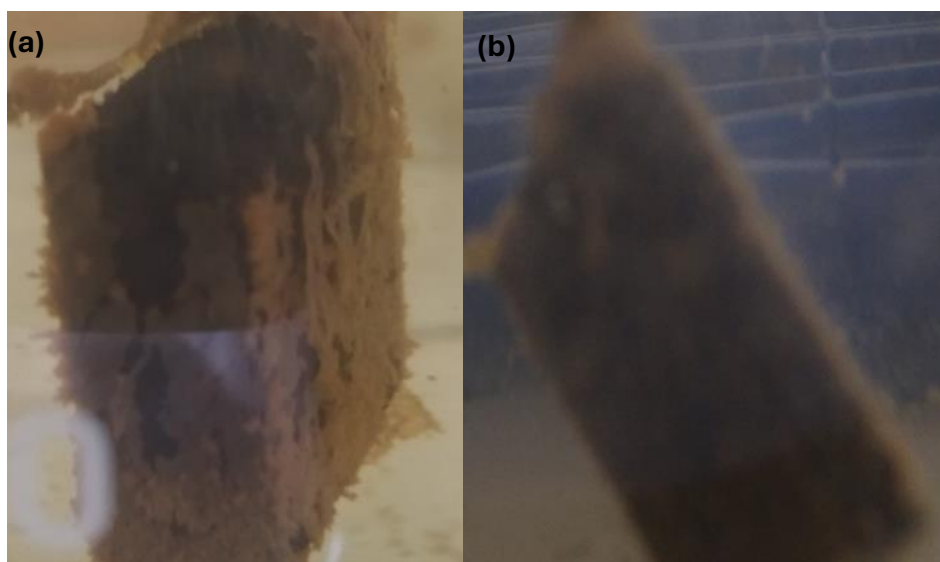


Figure 0.9: *Sclerocarya birrea* leaf inhibitor molecules absorbed on (a) API 5L X42 pipeline steel and (b) Aluminium (AA1100) as observed in between weight loss experiments.

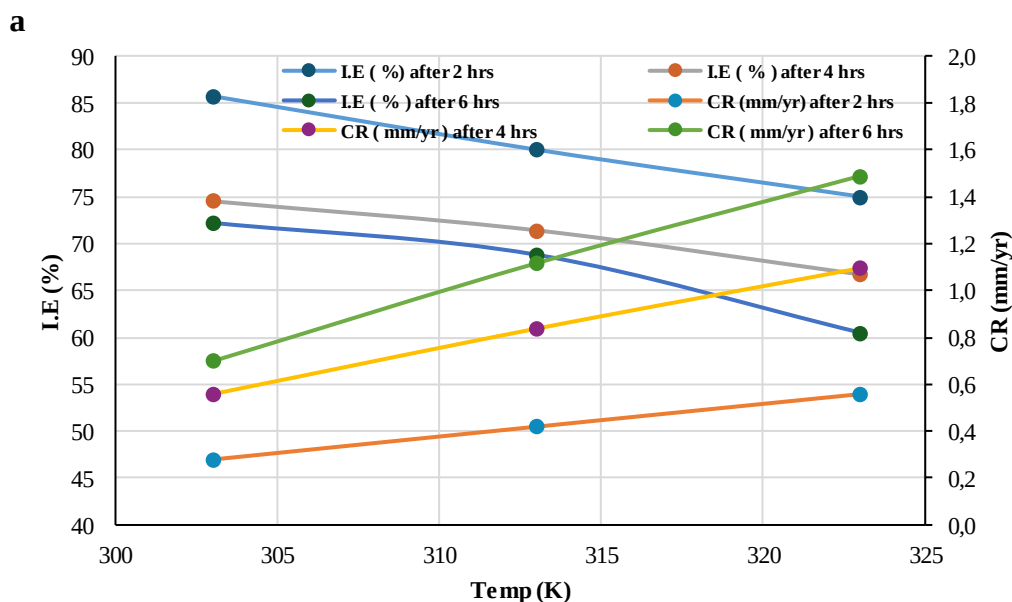
4.3 Thermodynamics and adsorption studies

4.3.1 Effect of temperature on both the inhibition efficiency and corrosion rate of metal samples exposed to 1 M H₂SO₄ and 3.5 % NaCl with varying extract concentrations.

Adsorption and corrosion inhibition are both substantially affected by temperature, with higher temperatures causing desorption of inhibitor molecules that had previously been adsorbed to metallic surfaces. Raising the temperature triggers the molecule's kinetic energy to increase, resulting in desorption from the surface, removing the coating layer that has been covering the metal from the corrosive agents, and leaving the surface exposed (Gómez-Sánchez et al., 2023). Elevated temperatures may also enhance the solubility of the metals' protective coatings, increasing the metal's vulnerability to degradation (Dauda et al., 2013). In terms of chemisorption, temperature increases lead to an increase in molecule adsorption, but only up to a point, beyond which additional increases favour desorption.

4.3.1.1 Effect of temperature (303 – 323 K) on both the inhibition efficiency and corrosion rate of metal samples exposed to 3.5 % NaCl in the presence and absence of Sclerocarya birrea inhibitor.

From the observation in Figure 4.10 a and b it can be noted that inhibition efficiencies are high at the shortest exposure durations (2 hrs) and lowest temperature of 303 K. As the temperatures are raised the inhibition efficacy decreases. Figures 4.10 a & b to 4.12 e & f show that inhibitory effectiveness increases as extract concentration increases; this is because at high concentrations, more molecules adhere to the surface layer, resulting in a much more formidable thick layer. High inhibition efficiencies were achieved at a lower temperature (303 K) , it greatly reduced with each rise in temperature and the lowest efficacy was achieved at 323 K. Higher temperatures favors desorption as molecules possesses are energised and in motion. A striking tendency in the data is that as the exposure length increases, inhibition efficiency falls and corrosion rate increases, which may be attributed to the molecules' desorption back into the electrolyte owing to stability loss.



b

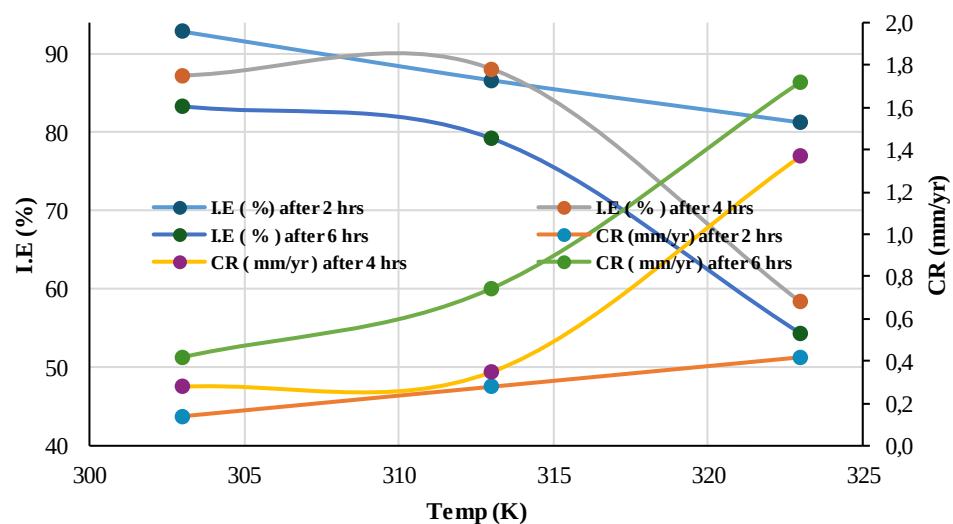
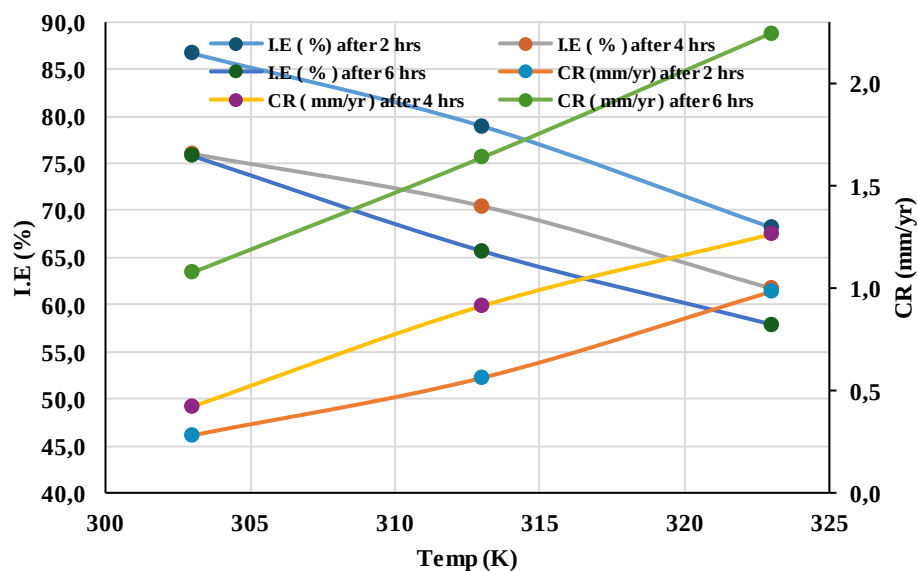


Figure 0.10: Inhibition efficiency and corrosion rate of mild steel in 3.5 % NaCl for a) 10 g/L and b) 20 g/L *Sclerocarya birrea* extract concentration.

c



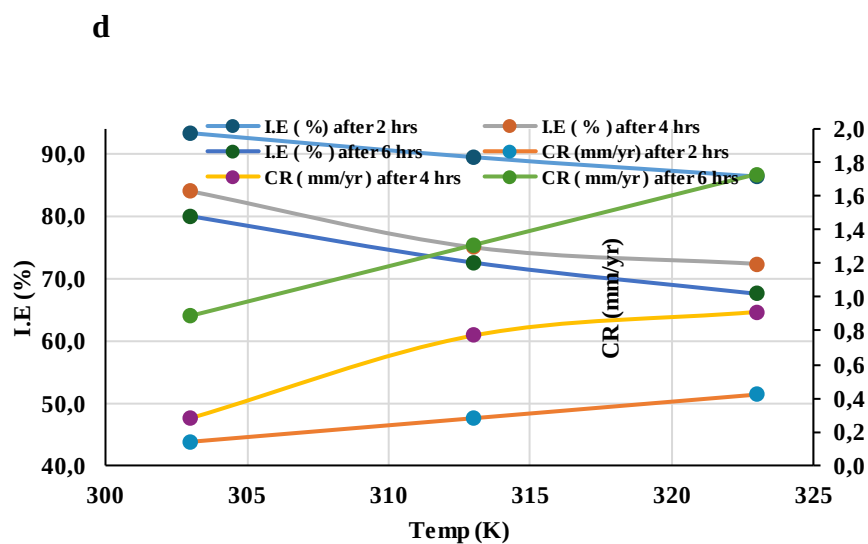
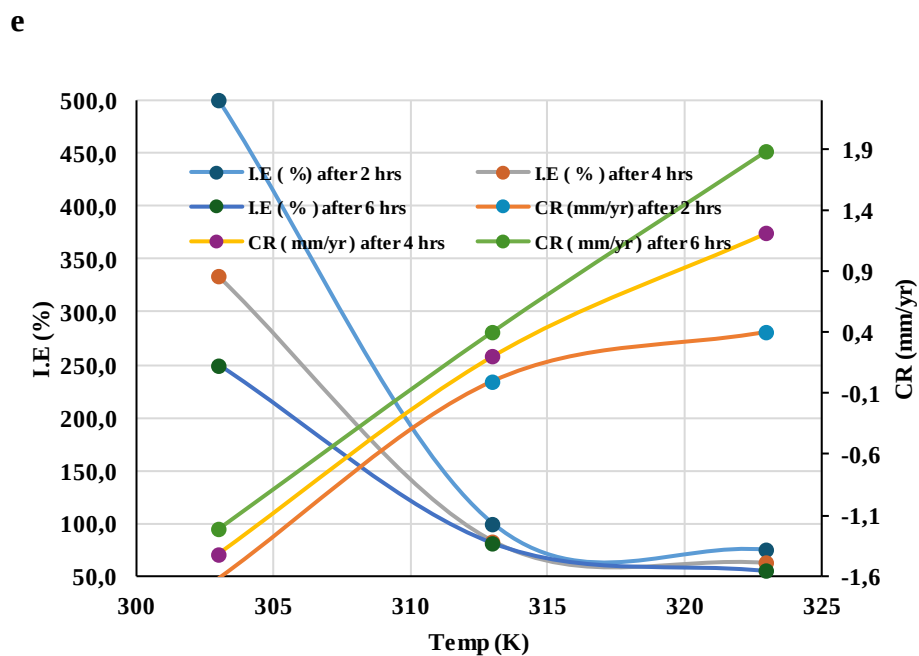


Figure 0.11: Inhibition efficiency and corrosion rate of API 5L X42 Pipeline steel in 3.5 % NaCl for c) 10 g/L and d) 20 g/L *Sclerocarya birrea* extract concentration.



f

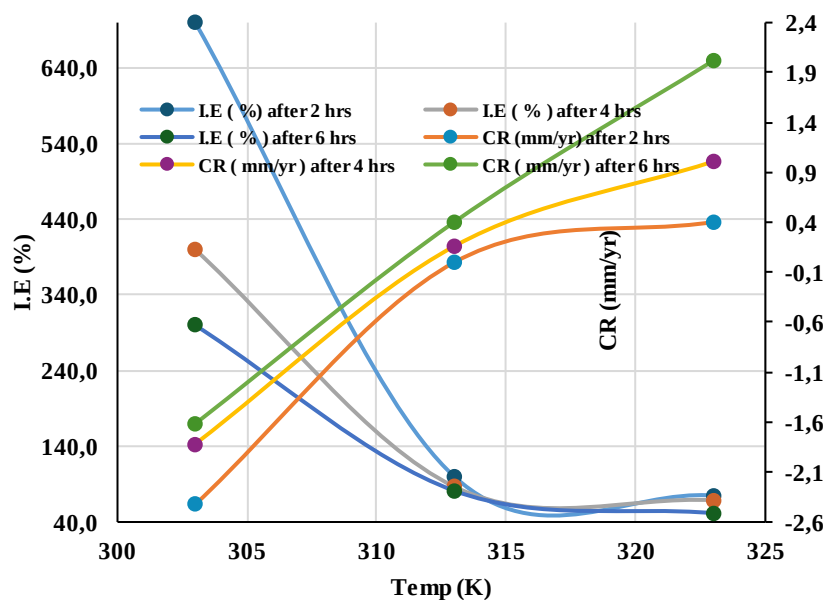
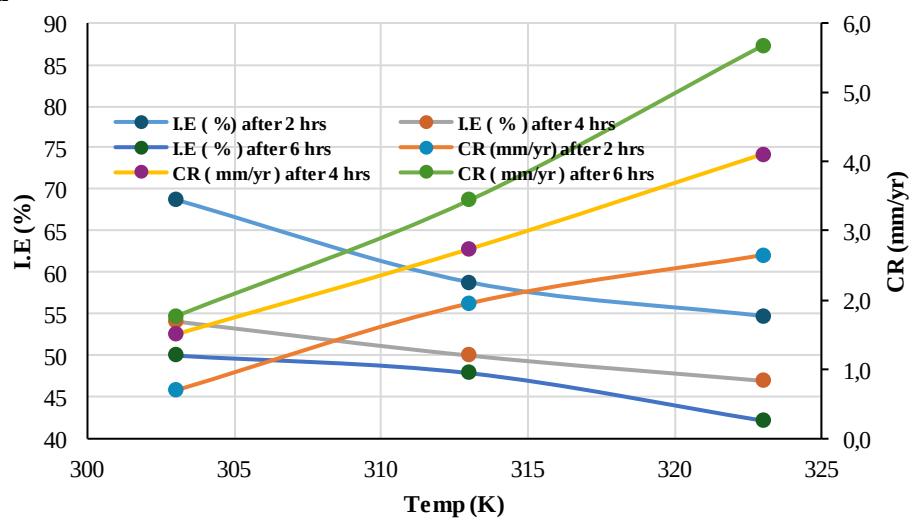


Figure 0.12: Inhibition efficiency and corrosion rate of aluminium (AA1100) in 3.5 % NaCl for e) 10 g/L and f) 20 g/L *Sclerocarya birrea* extract concentration.

4.3.1.2 Effect of temperature (303 -323 K) on both the inhibition efficiency and corrosion rate of metal samples exposed to 1 M H_2SO_4 solution in the presence and absence of *Sclerocarya birrea* inhibitor.

a



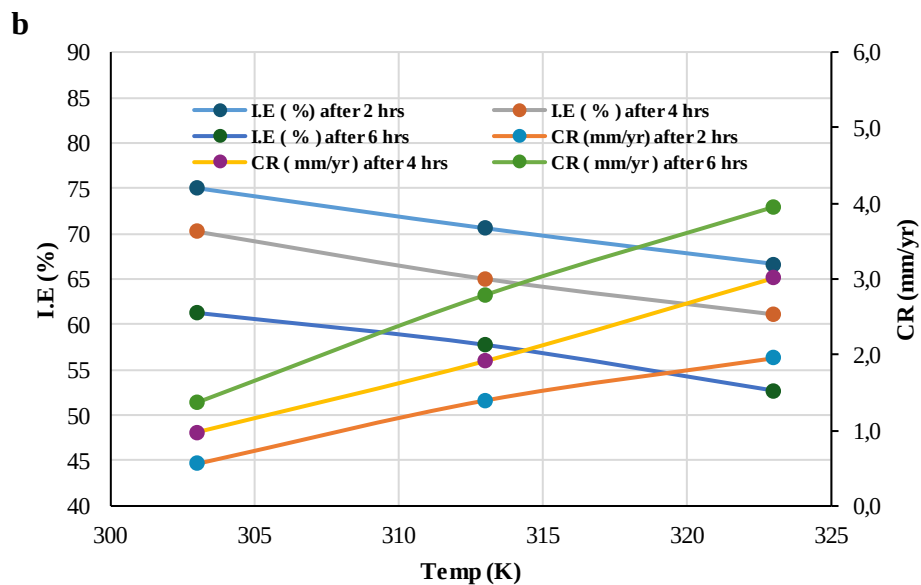
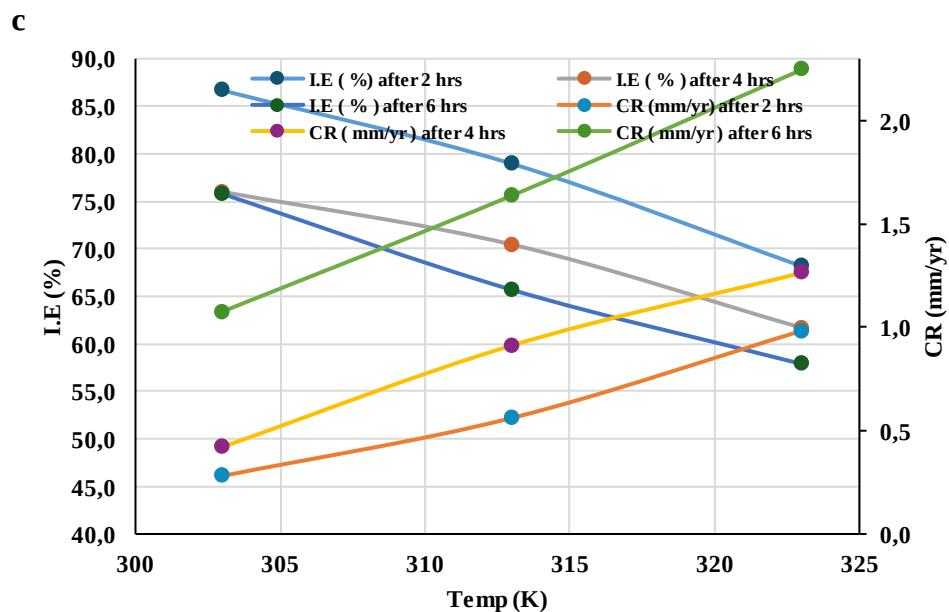


Figure 0.13: Inhibition efficiency and corrosion rate of mild steel in 1 M H₂SO₄ for a) 10 g/L and b) 20 g/L *Sclerocarya birrea* extract concentration.



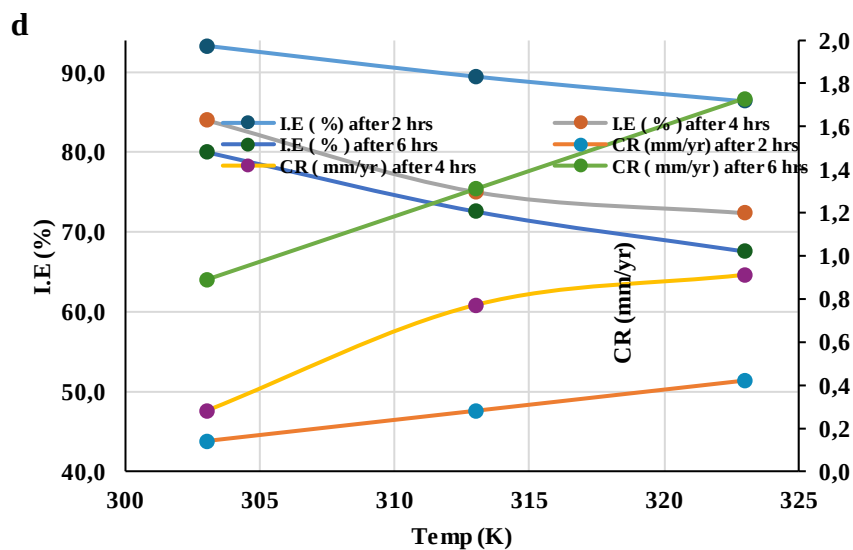
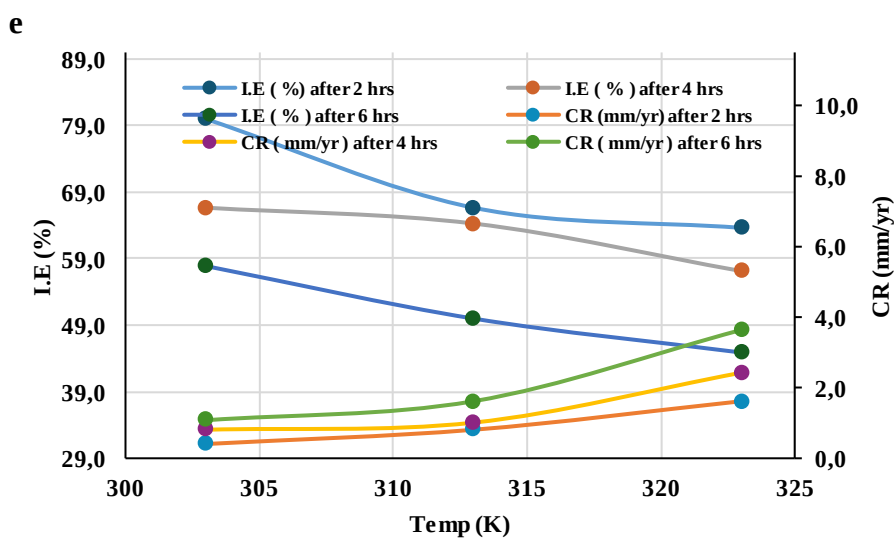


Figure 0.14: Inhibition efficiency and corrosion rate of API 5L X42 Pipeline steel in 1 M H_2SO_4 for c) 10 g/L and d) 20 g/L *Sclerocarya birrea* extract concentration.



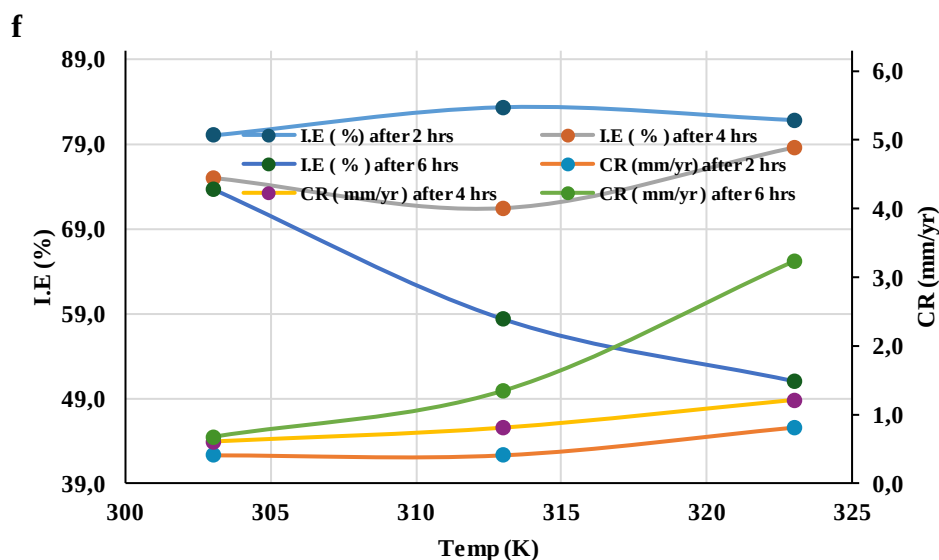


Figure 0.15: Inhibition efficiency and corrosion rate of Aluminium (AA1100) in 1 M H₂SO₄ for e) 10 g/L and f) 20 g/L *Sclerocarya birrea* extract concentration.

4.3.1.3 Effect of exposure duration on the corrosion rate of the metals in the absence and presence of varying concentrations of *Sclerocarya birrea* leaf extract inhibitor.

Low inhibition efficiency was observed for samples subjected to 1 M H₂SO₄ (Figure 4.13 a & b to 4.15 e & f) due to the destructive or aggressive nature of the acid to metals when compared to the simulated seawater (3.5 % NaCl). Despite low inhibition efficiency and high corrosion rates the same trend of temperature's impact on the inhibitor's performance was apparent. As the temperature increased the inhibitory efficacy decreased, whereas the corrosion rate rose significantly. The lower I.E. % reached can be ascribed to quicker migration of protons and sulphate anions (Ezughu & Aralu, 2023). These protons and sulphate anions with higher kinetic energies might interfere with inhibitory adsorption, subsequently minimal adsorption (Aralu et al., 2021). For all these metals under investigation, AA1100 suffered less degradation in both media followed by mild steel and lastly API 5L X42 pipeline steel. The oxide film in aluminium together with adsorbed molecules on the aluminium substrate blocked corrosive agents into reaching the active sites of the metal.

The effect of exposure duration on all the three metals in both 3.5 % NaCl and 1 M H₂SO₄ environments with and without different *Sclerocarya birrea* inhibitor dosages reflect the same trend pattern. Figures 4.16 to 4.18 depict the observations made over a period of 6 hours, with the corrosion rate increasing linearly with prolonged exposure. Corrosion rate as expected is more pronounced in blank exposed samples and decreases with increase in inhibitor dosage. Initially after then inhibitor has been introduced to the corrosive medium, inhibiting molecules

tend to safeguard the metal by adhering to its surface, but with prolonged exposure those molecules desorb back to the solution leaving the metal surface unprotected (Shaha et al., 2024). After six hours, high corrosion rates were noted in all the aggressive solutions, with samples exposed to an acidic environment corroding more quickly than those in simulated seawater medium.

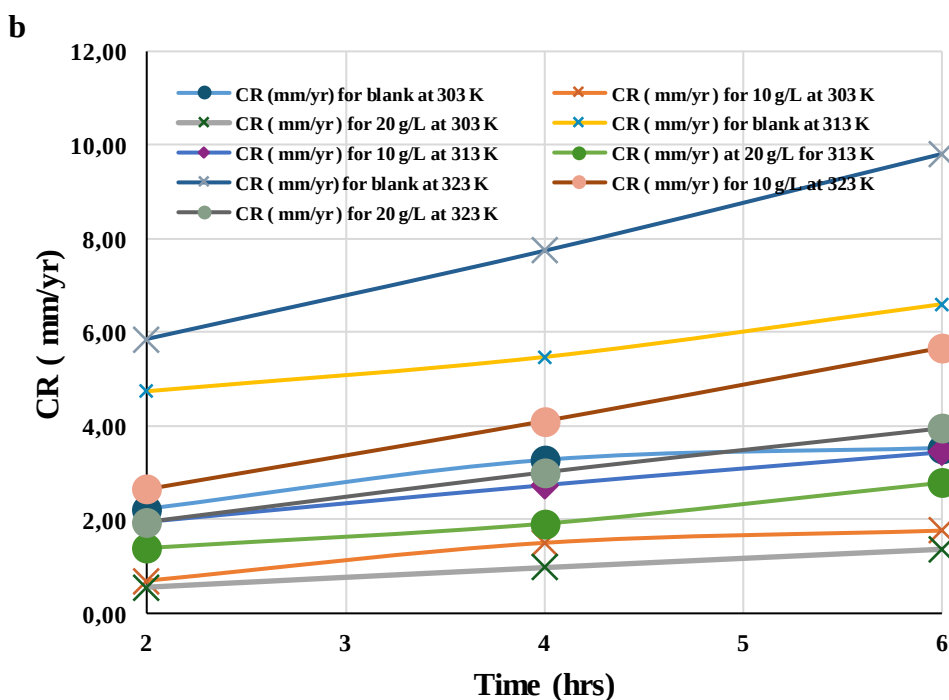
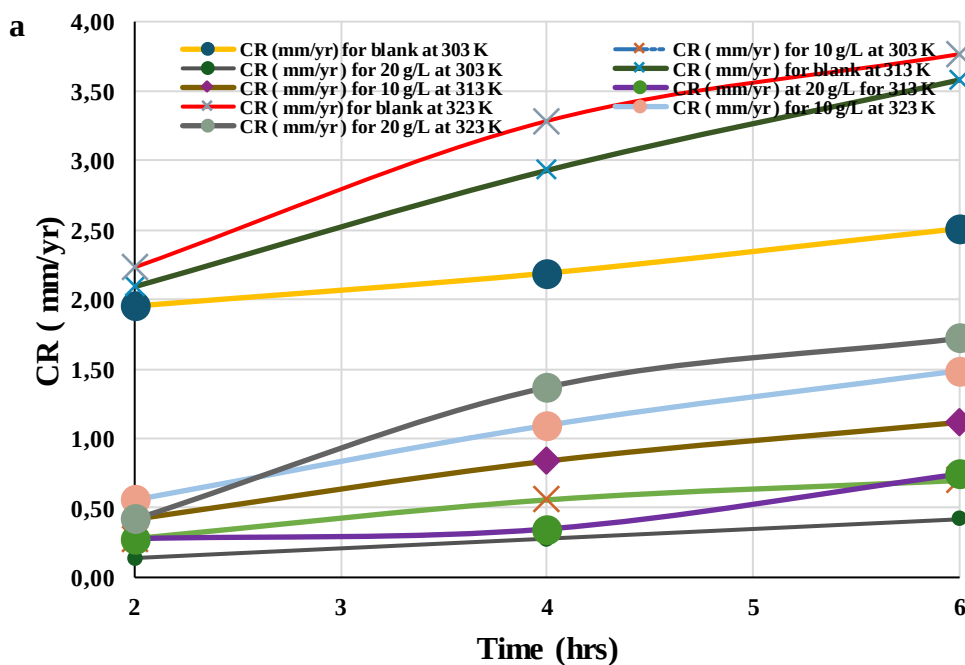
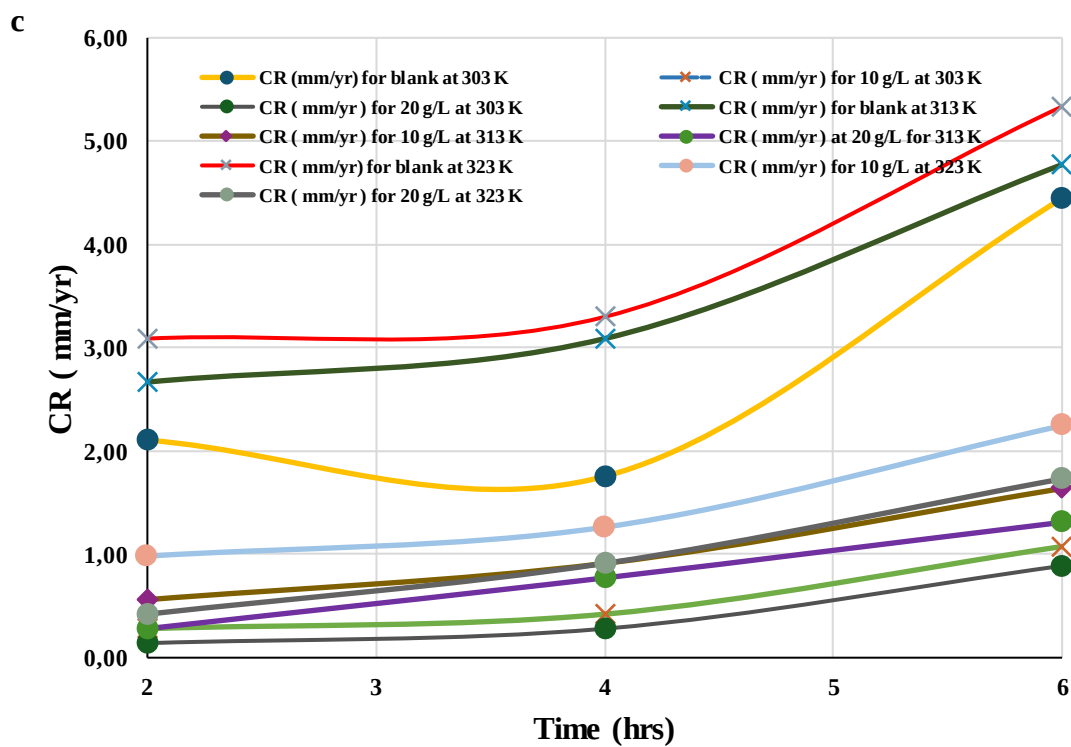


Figure 0.16: Corrosion rate versus exposure duration for mild steel at different temperatures and varying extract concentrations in a) 3.5 % NaCl and b) 1 M H₂SO₄.



d

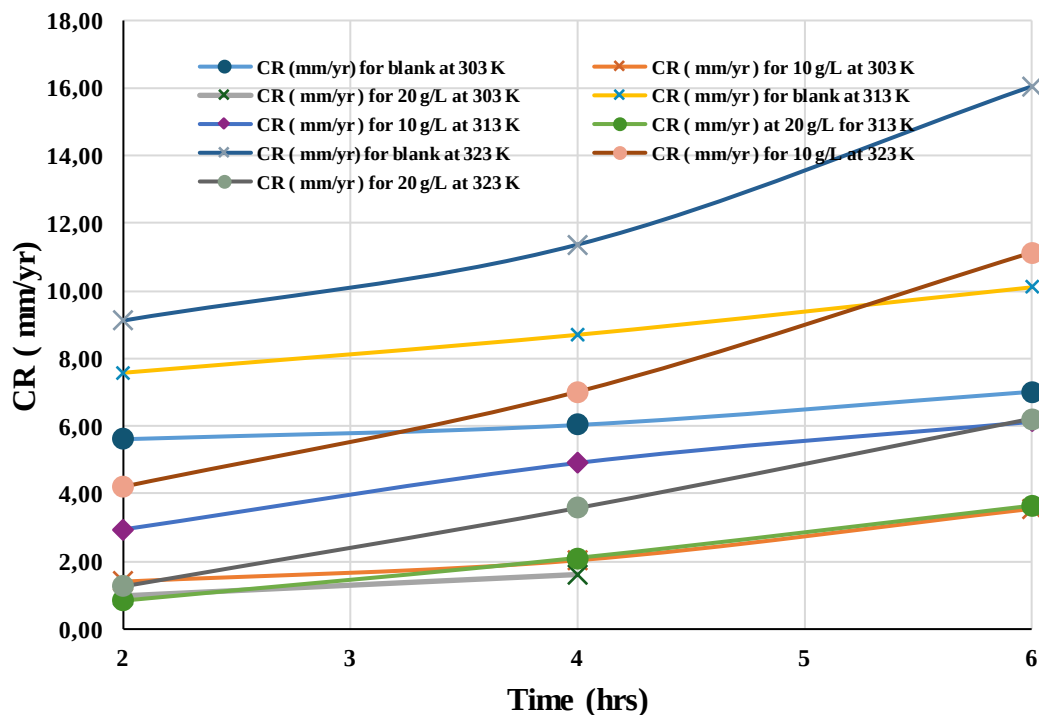
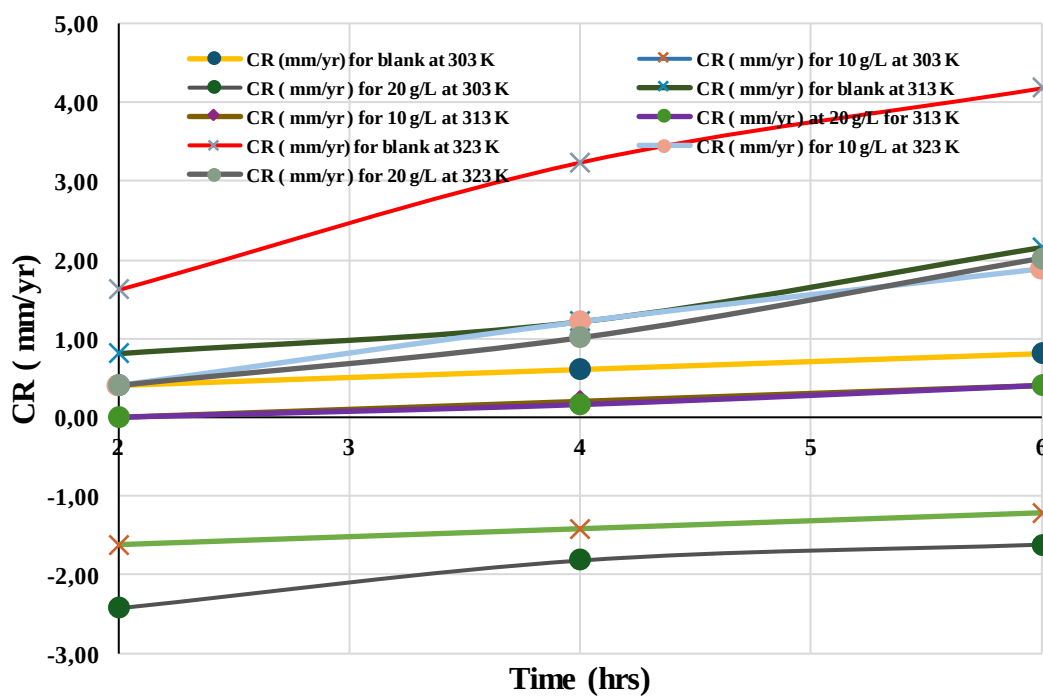


Figure 0.17: Corrosion rate versus exposure duration for API 5L X42 Pipeline steel at different temperatures and varying extract concentrations in a) 3.5 % NaCl and b) 1 M H₂SO₄.

e



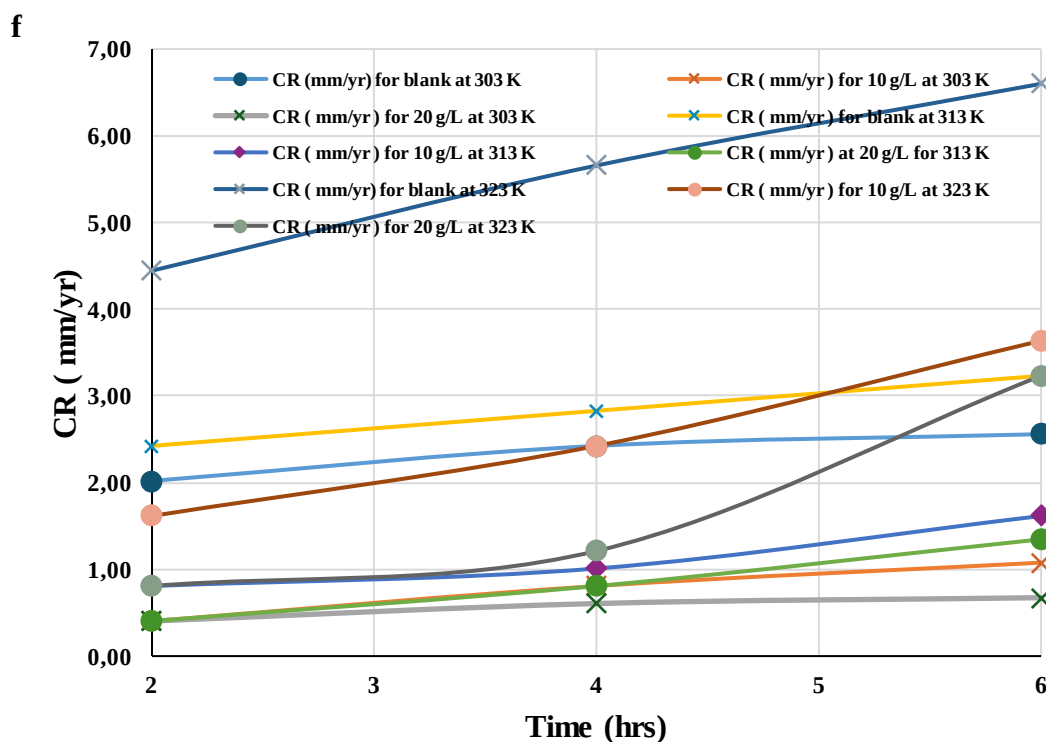
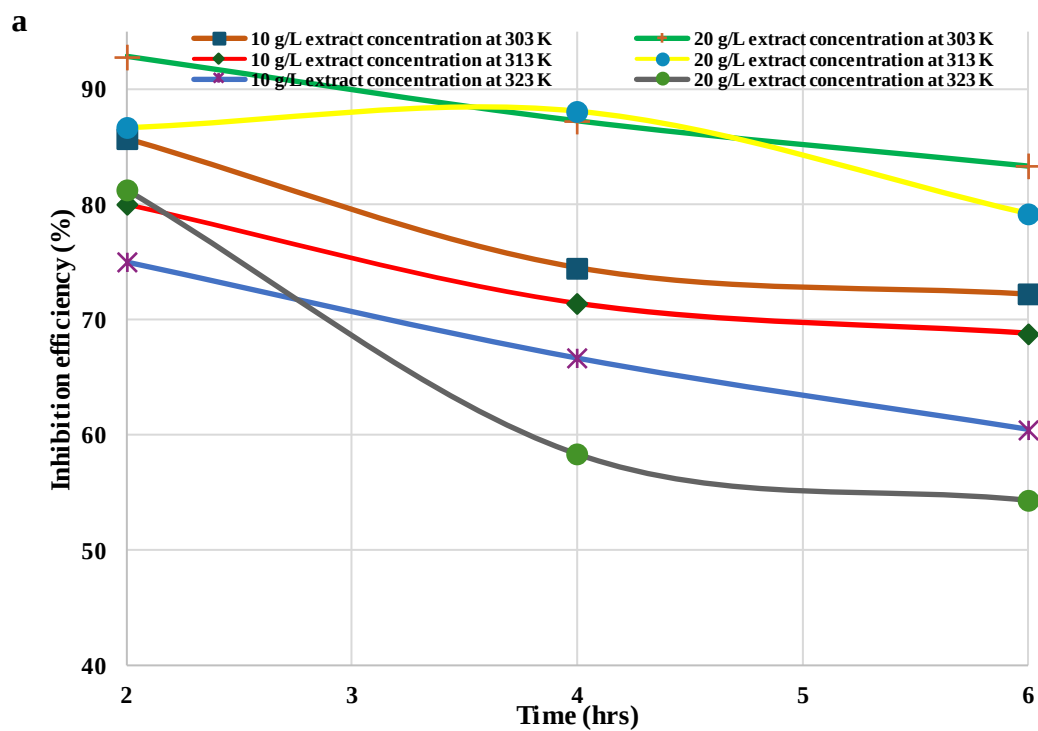


Figure 0.18: Corrosion rate versus exposure duration for aluminium (AA 1100) at different temperatures and varying extract concentrations in a) 3.5 % NaCl and b) 1 M H₂SO₄.

4.3.2 Effect of exposure duration on the inhibition efficiency of *Sclerocarya birrea* leaf inhibitor in 3.5 % NaCl and 1 M H₂SO₄ at various temperatures.

As observed in Figures 4.19 to 4.21, the impact of exposure duration on the leaf extract's inhibitory efficacy exhibits a clear temporal dependence on both 1 M H₂SO₄ and simulated seawater corrosive environments. The temporary adsorption of inhibiting molecules on the metal surfaces provides a thin coating which results in high inhibition efficiencies over shorter exposure duration. After two hours, inhibition efficiencies are noticeably high for all the metals, suggesting that inhibitor molecules are fast and efficiently adhering to the metal surfaces. On the other hand, efficiency shows a linear reduction with increasing exposure, which is most noticeable after 6 hours. The inhibitor molecules surface desorption is driven on by extended exposure to corrosive environments and the possible deterioration of the extract's active constituents over time. The aggressive character of the acidic medium is revealed by the reduced efficiency when compared to simulated seawater setting, where the high pH and ion concentration greatly speed up desorption and the disintegration of protective coatings (Alar et al., 2022). On the other hand, the 3.5 % NaCl environment's milder corrosivity allows for a longer-lasting protective effect, but it still fades overtime. These findings highlight the need to

adjust inhibitor concentration and application schedules to prevent time-dependent efficiency loss, especially under extremely harsh acidic conditions.



b

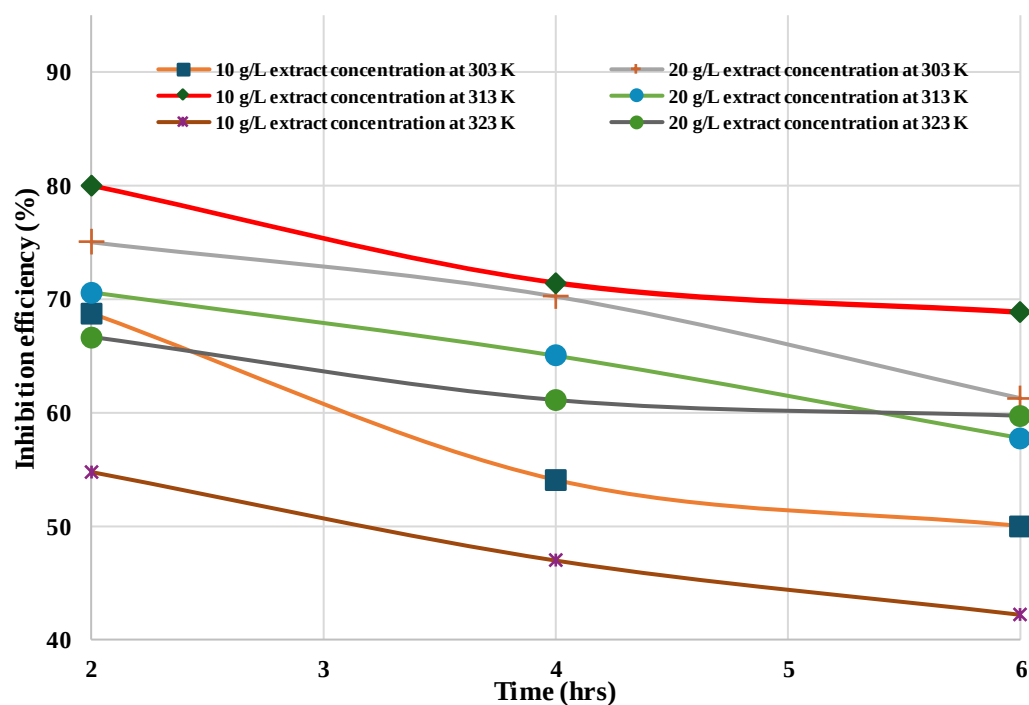
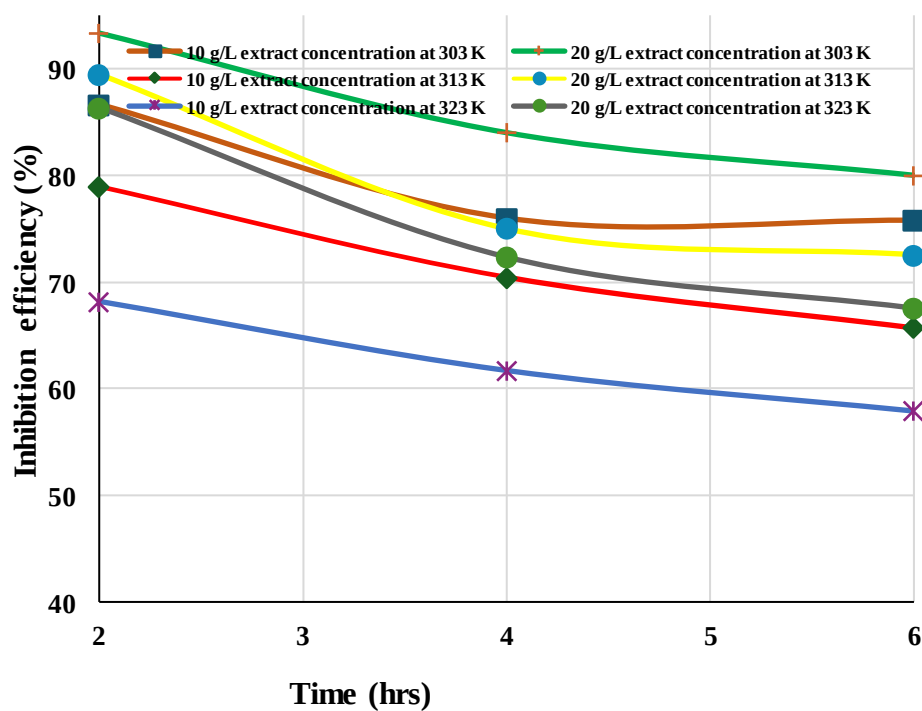


Figure 0.19: Exposure duration versus inhibition efficiency for *Sclerocarya birrea* inhibitor in mild steel at different temperatures and varying extract concentrations in a) 3.5 % NaCl and b) 1 M H₂SO₄.

c



d

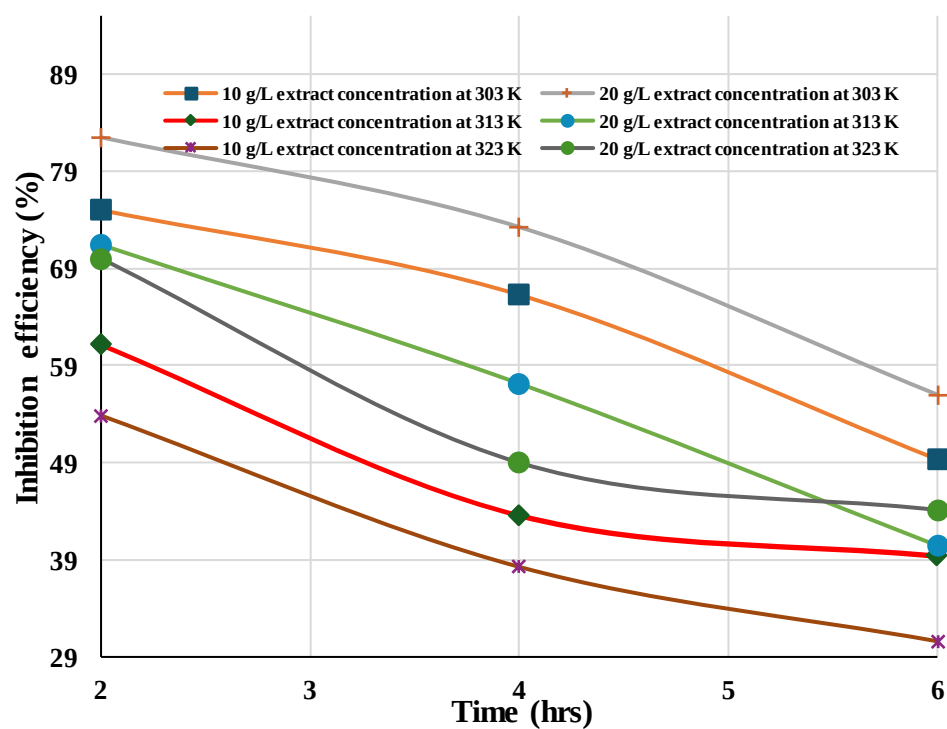
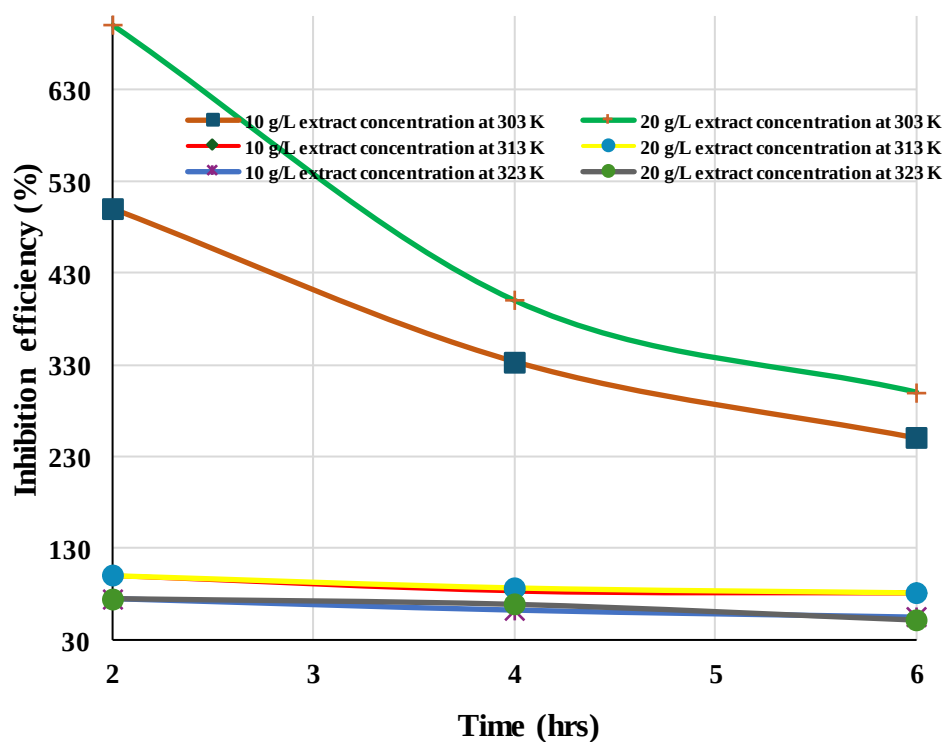


Figure 0.20: Exposure duration versus inhibition efficiency for *Sclerocarya birrea* inhibitor in API 5L X42 Pipeline steel at different temperatures and varying extract concentrations in c) 3.5 % NaCl and d) 1 M H₂SO₄.

e



f

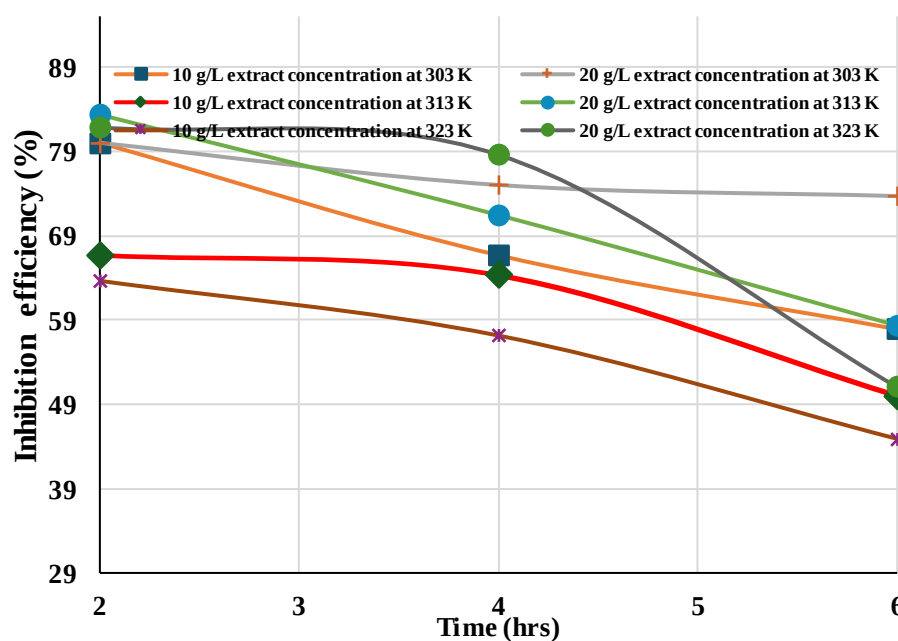
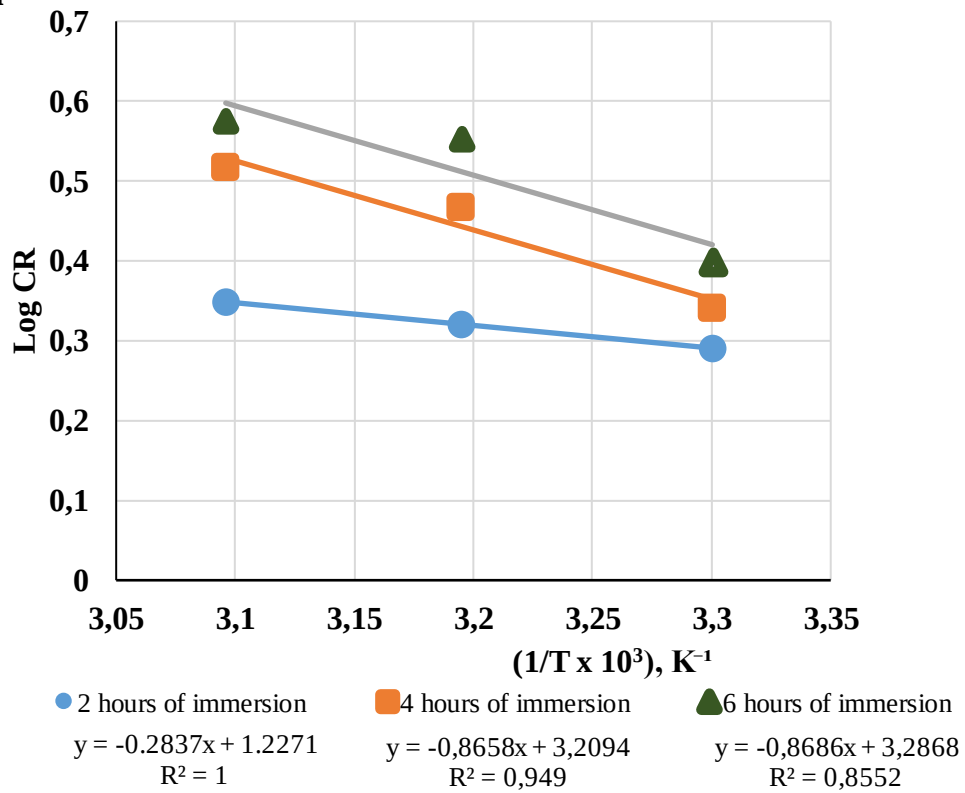


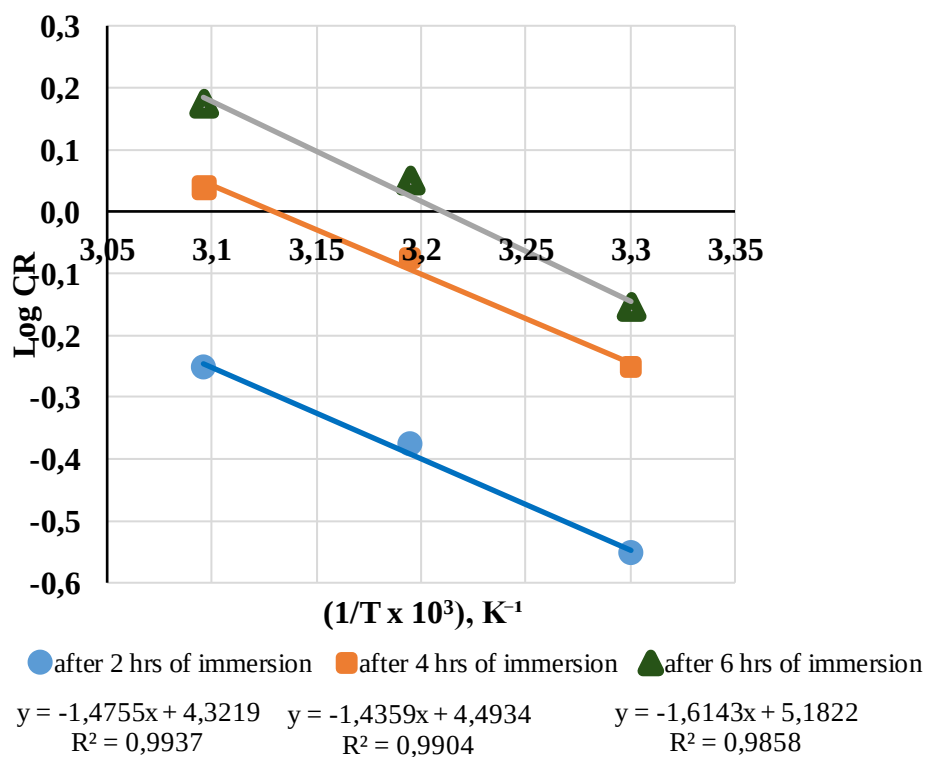
Figure 0.21: Exposure duration versus inhibition efficiency for *Sclerocarya birrea* inhibitor in aluminium (AA1100) alloy at different temperatures and varying extract concentrations in e) 3.5 % NaCl and f) 1 M H₂SO₄.

4.3.3 Arrhenius Plots for the metal specimens.

a



b



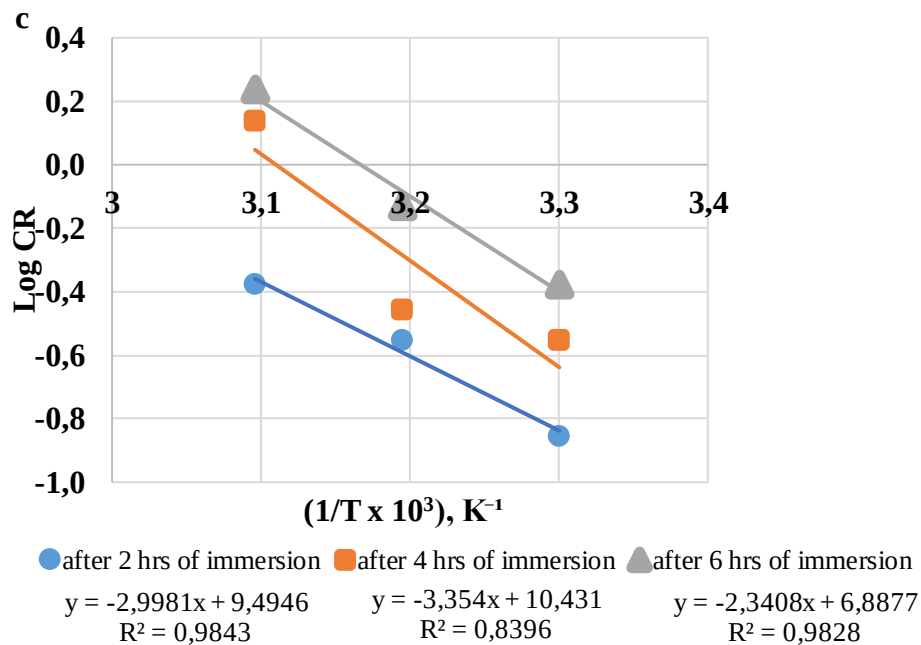
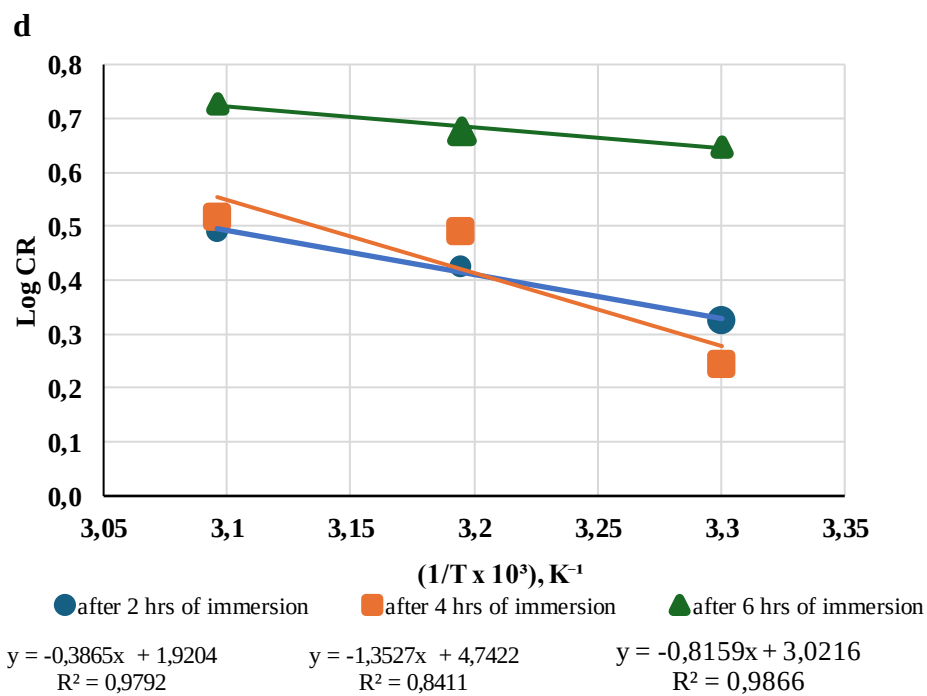


Figure 0.22: Plot of Log CR vs $(1/T \times 10^3)$ for mild steel corrosion in 3.5 % NaCl at a) blank , b) 10 g/L and c) 20 g/L of *Sclerocarya birrea* leaf extracts.



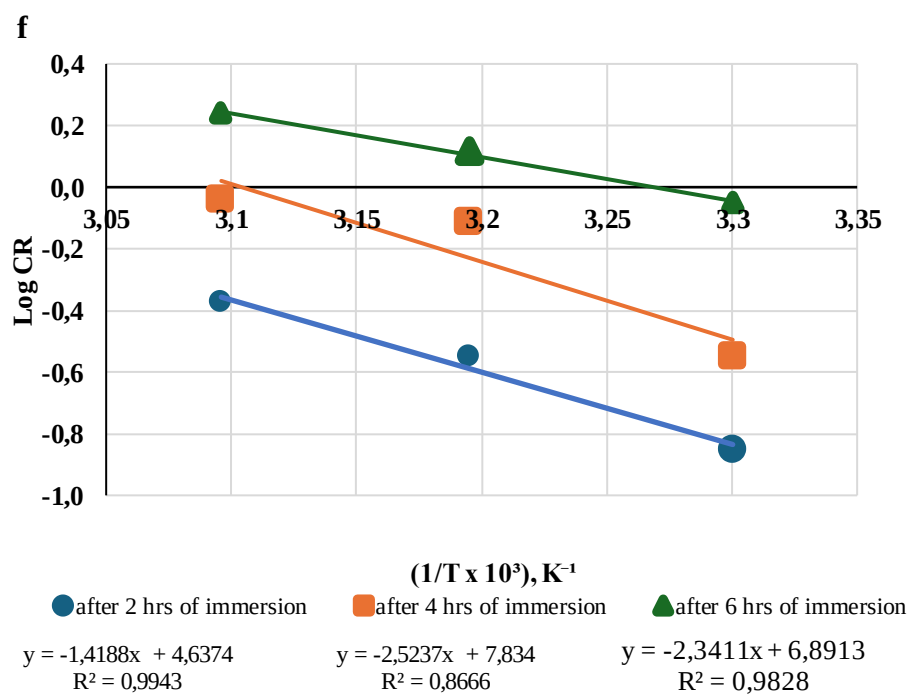
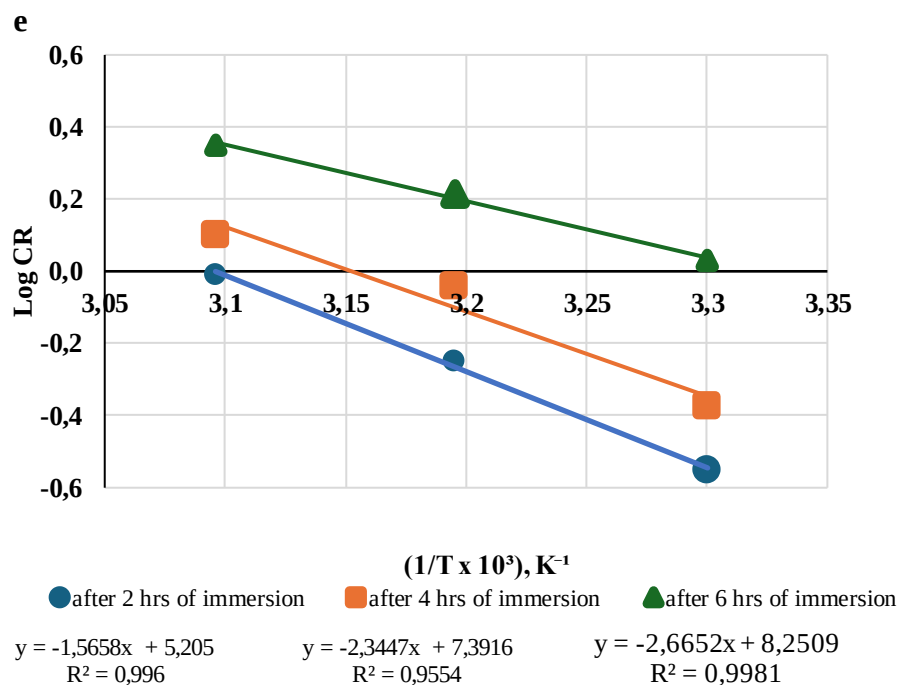
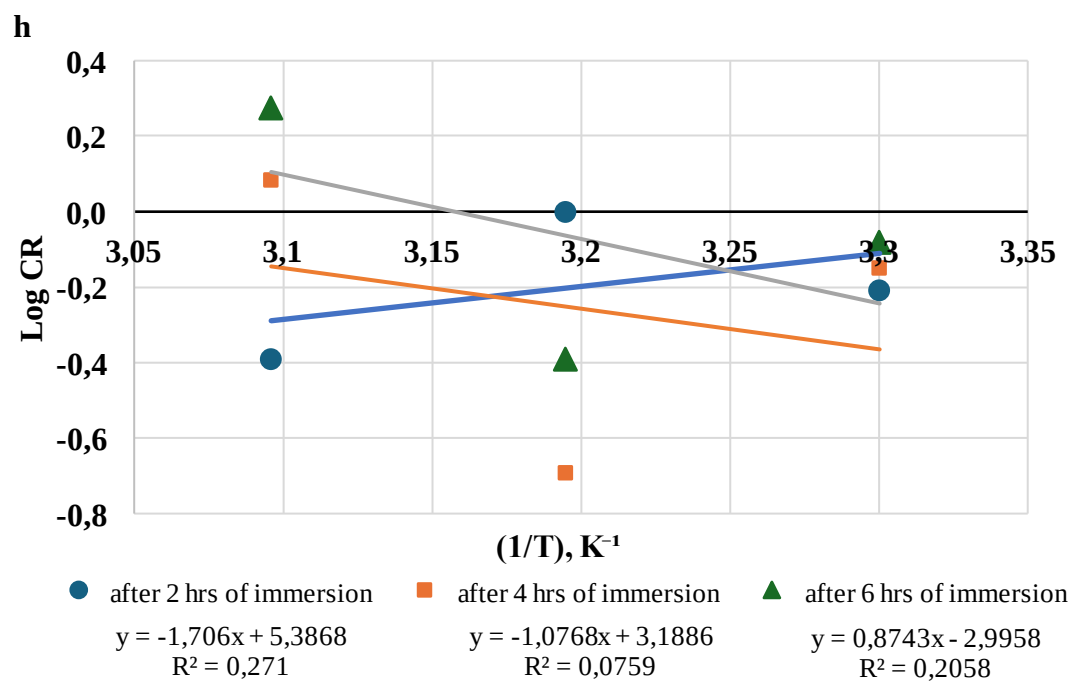
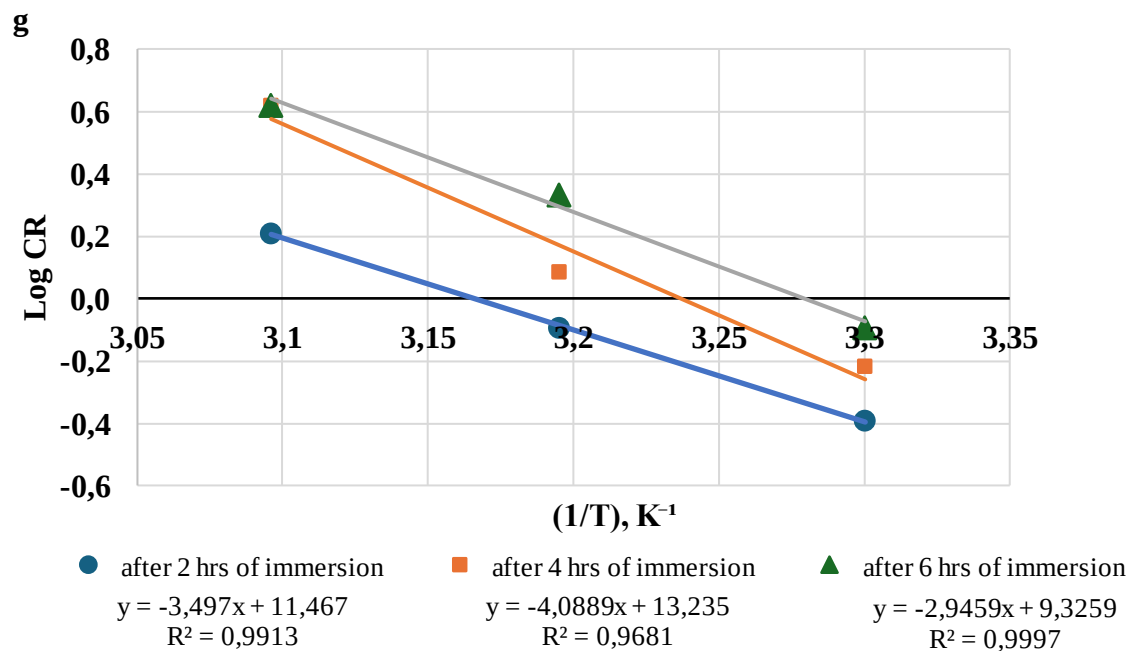


Figure 0.23: Plot of Log CR vs $(1/T \times 10^3)$ for API 5L X42 Pipeline steel corrosion in 3.5 % NaCl at d) blank , e) 10 g/L and f) 20 g/L of *Sclerocarya birrea* leaf extracts.



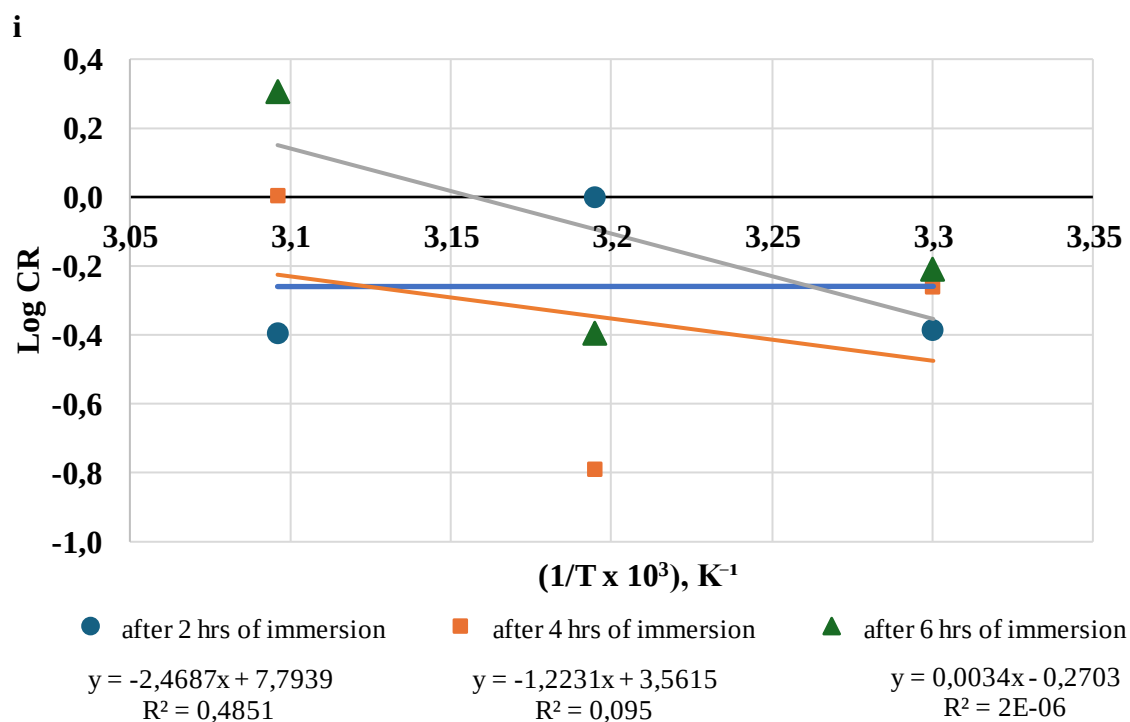
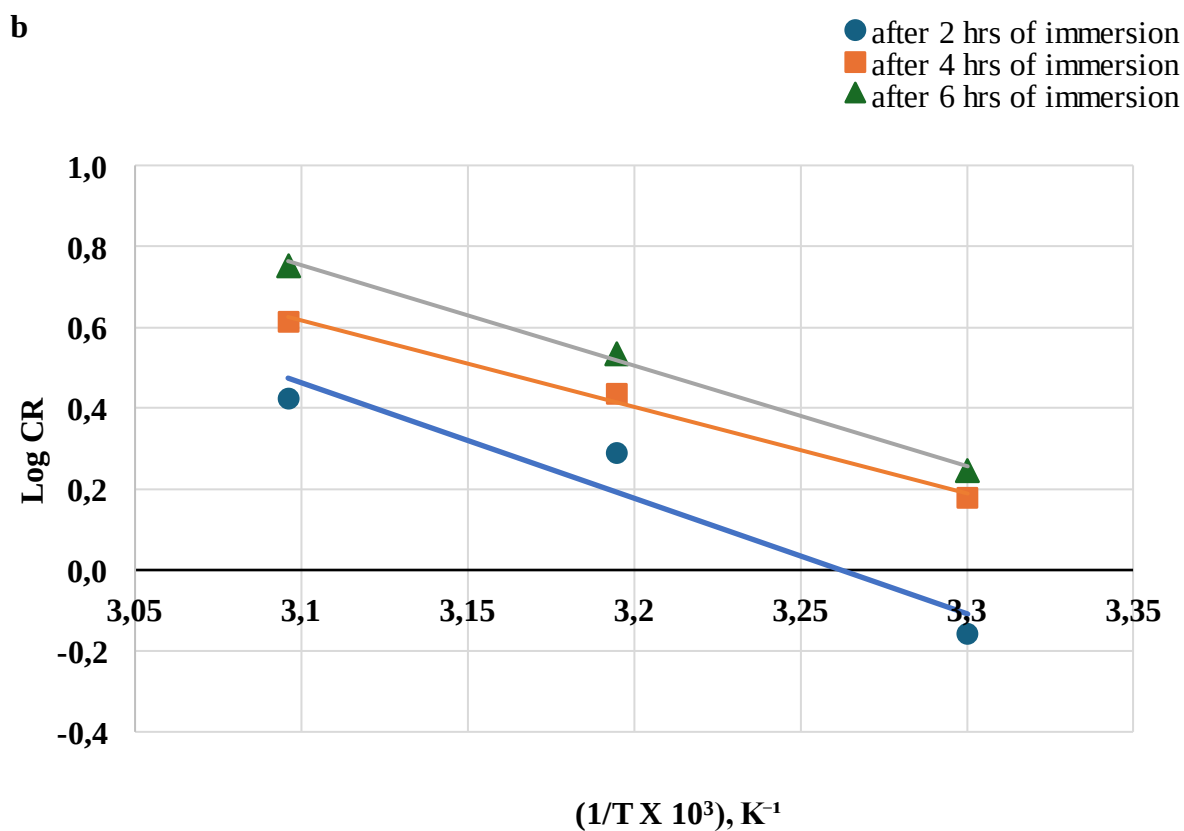


Figure 0.24: Plot of Log CR vs (1/T X 10³) for aluminium (AA1100) alloy corrosion in 3.5 % NaCl at g) blank , h) 10 g/L and i) 20 g/L of *Sclerocarya birrea* leaf extracts.



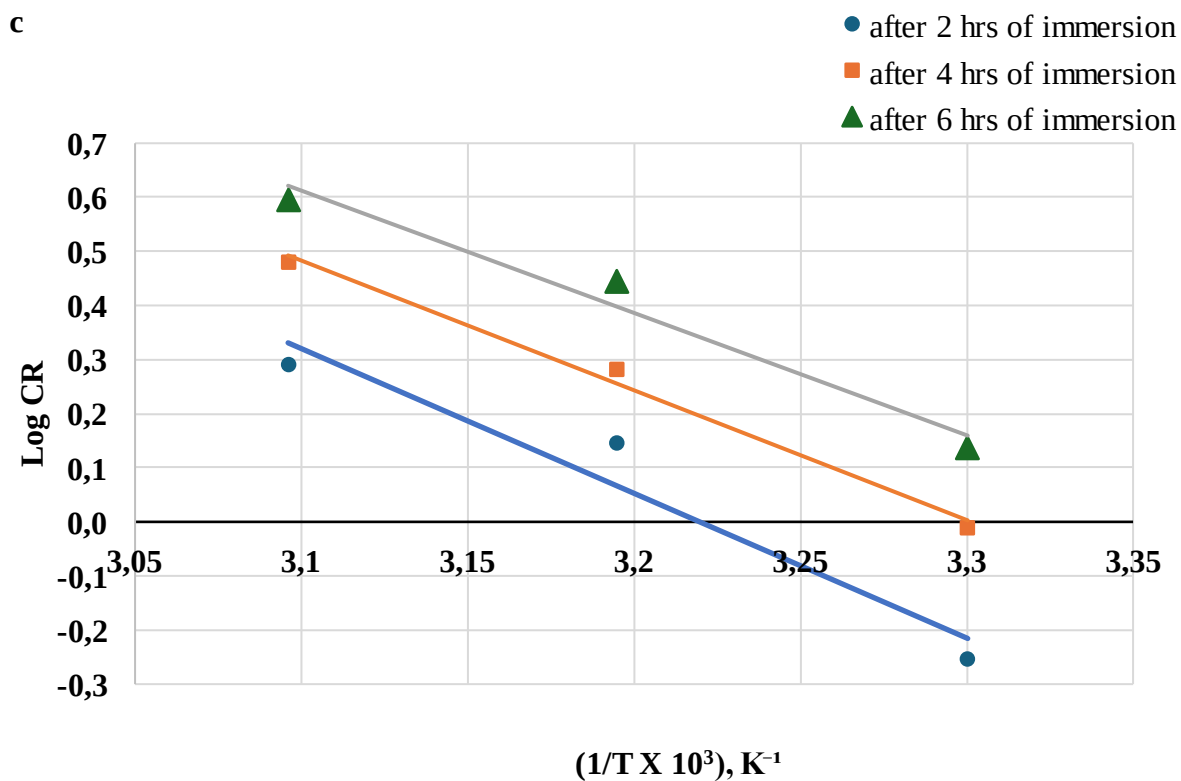
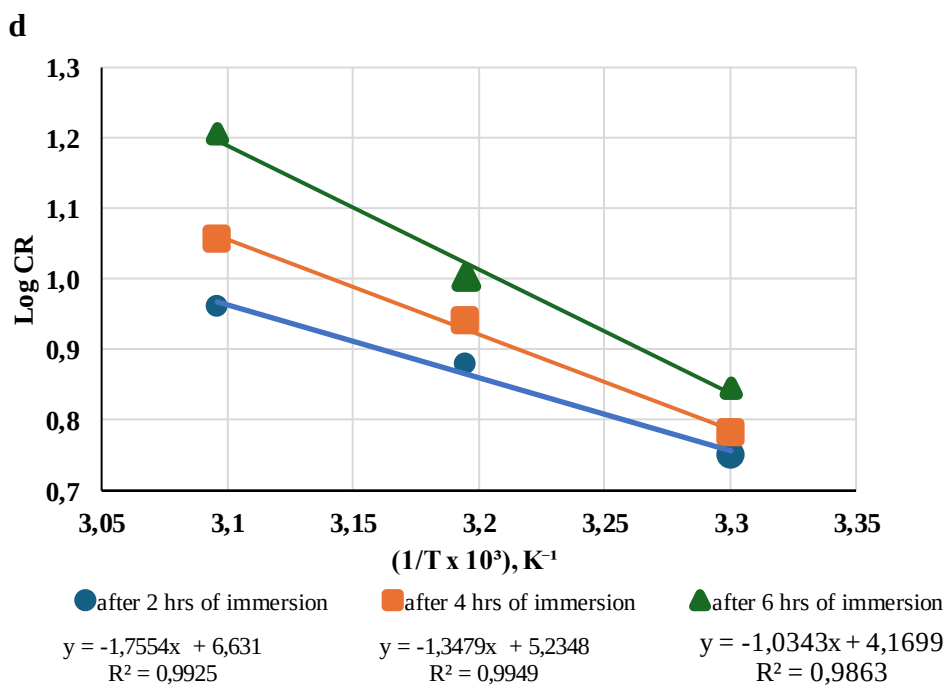


Figure 0.25: Plot of Log CR vs $(1/T \times 10^3)$ for mild steel corrosion in 1 M H_2SO_4 at b) 10 g/L and c) 20 g/L of *Sclerocarya birrea* leaf extracts.



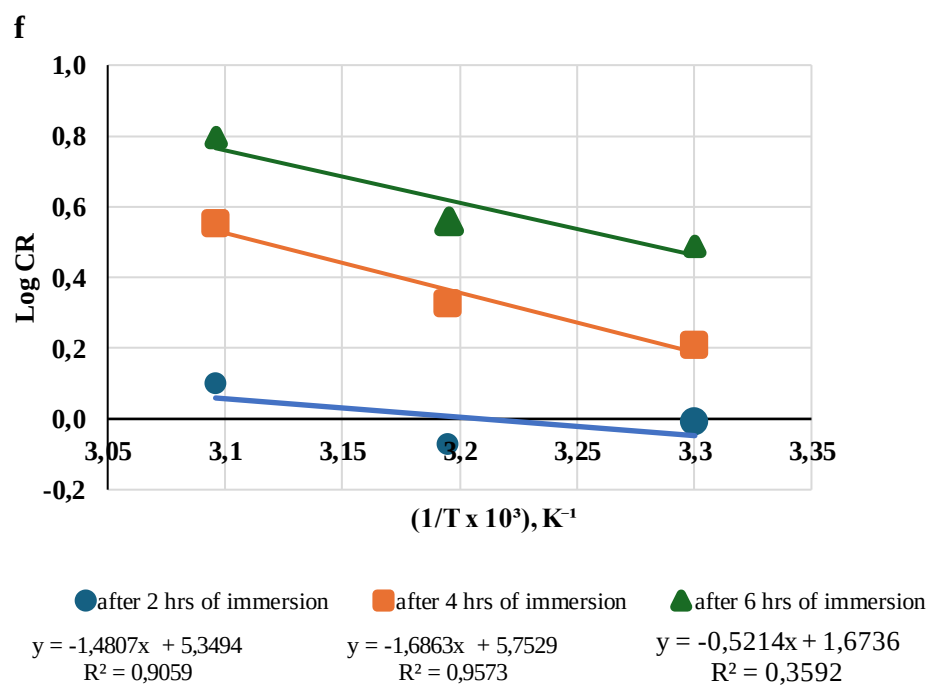
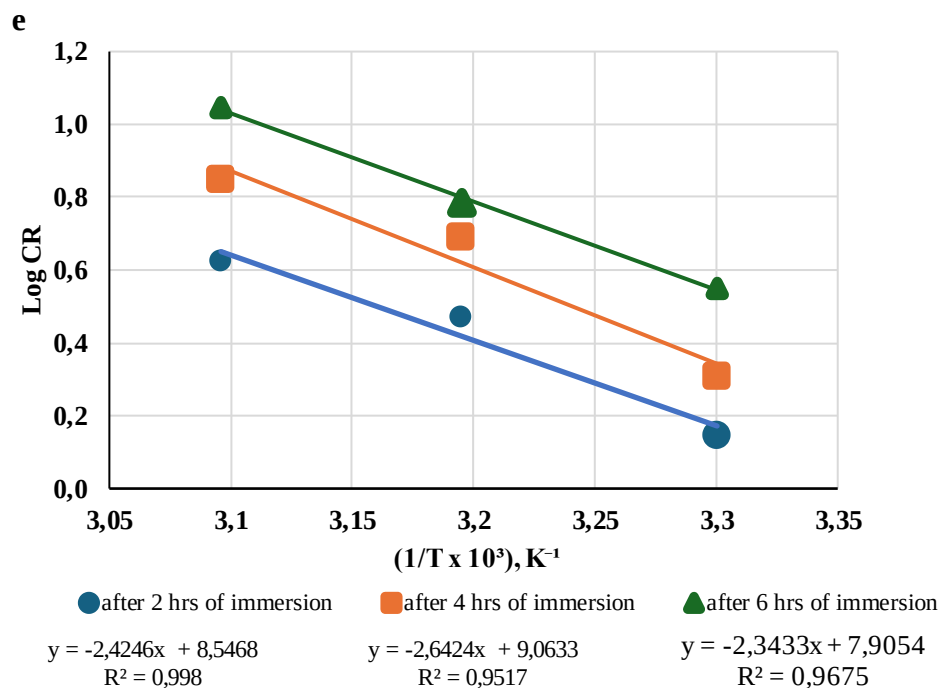
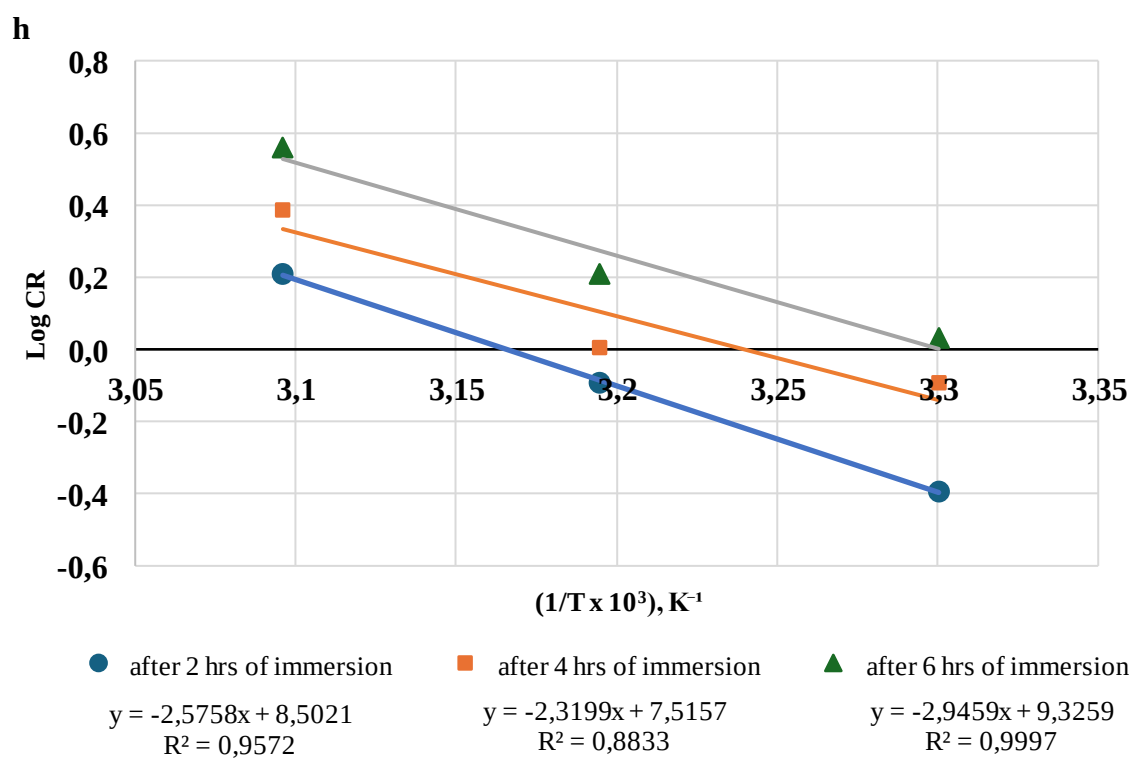
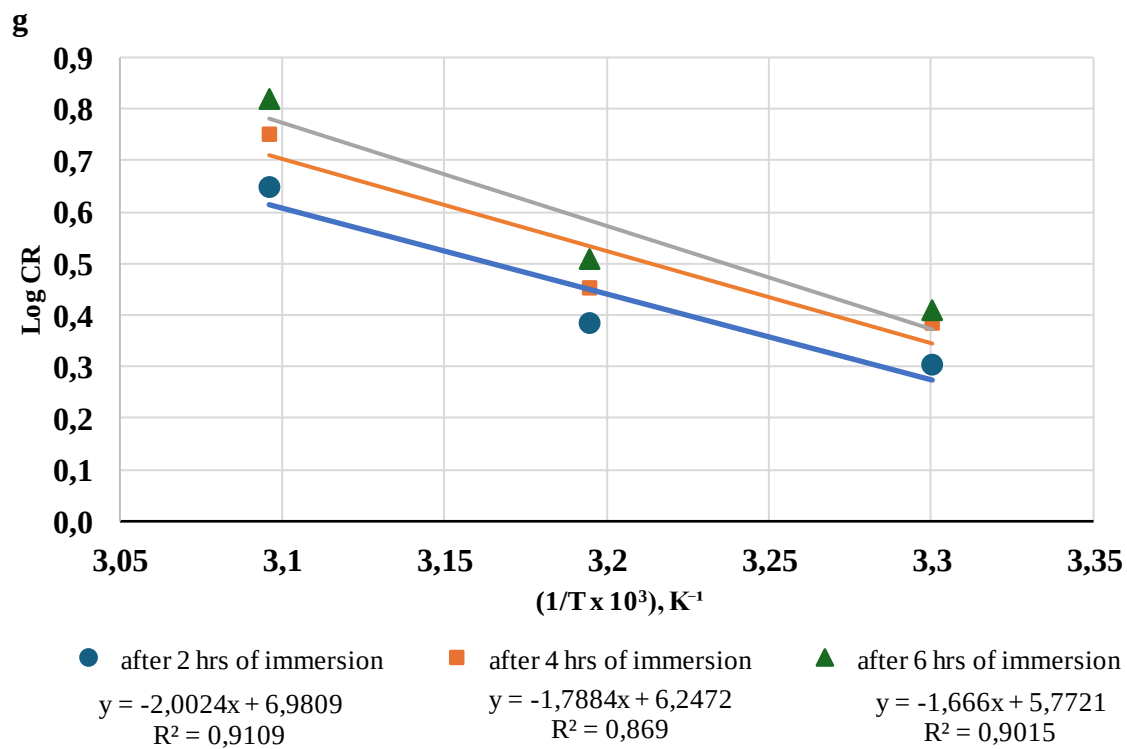


Figure 0.26: Plot of Log CR vs (1/T X 10³) for API 5L X42 Pipeline steel corrosion in 1 M H₂SO₄ at d) blank , e) 10 g/L and f) 20 g/L of *Sclerocarya birrea* leaf extracts.



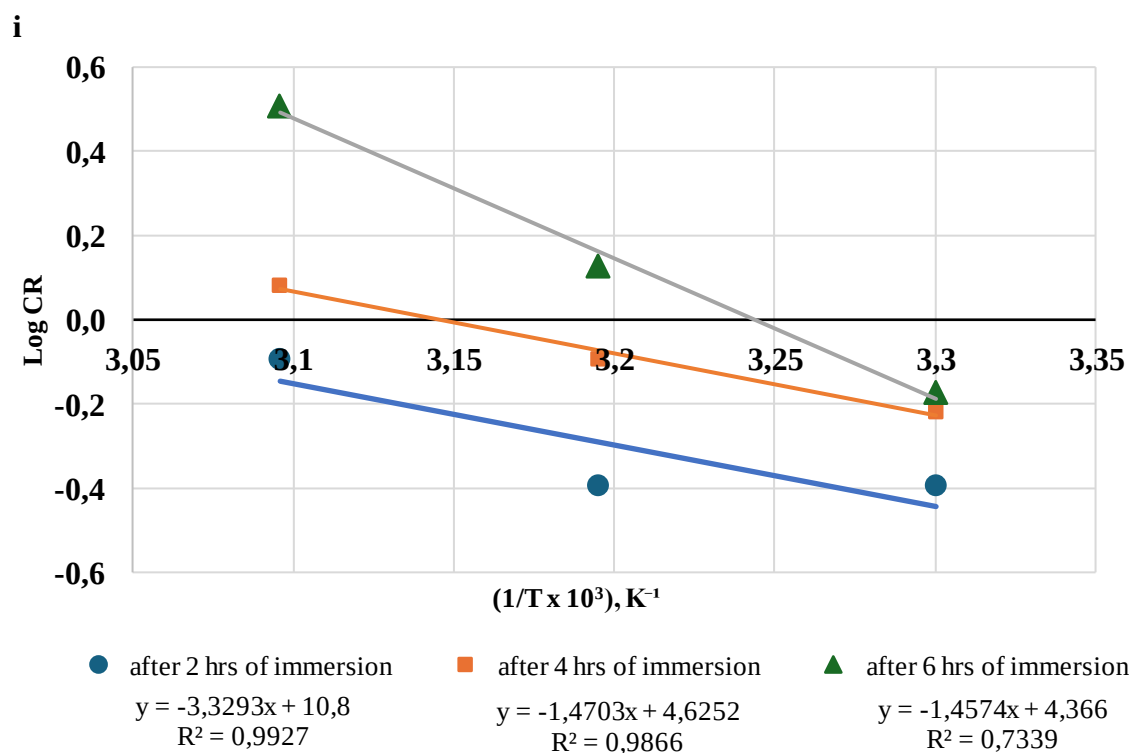
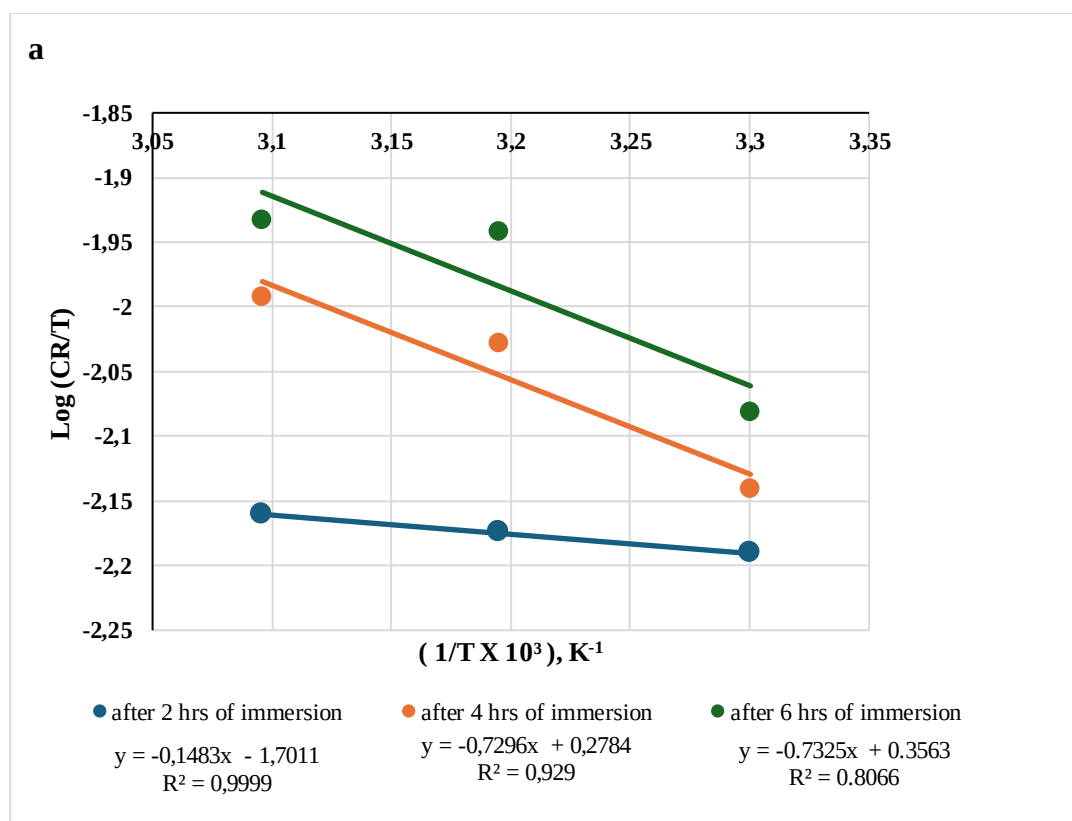


Figure 0.27: Plot of Log CR vs $(1/T \times 10^3)$ for Aluminium (AA1100) corrosion in 1 M H_2SO_4 at g) blank, h) 10 g/L and i) 20 g/L of *Sclerocarya birrea* leaf extracts.

4.3.4 Transition state plots for the metallic samples



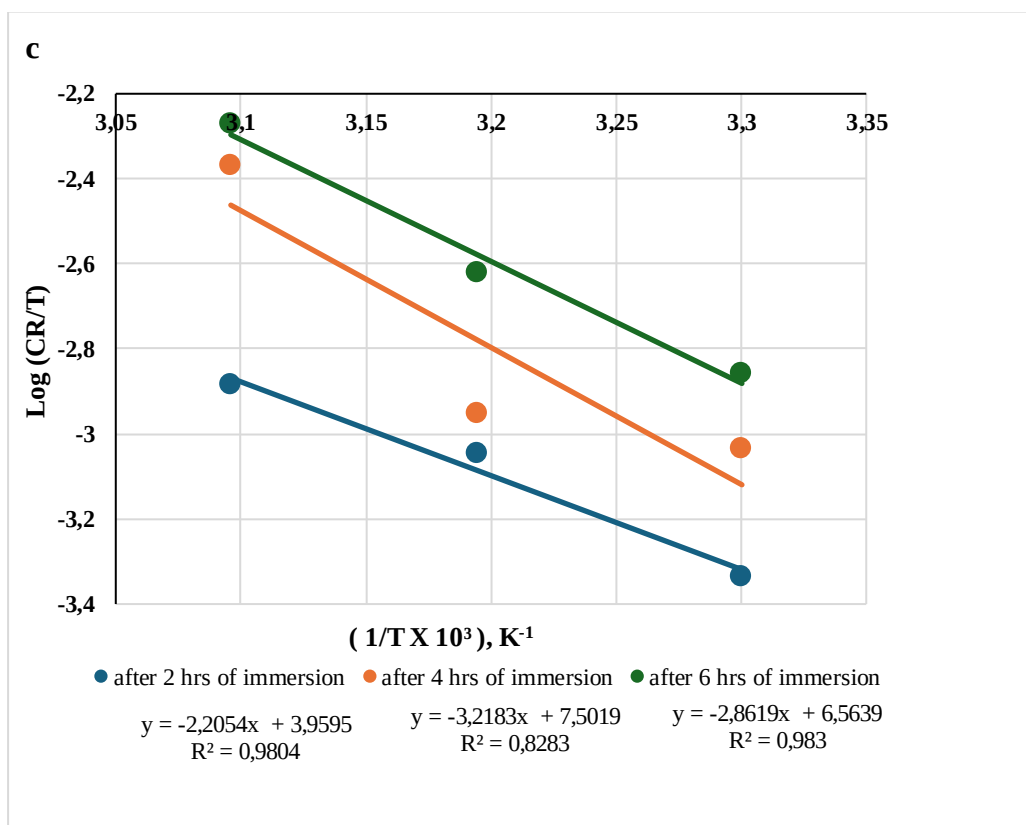
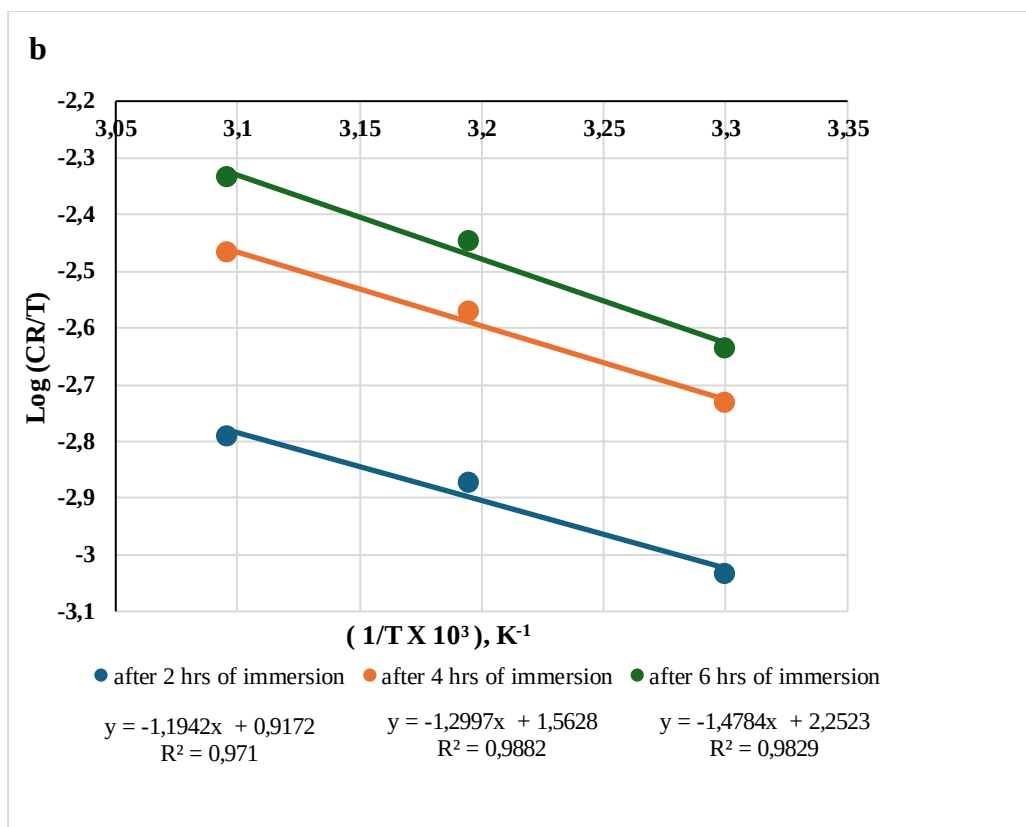
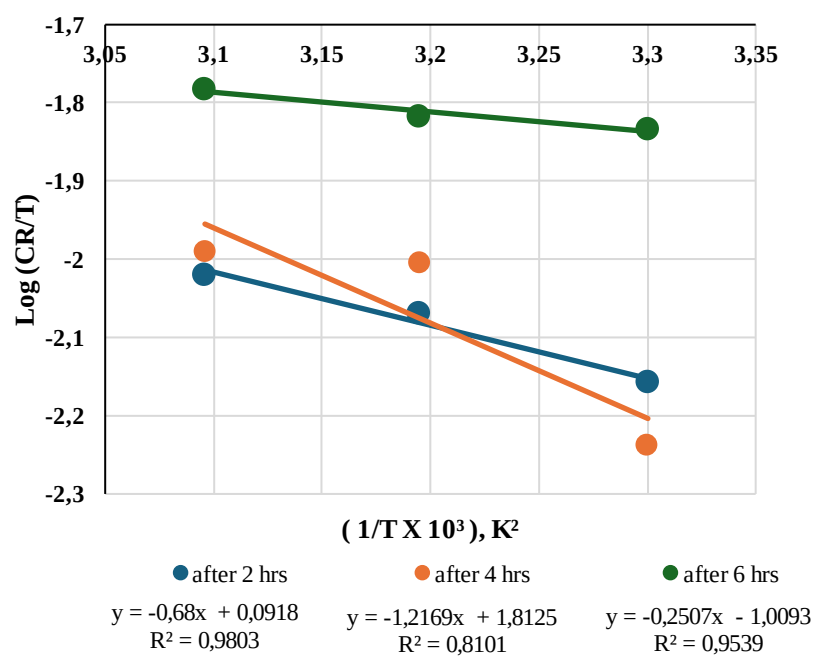
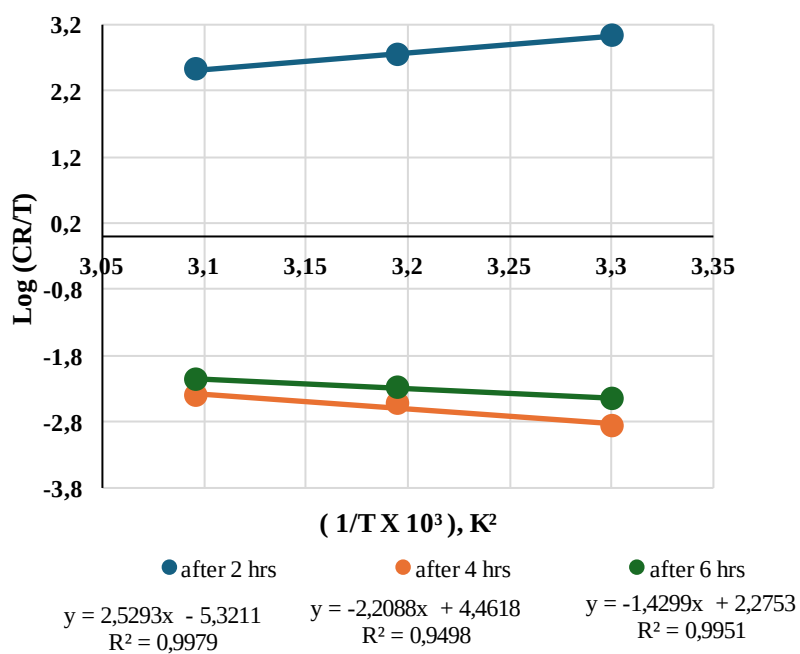


Figure 0.28: Plot of $\text{Log}(\text{CR}/T)$ versus $(1/T \times 10^3)$ for mild steel samples immersed in 3.5 % NaCl with a) blank, b) 10 g/L and c) 20 g/L of extract concentration.

d



e



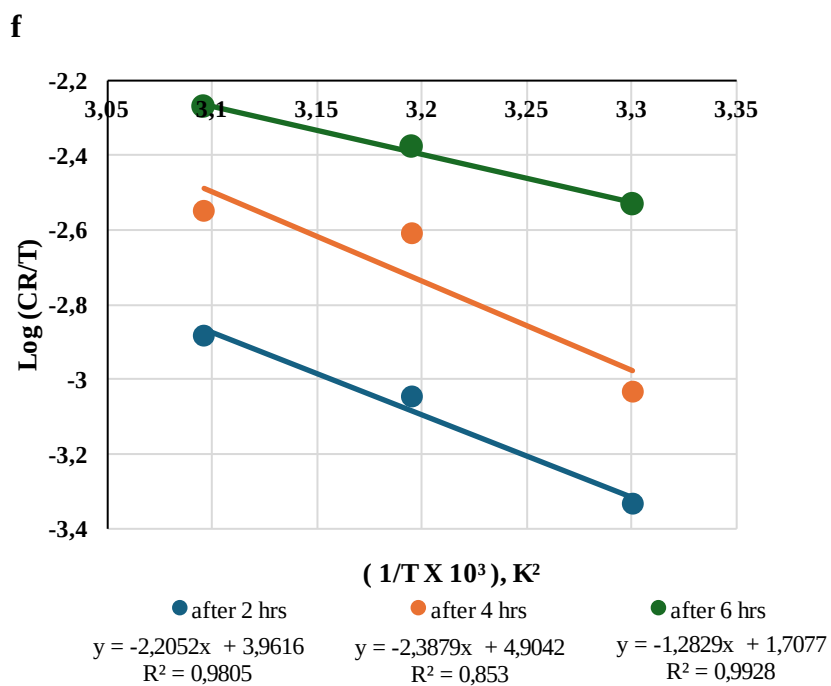


Figure 0.29: Plot of Log (CR/T) versus $(1/T \times 10^3)$ for API 5L X42 Pipeline steel samples immersed in 3.5 % NaCl with d) blank, e) 10 g/L and f) 20 g/L of extract concentration.

i

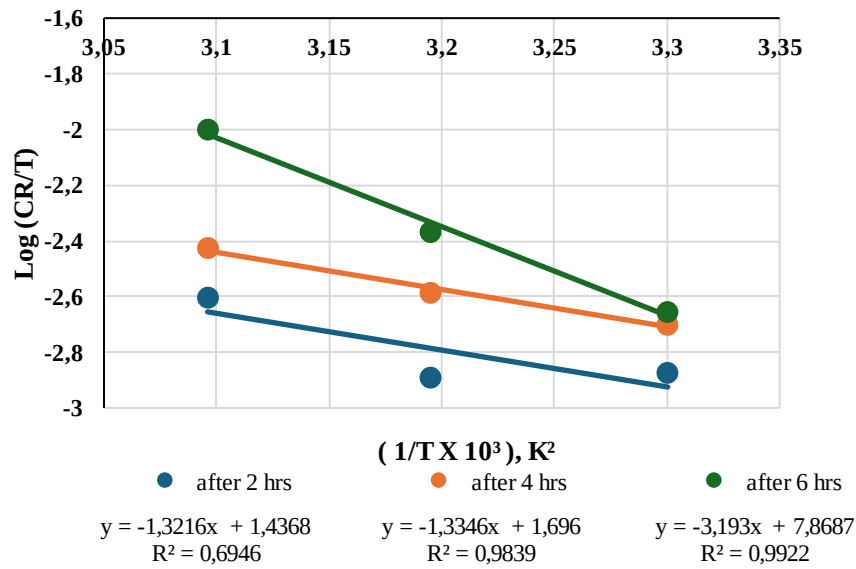
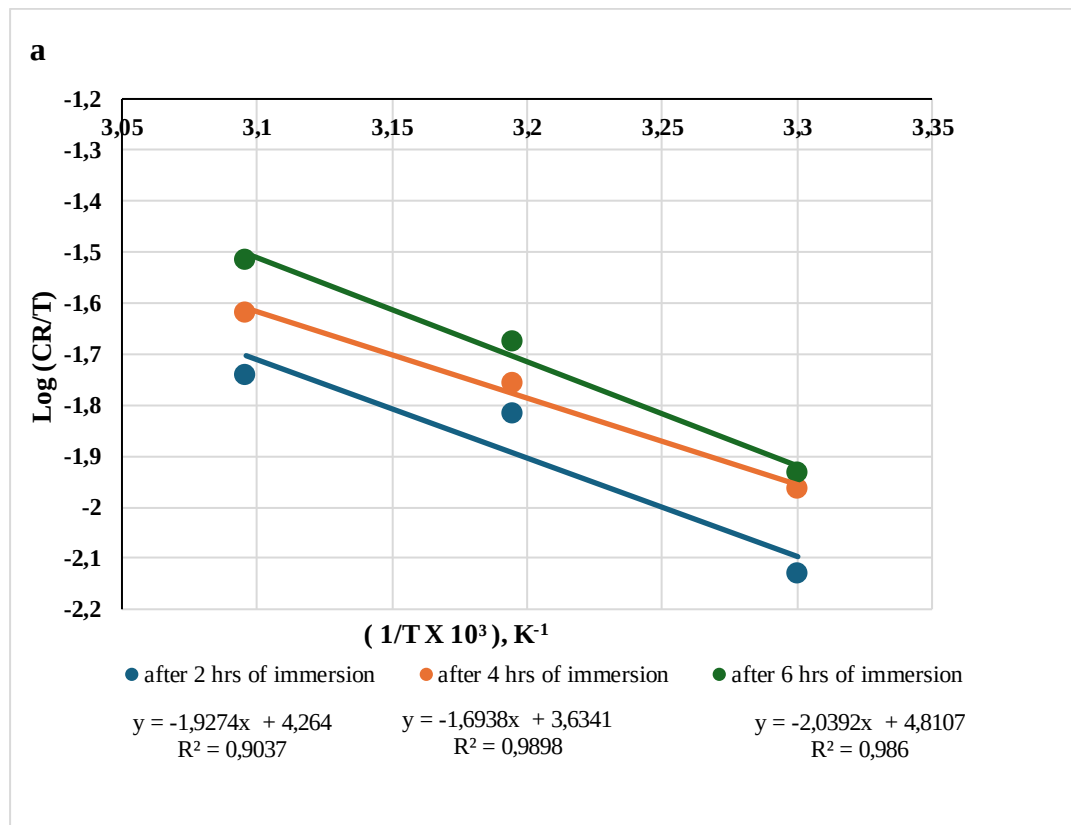
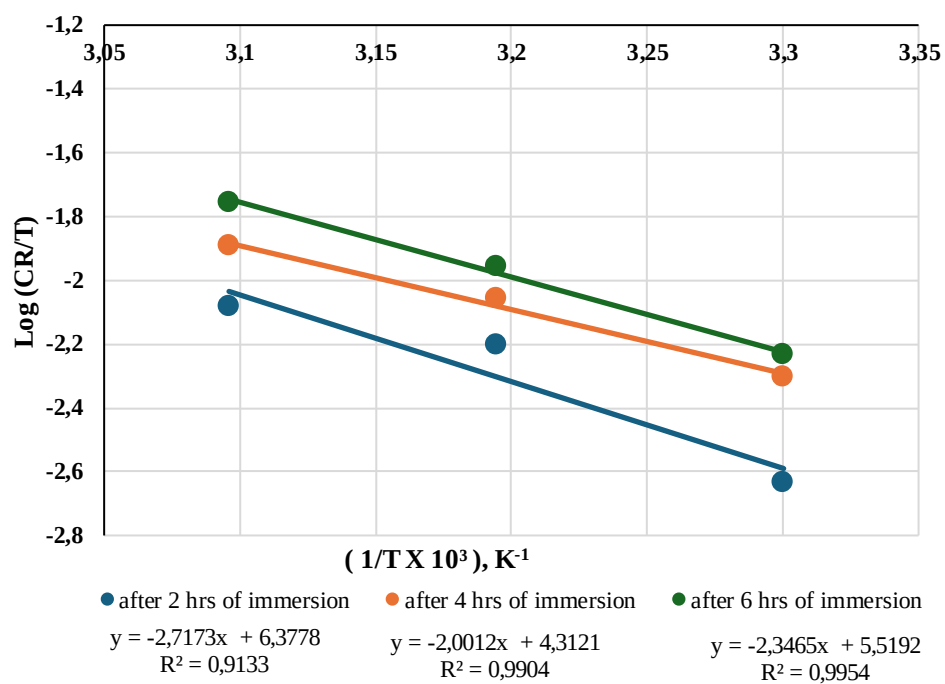


Figure 0.30: Plot of Log (CR/T) versus $(1/T \times 10^3)$ for Aluminium (AA1100) samples immersed in 3.5 % NaCl with i) 20 g/L of extract concentration.



b



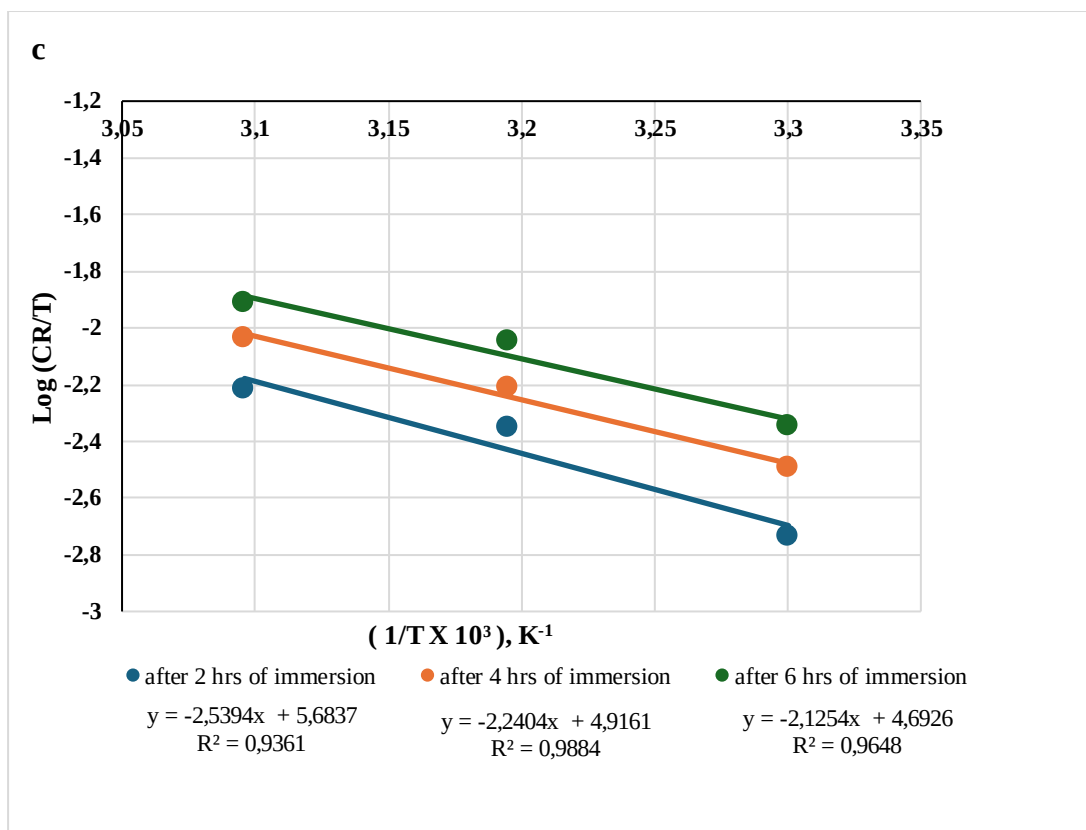
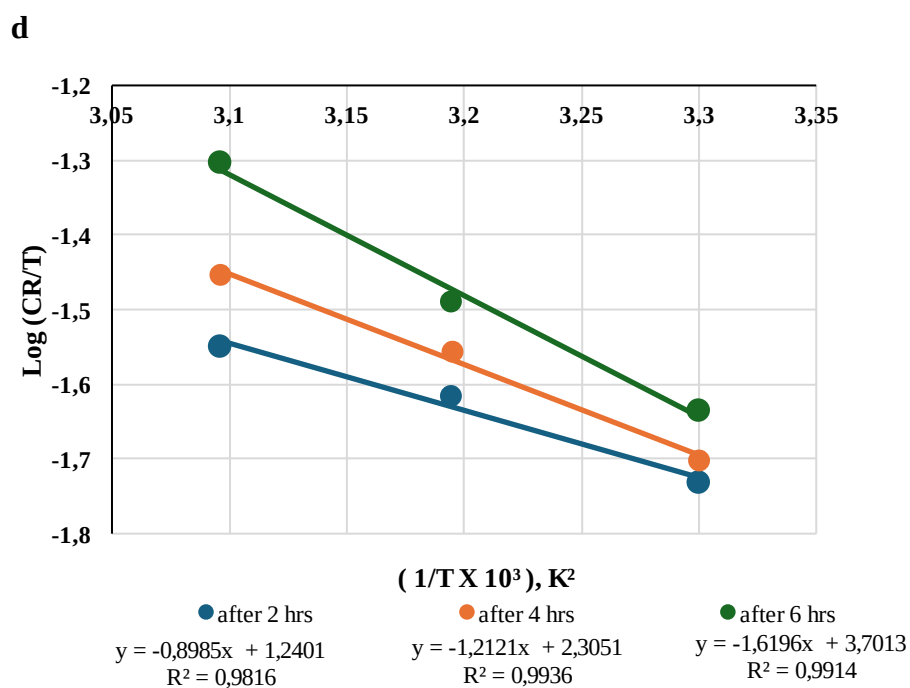


Figure 0.31: Plot of Log (CR/T) versus $(1/T \times 10^3)$ for mild steel samples immersed in 1 M H_2SO_4 with a) blank, b) 10 g/L and c) 20 g/L of extract concentration.



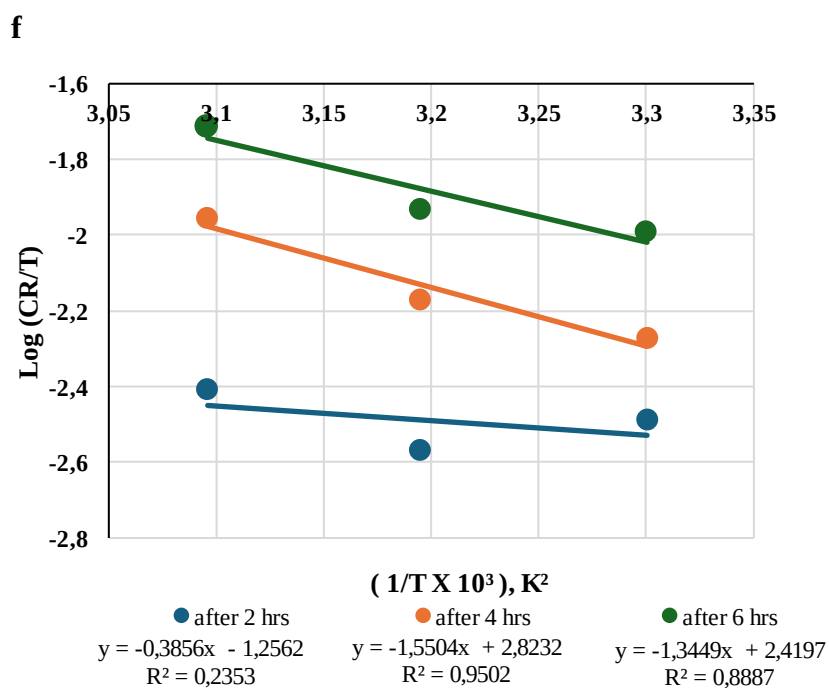
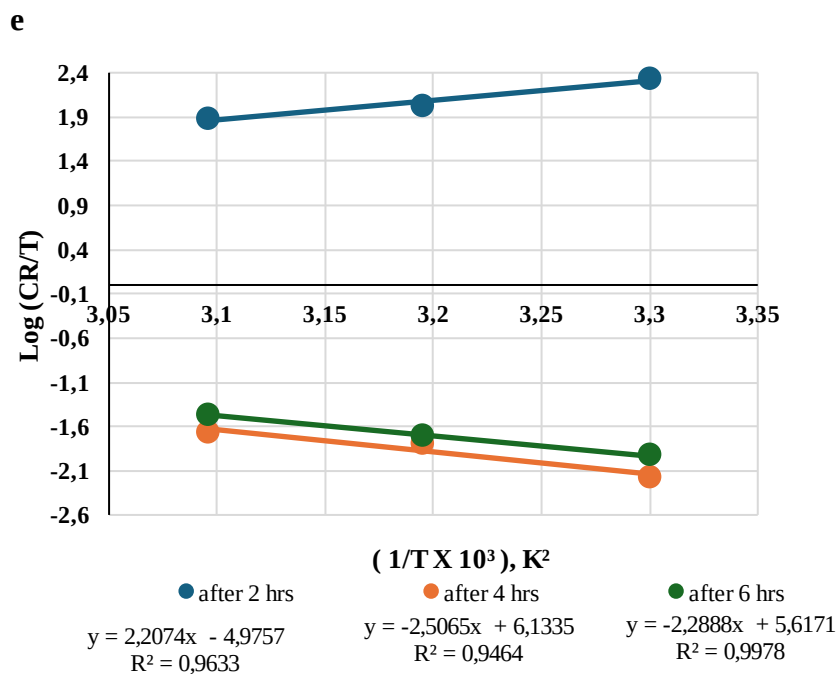


Figure 0.32: Plot of Log (CR/T) versus ($1/T \times 10^3$) for mild steel samples immersed in 1 M H₂SO₄ with d) blank, e) 10 g/L and f) 20 g/L of extract concentration.

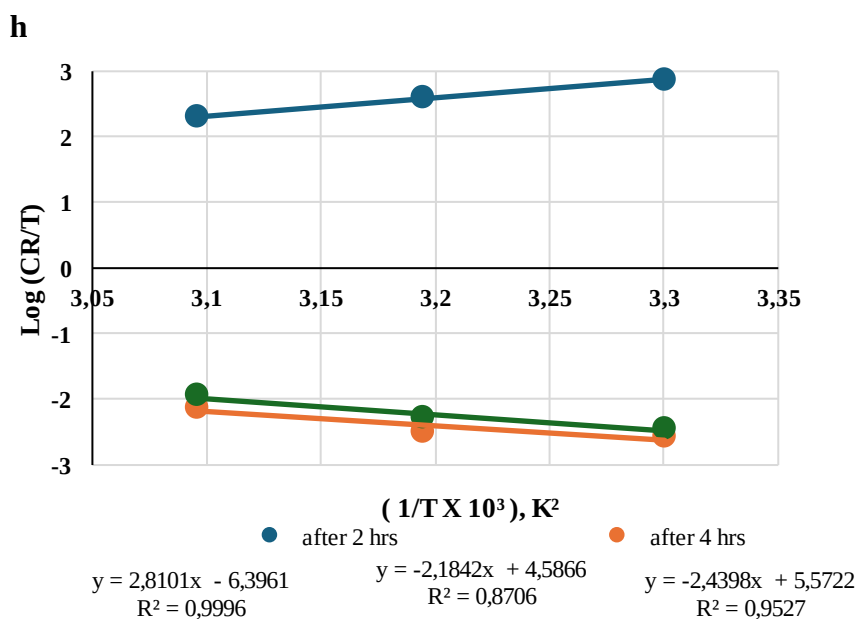
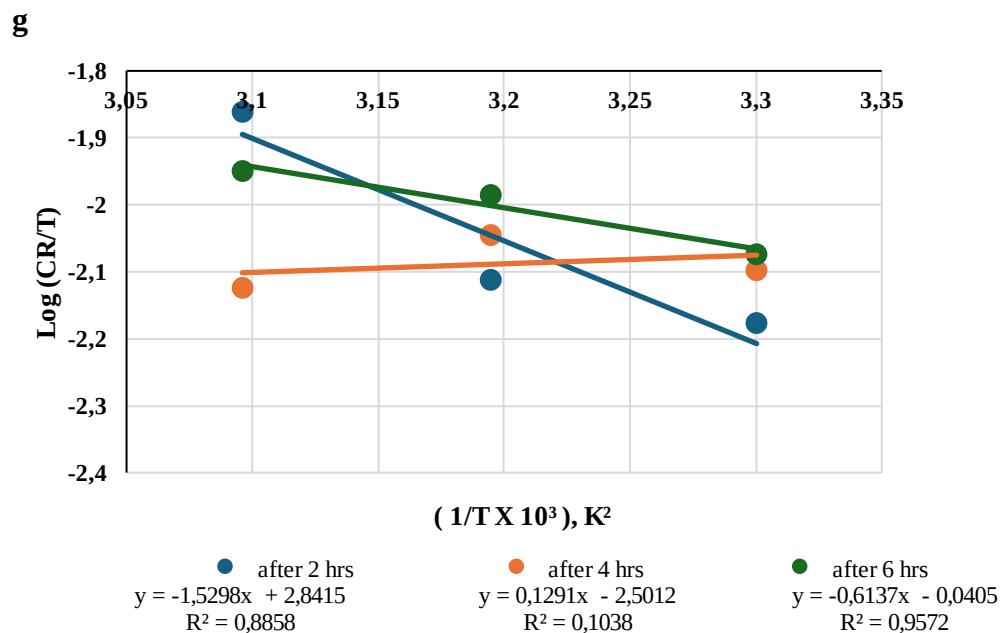


Figure 0.33: Transition state plot for mild steel samples immersed in 1 M H_2SO_4 with g) blank, h) 10 g/L and i) 20 g/L of extract concentration.

4.3.5 Computation of thermodynamic and activation parameters from the transition state and Arrhenius plots.

Activation, thermodynamic, inhibition and dissolution factors were calculated for all three metals (mild steel, AA1100, and API 5L X42 pipeline steel) in both 1 M H_2SO_4 and 3.5 % NaCl corrosive environments. The findings are summarised in the corresponding Tables 4.6, 4.7, and 4.8.

Enthalpy of activation, entropy of activation, and activation energy (E_a) were calculated for all the metals dissolution process using thermodynamic and activation characteristics. The Arrhenius plots slopes are shown by Figures 4.22 to 4.24 for samples exposed to 3.5 % NaCl and Figures 4.25 to 4.27 for specimens immersed in 1 M H_2SO_4 , the slopes were used to calculate activation energies (E_a). For mild steel and API 5L X42 pipeline steel activation energies (E_a) as depicted in Tables 4.6 and 4.7 are positive and higher for inhibited samples as compared to uninhibited samples. More prolonged exposure hours result in a drop in activation energies as the molecules that were previously adsorbed on the metal surfaces resorb into the solution, inferring physisorption (Obot et al., 2011). Aluminium samples exposed to 1 M H_2SO_4 followed the same trend with high E_a values observed for inhibited samples in contrast to uninhibited samples, the E_a increases with inhibitor dosage ensuring least energy requirement for metal degradation process is increased. For metal samples exposed to 3.5 % NaCl activation energies were between 5.43 KJ/mol and 64.22 KJ/mol whereas specimens immersed in 1 M H_2SO_4 have E_a of between 35.04 KJ/mol and 54.63 KJ/mol. The activation energies (E_a) in both corrosive media are below 80 KJ/mol, suggesting physisorption as the ideal method by which inhibitory molecules adsorb to the metal surface (Akinbulumo et al., 2020; Finšgar & Jackson, 2014). A complex material that forms between the metal and *Sclerocarya birrea* inhibitor and acts as a barrier to stop metal breakdown is implied by the E_a results, albeit this substance destabilizes over extended contact (Umoren et al., 2022). According to numerous reports, chemical adsorption is indicated when $E_a > 80$ kJ/mol, while a physical adsorption is implied when $E_a < 80$ kJ/mol (Olasehinde et al., 2012).

In the presence of *Sclerocarya birrea* inhibitor E_a values were lower than E_a for samples exposed to blank solution in 3.5 % NaCl which is indicative that the inhibitor lowers the activation energy (Ajike et al., 2024). When the activation energy values in blank solutions are higher than for inhibited samples as it is observed with aluminium samples (Table 4.8) in 3.5 % NaCl it implies chemisorption adsorption (Kumar et al., 2018; Sehmi et al., 2020). The activation energies for Al in 3.5 % NaCl decrease with increase in inhibitor dosage because of the progressive attachment of the inhibiting particles to the Al surface resulting in coordinative bonds between the metal and inhibitor hence lowering the subsequent activation energy (Raviprabha et al., 2023). At higher degrees of inhibition, the shift of the net corrosion reaction from the uncovered to covered area of the metal substrate produces a drop in corrosion activation energy (Oguzie, 2007).

The heat of enthalpy , heat of entropy and Gibbs free energy were calculated from slopes of the Transition state plots from Figures 4.29 to 4.33. The heat of enthalpy values (ΔH°) bears a positive sign for mild steel and API 5L X42 Pipeline steel in both the corrosive media (3.5 % NaCl and 1 M H_2SO_4) , indicating an endothermic reaction. Additionally, the endothermic process indicates mild steel dissolves slowly at modest temperatures while at elevated temperatures the dissolution process becomes thermodynamically favorable (Noor & Al-Moubaraki, 2008). Most of the ΔH° values achieved are below 40 KJ/mol, confirming that physisorption is dominant (Adejo et al., 2014). Exceptions were recorded for 10.0 g/L after 2 hrs of exposure and uninhibited sample after 4 hrs of exposure were ΔH° negatives of -53.81 KJ/mol and -2.47 KJ/mol were recorded. The negative enthalpy changes ($\Delta H^\circ < 0$) observed is an indicative that passive film formation becomes more favorable than active metal dissolution at these time points (Al-Amiery et al., 2023; El-Sayed et al., 2023). Passive film formation is an exothermic process which releases heat hence resulting in a negative enthalpy change couple with corrosion current density decrease (Tian et al., 2020). Negative ΔS° values indicate the creation of an activated complex during the rate determining phase, which indicates of association rather than dissolution (Abdel-Gaber et al., 2006; Amin et al., 2011; Behpour et al., 2009). This implies that disorder decreases as the reaction progresses from reactants to the activated complex (Kannan et al., 2018). These results are quite significant as they indicate the ability of the *Sclerocarya birrea* inhibitor to form a robust and efficient barrier at the metal solution interface to impede metal degradation.

Table 0.6: Thermodynamic and kinetic parameters for mild steel immersed in 3.5 % NaCl and 1 M H_2SO_4 with varying extract concentrations.

Media	Extract concentration (g/L)	E_a (kJ/mol)			ΔH (kJ/mol)			ΔS (J/mol/k)		
		Time (hrs)			Time (hrs)			Time (hrs)		
3.5 % NaCl		2	4	6	2	4	6	2	4	6
	Blank (0)	16.63	16.58	5.43	14.03	13.97	2.84	-230.15	-192.25	-190.75
	10.0	30.91	28.25	27.49	28.31	24.86	22.87	-180.01	-167.65	-154.45
	20.0	64.22	57.41	44.82	61.62	54.80	42.23	-121.76	-71.90	-54.94
1M H_2SO_4	Blank (0)	41.65	39.50	35.04	39.04	36.90	32.43	-127.99	-115.93	-105.46
		54.63	47.53	40.91	52.03	44.93	38.32	-115.01	-91.90	-75.46
	10.0									
	20.0	41.65	39.51	35.04	48.62	42.90	40.70	-107.72	-103.45	-88.75

Table 0.7: Thermodynamic and kinetic parameters for API 5L X42 Pipeline steel immersed in 3.5 % NaCl and 1 M H₂SO₄ with varying extract concentrations.

Media	Extract concentration (g/L)	E _a (kJ/mol)			ΔH (kJ/mol)			ΔS (J/mol/k)		
3.5 % NaCl		Time (hrs)			Time (hrs)			Time (hrs)		
		2	4	6	2	4	6	2	4	6
	Blank (0)	7.40	25.90	15.62	13.02	23.30	4.80	-195.82	-162.87	-178.25
	10.0	29.98	44.89	51.03	48.43	42.28	27.38	-95.69	-112.14	-154.01
1 M H ₂ SO ₄	20.0	27.14	48.32	44.83	42.22	45.27	24.56	-121.72	-103.67	-164.88
	Blank (0)	33.61	25.81	19.80	17.20	23.21	31.01	-173.83	-153.44	-126.71
	10.0	46.42	50.94	44.87	42.27	47.99	43.82	-292.85	-80.14	-90.02
	20.0	28.35	32.29	9.98	7.38	29.69	25.75	-221.63	-143.52	-151.25

Table 0.8: Thermodynamic and kinetic parameters for aluminium (AA100) immersed in 3.5 % NaCl and 1 M H₂SO₄ with varying extract concentrations.

Media	Extract concentration (g/L)	E _a (kJ/mol)			ΔH (kJ/mol)			ΔS (J/mol/k)		
3.5 % NaCl		Time (hrs)			Time (hrs)			Time (hrs)		
		2	4	6	2	4	6	2	4	6
	Blank (0)	66.96	78.29	56.41	-	-	-	-	-	-
	10.0	32.67	20.62	16.74	-	-	-	-	-	-
1 M H ₂ SO ₄	20.0	47.27	23.42	0.065	-	-	-	-	-	-
	Blank (0)	38.34	34.24	31.90	29.29	-2.47	11.75	-143.17	-245.47	-198.35
	10.0	49.32	44.42	56.41	-	41.82	46.72	-320.04	-109.76	-90.88
	20.0	63.75	28.15	27.91	53.81	25.30	25.55	-170.07	-165.10	-46.91

4.3.6 Adsorption isotherms

4.3.6.1 Langmuir Adsorption isotherm

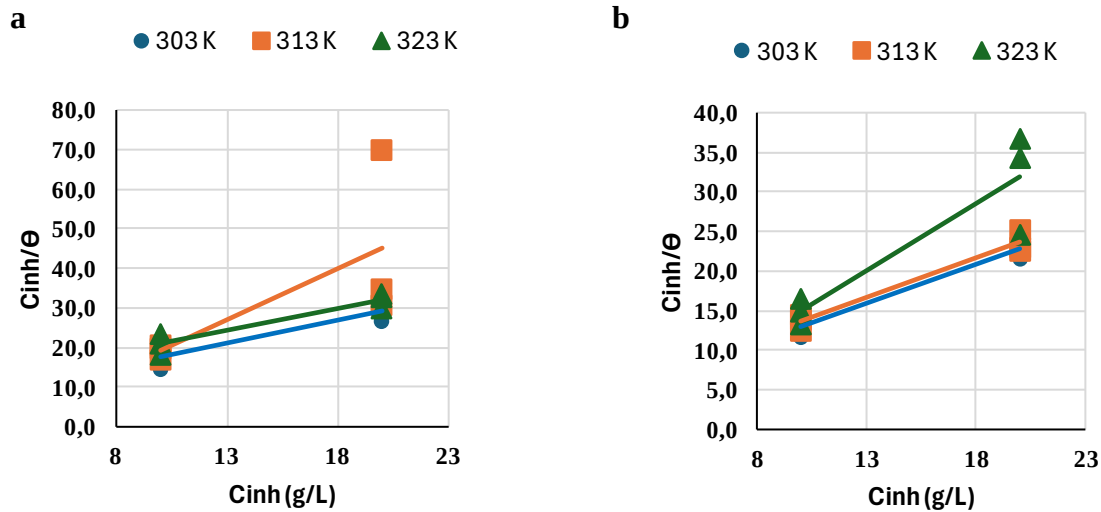


Figure 0.34: Langmuir adsorption isotherm for mild steel a) 3.5 % NaCl and b) 1 M H_2SO_4 with various extract concentrations after 2 hrs, 4 hrs and 6 hrs of immersion.

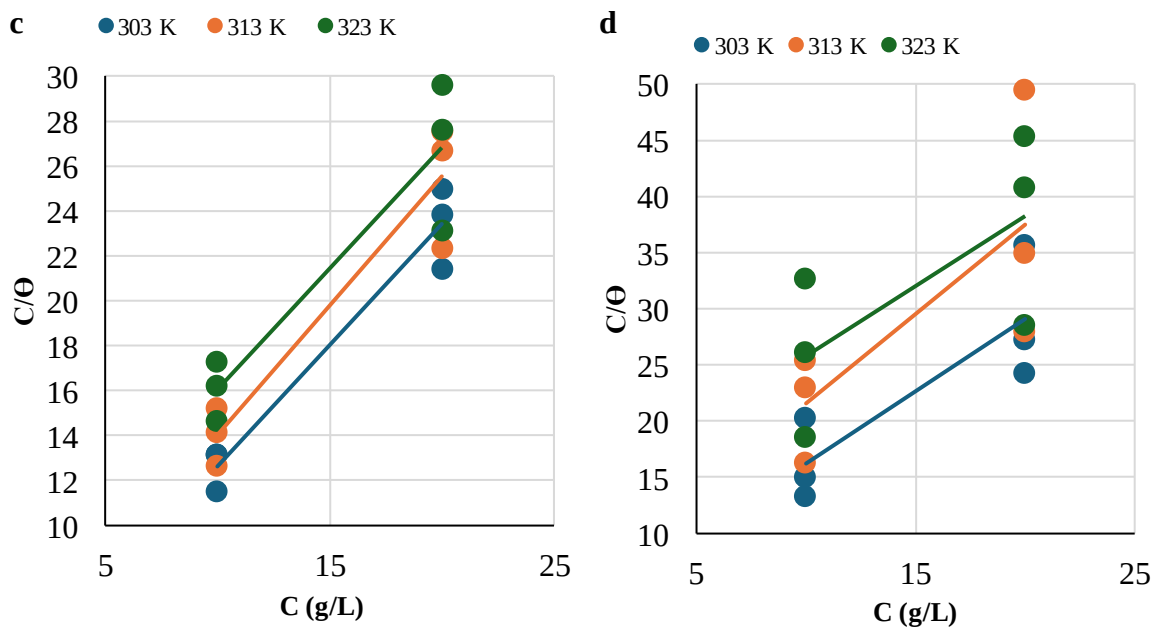


Figure 0.35: Langmuir adsorption isotherm for API 5L X42 Pipeline steel c) 3.5 % NaCl and d) 1 M H_2SO_4 with various extract concentrations after 2 hrs, 4 hrs and 6 hrs of immersion.

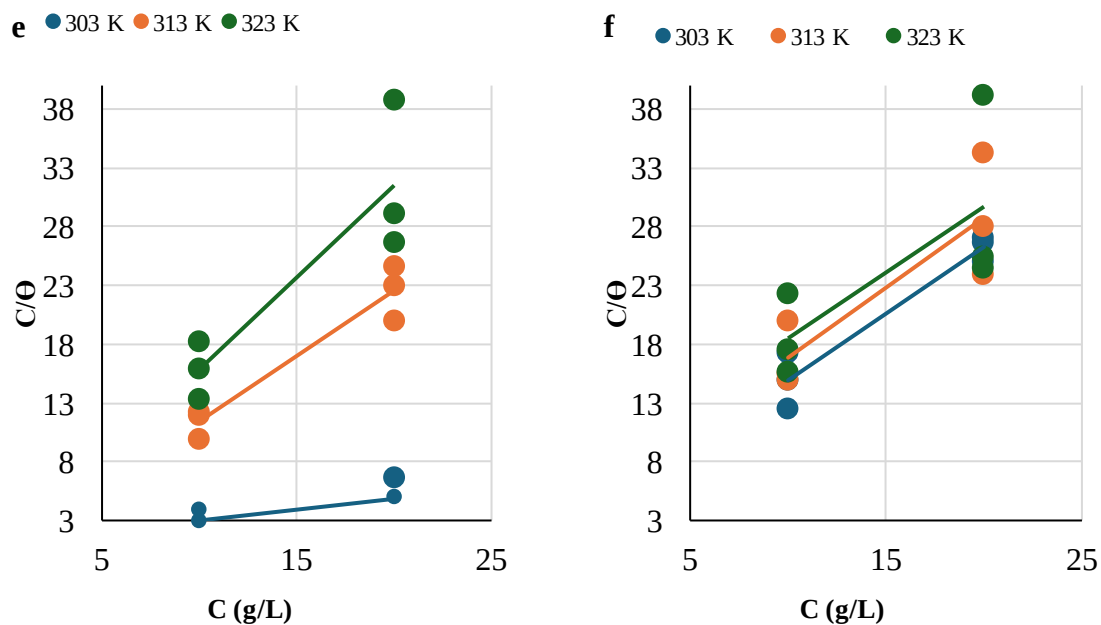


Figure 0.36: Langmuir adsorption isotherm for AA1100 e) 3.5 % NaCl and f) 1 M H₂SO₄ with various extract concentrations after 2 hrs, 4 hrs and 6 hrs of immersion.

4.3.6.2 Freundlich adsorption isotherm

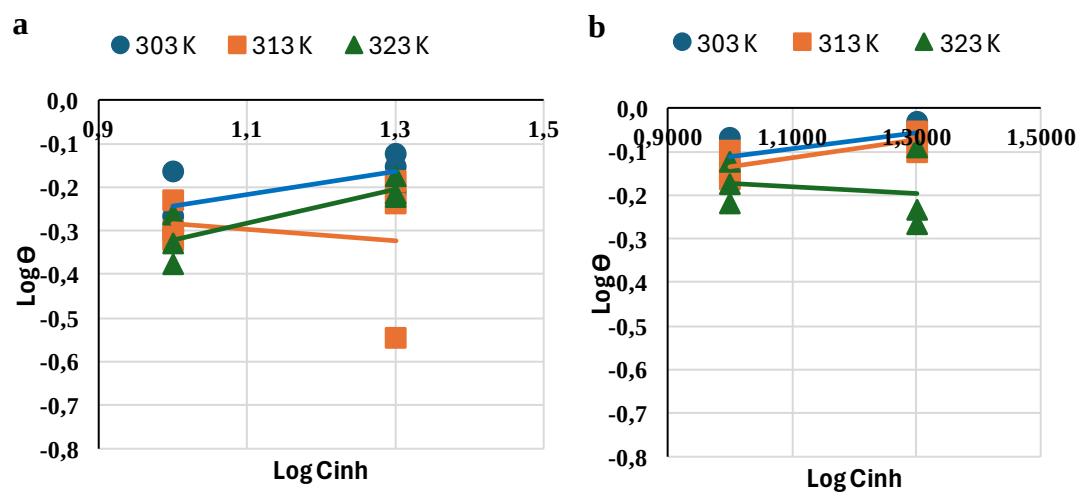


Figure 0.37: Freundlich adsorption isotherm for mild steel immersed in a) 3.5 % NaCl and b) 1 M H₂SO₄ with various extract concentrations after 2 hrs, 4 hrs and 6 hrs of immersion.

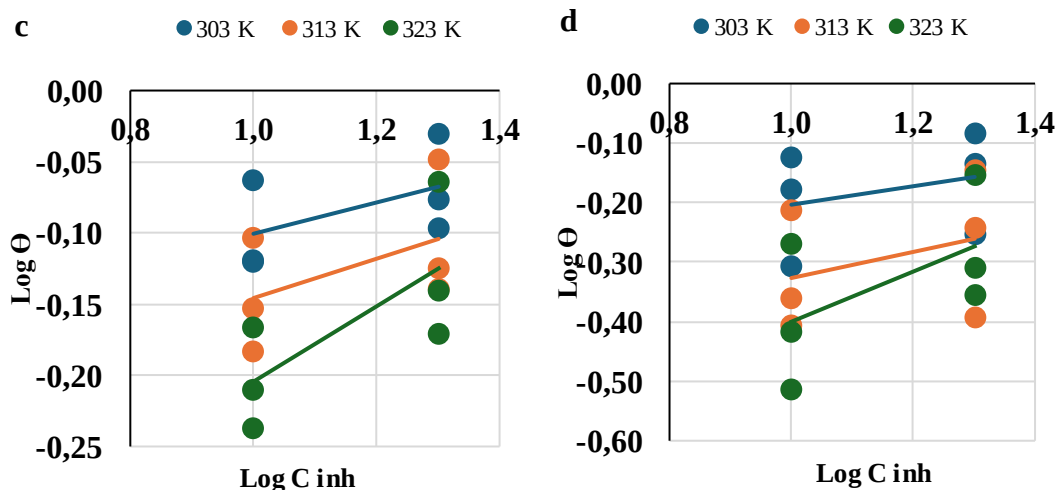


Figure 0.38: Freundlich adsorption isotherm for mild steel immersed in c) 3.5 % NaCl and d) 1 M H_2SO_4 with various extract concentrations after 2 hrs, 4 hrs and 6 hrs of immersion.

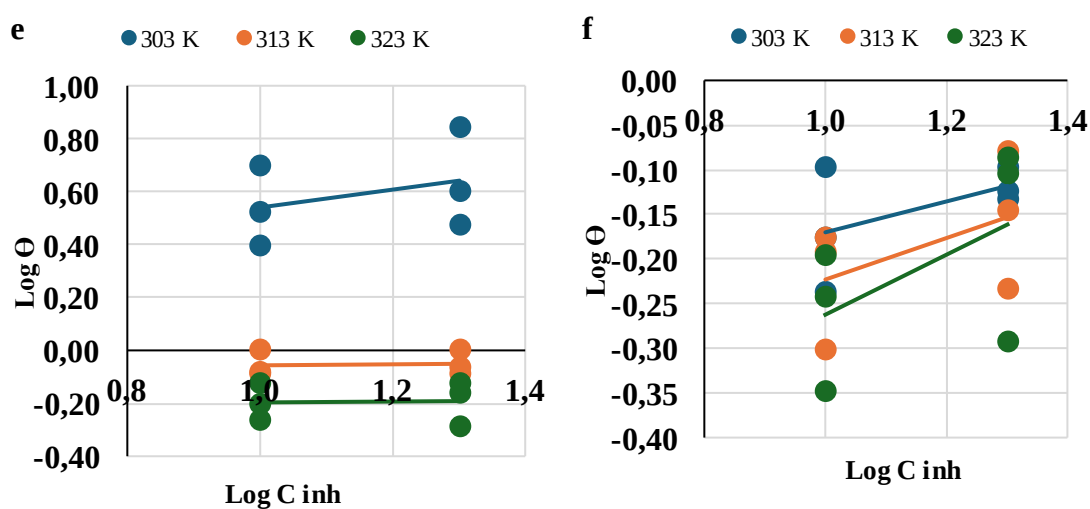


Figure 0.39: Freundlich adsorption isotherm for aluminium (AA1100) immersed in e) 3.5 % NaCl and f) 1 M H_2SO_4 with various extract concentrations after 2 hrs, 4 hrs and 6 hrs of immersion.

4.3.6.3 El-awady adsorption isotherm

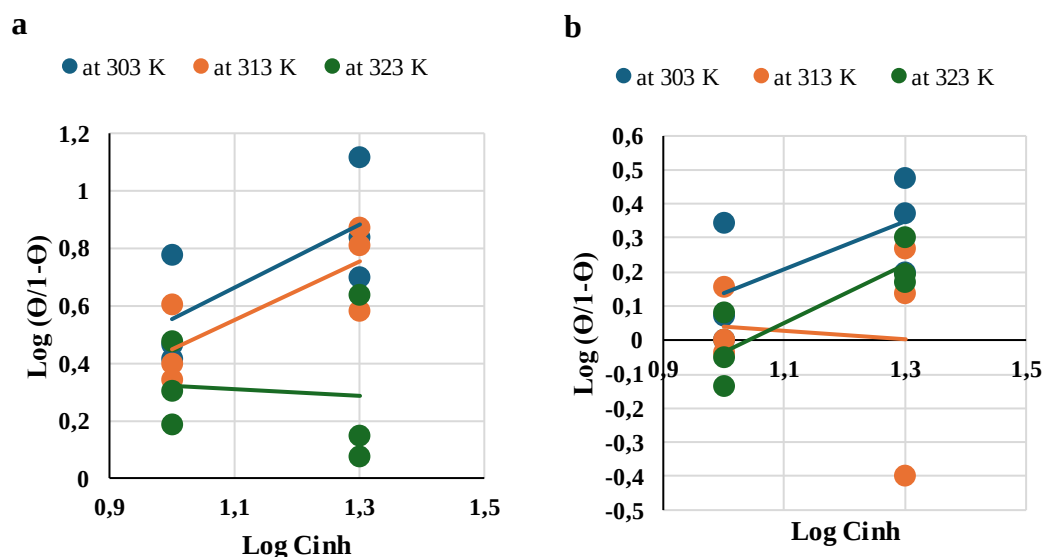


Figure 0.40: El-awady's adsorption isotherm for mild steel immersed in a) 3.5% NaCl and b) 1 M H₂SO₄ with various extract concentrations after 2 hrs , 4 hrs and 6 hrs of exposure.

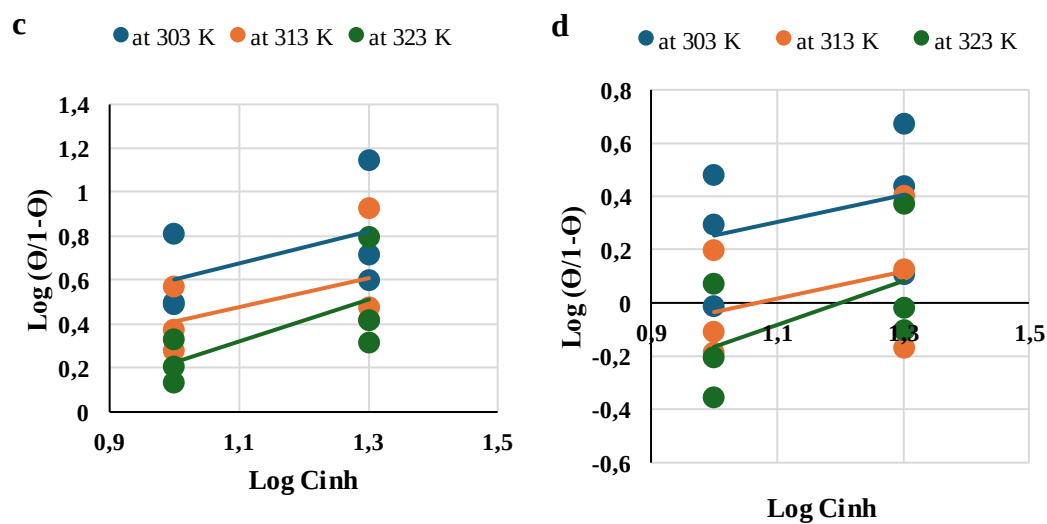


Figure 0.41: El-awady's adsorption isotherm for API 5L X42 Pipeline steel immersed in c) 3.5 % NaCl and d) 1 M H₂SO₄ with various extract concentrations after 2 hrs , 4 hrs and 6 hrs of exposure.

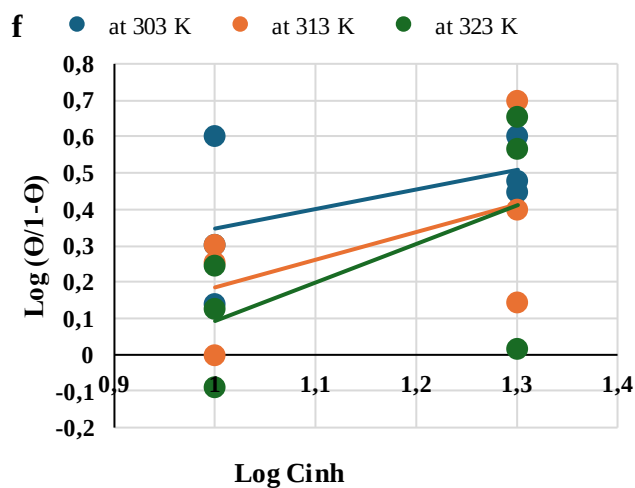


Figure 0.42: El-awady's adsorption isotherm for aluminium (AA1100) immersed in f) 1 M H_2SO_4 with various extract concentrations after 2 hrs , 4 hrs and 6 hrs of exposure.

4.3.6.4 Temin adsorption isotherm

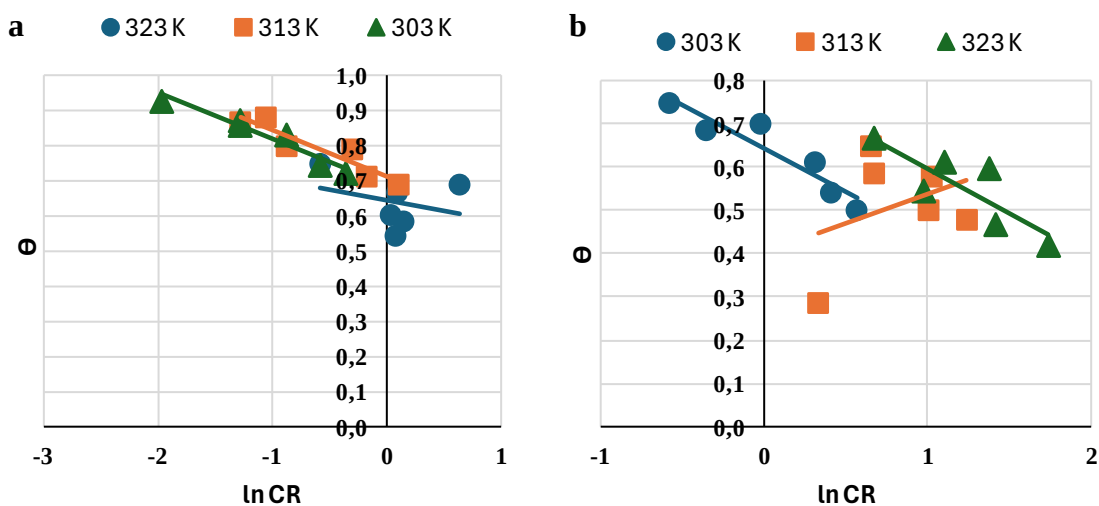


Figure 0.43: Temkin adsorption isotherm for mild steel immersed in a) 3.5 % NaCl and b) 1 M H_2SO_4 with various extract concentrations after 2 hrs , 4 hrs and 6 hrs of exposure.

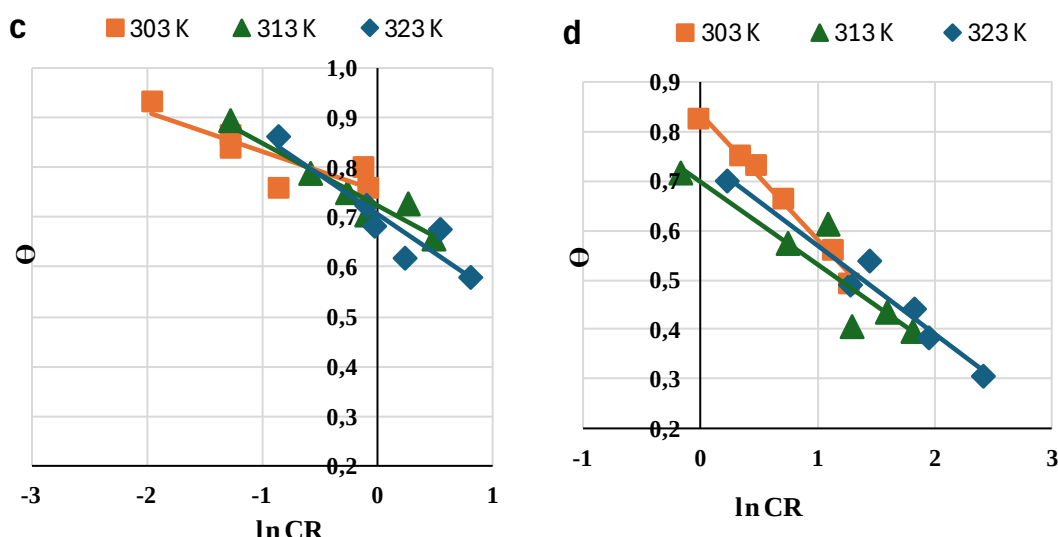


Figure 0.44: Temkin adsorption isotherm for API 5L X42 Pipeline steel immersed in c) 3.5 % NaCl and d) 1 M H₂SO₄ with various extract concentrations after 2 hrs , 4 hrs and 6 hrs of exposure.

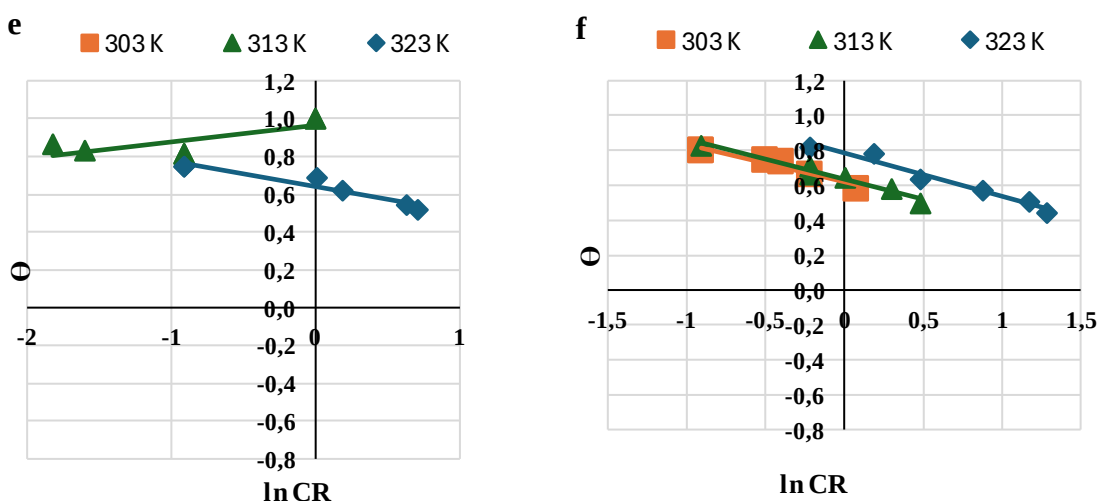


Figure 0.45: Temkin adsorption isotherm for mild steel immersed in e) 3.5 % NaCl and f) 1 M H₂SO₄ with various extract concentrations after 2 hrs , 4 hrs and 6 hrs of exposure.

4.3.7 The equilibrium constant (K_{ads})

The equilibrium constant (K_{ads}) for the various adsorption isotherms in were computed and summarized as in Table 4.9 to Table 4.11. Generally, K_{ads} values are low which is an indication of electrostatic interactions between the *Sclerocarya birrea* inhibiting molecules and mild steel surface (Adejo et al., 2012). The K_{ads} were computed from the slopes of the isotherm's graphs from Figures 4.34 to 4.45. In an astonishing outcome a high value of K_{ads} is recorded for

Temkin adsorption isotherm in aluminium exposed to 3.5 % NaCl, 56763.66 at 313 K. High values achieved for Temkin adsorption isotherm signify greater adsorption and potential of achieving greater inhibition (Jimoh & Usman, 2021). In addition, at temperature of 313 K the thermal mobility of inhibiting molecules is increased hence increasing the adsorption rates which in turn lead to high values of adsorption constants (Huang et al., 2024). According to (Chu, 2021) Temkin adsorption isotherm suffers from a fundamental flaw of inconsistency so the anomaly value observed can also be ascribed to that.

Table 0.9: The K_{ads} for mild steel exposed to 3.5 % NaCl and 1 M H_2SO_4 in the presence and absence of varying extract concentrations.

Media	Temperature (K)	$K_{ads} (mol^{-1})$			
		Langmuir	Freundlich	Temkin	El-awady
3.5 % NaCl	303	0.863	0.310	0.0053	0.287
	313	0.387	0.704	0.0045	0.302
	323	0.910	0.195	0.0000223	2.737
1 M H_2SO_4	303	1.016	0.507	0.0405	0.272
	313	1.001	0.455	19.688	1.455
	323	0.590	0.802	48.98	0.128

Table 0.10: The K_{ads} for API 5L X42 Pipeline steel exposed to 3.5 % NaCl and 1 M H_2SO_4 in the presence and absence of varying extract concentrations.

Media	Temperature (K)	$K_{ads} (mol^{-1})$			
		Langmuir	Freundlich	Temkin	El-awady
3.5 % NaCl	303	0.928	0.616	0.0000734	0.746
	313	0.870	0.520	0.00310	0.565
	323	0.930	0.340	0.0112	0.187
1 M H_2SO_4	303	0.778	0.438	0.0372	0.559
	313	0.629	0.285	0.0152	0.286
	323	0.803	0.151	0.0151	0.102

Table 0.11: The K_{ads} for aluminium (AA1100) exposed to 3.5 % NaCl and 1 M H_2SO_4 in the presence and absence of varying extract concentrations.

Media	Temperature (K)	$K_{ads} (mol^{-1})$			
		Langmuir	Freundlich	Temkin	El-awady
3.5 % NaCl	303	5.432	1.595	-	-
	313	0.899	0.841	56763.66	-
	323	0.639	0.612	0.0115	-
1 M H_2SO_4	303	0.881	0.454	0.0545	0.646
	313	0.840	0.351	0.0629	0.175

323	0.893	0.252	0.0421	0.122
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4.3.8 Gibbs free energy (ΔG_{ads})

The values of ΔG_{ads} obtained for the isotherms under consideration were tabulated in Tables 4.12 to 4.14. All the values were negative for Langmuir, Freundlich and El-awady at studied temperatures and corrosive environments which is indicative of spontaneous adsorption process of inhibitor molecules on the metal substrate and confirm formation of strong interactions at the metal-inhibitor surface (Akpan et al., 2024; Ebenso & Obot, 2010; Miralrio & Espinoza Vázquez, 2020). The values varied from -4.656 KJ/mol to -14.384 KJ/mol. This reflects the spontaneity of the inhibitor compounds binding onto the metal surfaces. Physisorption is compatible with $\Delta G_{\text{ads}} \leq 20$ KJ/mol while chemisorption is compatible with $\Delta G_{\text{ads}} \geq -40$ KJ/mol (Ahanotu et al., 2022; Okewale & Adesina, 2020). The Temkin adsorption isotherm for pipeline steel exposed to 1 M H_2SO_4 shows the same trends, with ΔG values ranging from -2.041 KJ/mol to -21.240 KJ/mol. Similarly, samples of aluminum exposed to the same media produced Gibbs free energies between -2.279 KJ/mol and -3.254 KJ/mol, indicating spontaneity of the process. So, from these findings the adsorption supports physisorption which involves a series of weak electrostatic interactions between metal atoms and adsorbate species. In contrast, Gibbs's free energy values for Temkin adsorption isotherm for samples exposed to 3.5% NaCl are all positive and increase with increase in temperature for mild steel and API 5L X42 pipeline steel bearing ΔG values between 1.277 KJ/mol and 17.981 KJ/mol. These observations imply that the adsorption process in Temkin adsorption in those media is non-spontaneous and requires external energy input to facilitate it (Ayawei et al., 2017; Ebelegi et al., 2020). Generally, $\Delta G > 0$ is indicative that energy required to adsorb *Sclerocarya birrea* inhibiting molecules to the metal surfaces is higher than energy released during the same process. In the context of leaf extract adsorption, it could imply that additional energy is required to absorb phytochemicals and other inhibiting organic compounds from the extract into the substrate.

Table 0.12: Gibbs free energy for mild steel exposed to 3.5 % NaCl and 1 M H_2SO_4 in the presence and absence of varying extract concentrations for all isotherms in mild steel.

Media	Temperature (K)	ΔG_{ads} (KJ/mol)			
		Langmuir	Freundlich	Temkin	El-awady
3.5 % NaCl	303	-9.748	-7.169	3.083	-6.975
	313	-7.983	-9.540	3.611	-7.337
	323	-10.534	-6.400	17.981	-13.492
1 M H_2SO_4	303	-10.160	-8.408	-2.041	-6.839
	313	-10.456	-8.404	-18.210	-11.430

323	-9.370	-10.195	-21.240	-5.266
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Table 0.13: Gibbs free energy for mild steel exposed to 3.5 % NaCl and 1 M H₂SO₄ in the presence and absence of varying extract concentrations for all isotherms in API 5L X42 Pipeline steel.

Media	Temperature (K)	ΔG_{ads} (KJ/mol)			
		Langmuir	Freundlich	Temkin	El-awady
3.5 % NaCl	303	-9.931	-8.899	13.866	-9.381
	313	-10.091	-8.752	4.581	-8.968
	323	-10.593	-7.890	1.277	-6.284
1 M H ₂ SO ₄	303	-9.487	-8.040	-1.827	-8.654
	313	-9.247	-7.186	0.443	-7.196
	323	-10.198	-5.710	0.475	-4.656

Table 0.14: Gibbs free energy for mild steel exposed to 3.5 % NaCl and 1 M H₂SO₄ in the presence and absence of varying extract concentrations for all isotherms in aluminium (AA1100).

Media	Temperature (K)	ΔG_{ads} (KJ/mol)			
		Langmuir	Freundlich	Temkin	El-awady
3.5 % NaCl	303	-14.384	-11.296	-	-
	313	-10.177	-10.003	-38.945	-
	323	-9.585	-9.469	1.169	-
1M H ₂ SO ₄	303	-9.800	-8.130	-2.789	-9.019
	313	-10.000	-7.729	-3.254	-5.917
	323	-10.484	-7.086	-2.279	-5.137

4.3.9 Correlation coefficient (R^2) of the adsorption isotherms

The correlation coefficient of the adsorption isotherms was tabulated in Tables 4.15 to 4.17. At low temperatures of 303 K in 3.5 % NaCl, the adsorption of inhibitor molecules for aluminum and API 5L X42 pipeline steel best fits Langmuir adsorption because it has substantial R^2 values of 0.954 and 0.929 respectively. At the same temperature in 1 M H₂SO₄ for these metals, Temkin adsorption isotherm is the most dominating model with an R^2 of 0.985 for API 5L X42 pipeline steel and 0.964 for Aluminum correspondingly. Langmuir adsorption isotherm showed the best fit for mild steel samples exposed to 1 M H₂SO₄ at 313 K with an R^2 value of 0.962 while Temkin in samples exposed to 3.5 % NaCl proved to be the ideal fit with an R^2 value of 0.932. Smaller R^2 values signifies highly favorable adsorption, $R^2 > 1$ unfavorable, $R^2 = 1$ linear, $0 < R^2 < 1$ favorable and if $R^2 = 0$ irreversible (Ezeugo et al., 2017). High R^2 values close to unity show favorable adsorption constants indicating efficient binding sites on the

adsorbent surface (Kaushal & Singh, 2017). These results depict that the adherence of *Sclerocarya birrea* inhibiting compounds on the studied metal surfaces is feasible while values close to unity indicate that there exists a strong and closely linked relationship between the variables (Pragathiswaran et al., 2013). In contrast to Freundlich and El-awady adsorption isotherms, Langmuir and Temkin best fitted the experimental results hence the adsorption of inhibitor molecules of *Sclerocarya birrea* on the metal surfaces be best described by Langmuir and Temkin models.

Table 0.15: R² values for all the adsorption isotherm considered in mild steel.

Media	Temperature (K)	Langmuir	Freundlich	Temkin	El-awady
3.5 % NaCl	303	0.853	0.399	0.932	0.495
	313	0.515	0.029	0.867	0.627
	323	0.893	0.725	0.094	0.0079
1 M H ₂ SO ₄	303	0.962	0.518	0.873	0.391
	313	0.962	0.621	0.121	0.0076
	323	0.830	0.036	0.704	0.746

Table 0.16: R² values for all the adsorption isotherm considered in API 5L X42 Pipeline steel.

Media	Temperature (K)	Langmuir	Freundlich	Temkin	El-awady
3.5 % NaCl	303	0.954	0.264	0.732	0.240
	313	0.913	0.244	0.927	0.229
	323	0.873	0.524	0.857	0.453
1 M H ₂ SO ₄	303	0.720	0.092	0.985	0.109
	313	0.573	0.113	0.825	0.126
	323	0.482	0.314	0.957	0.298

Table 0.17: R^2 values for all the adsorption isotherm considered in aluminium (AA1100).

Media	Temperature (K)	Langmuir	Freundlich	Temkin	El-awady
3.5 % NaCl	303	0.354	0.118	-	-
	313	0.929	0.0053	0.575	-
	323	0.797	0.0016	0.927	-
1 M H ₂ SO ₄	303	0.933	0.276	0.930	0.240
	313	0.756	0.256	0.964	0.276
	323	0.542	0.288	0.962	0.312

4.4 Corrosion inhibition monitoring by electrochemical methods

Measurements of Open circuit potential (OCP), Electrochemical impedance spectroscopy (EIS) and Potentiodynamic polarization (PDP) were performed on mild steel, API 5L X42 pipeline steel, and aluminum (AA 1100) samples that were exposed to 1 M H₂SO₄ and 3.5 % NaCl solutions with and without different dosages of *Sclerocarya birrea* inhibitor . The results from these electrochemical tests help in determining if the inhibitor is cathodic, anodic, or mixed type. Based on these results it is therefore possible to forecast the most likely corrosion inhibition mechanism that will occur based on the type of inhibitor.

4.4.1 Open Circuit Potential (OCP)

A basic electrochemical method for evaluating how materials would behave when corroded in various conditions is by first measuring its open circuit potential. With OCP, we learn about a material's inherent electrochemical stability as well as its propensity to passivate or corrode by letting it approach a steady-state potential without the need for external current (Eliaz, 2019b). In this investigation, mild steel, API 5L X42 pipeline steel, and aluminum samples were subjected to OCP tests in both a blank solution and to solutions containing 10 g/L and 20 g/L of *S.birrea* corrosion inhibitor concentrations. The blank solution depicts each metal's natural corrosion tendencies in the given environment, but the inhibitor-containing solution shows how the corrosion inhibitor reduces or prevents metal degradation (Ahmed et al., 2024) . Through this comparison, we may assess the material's inherent corrosion susceptibility and the effectiveness of the inhibitor in changing the OCP to higher positive values, suggesting less corrosion activity.

4.4.1.1 Open circuit potential (OCP) studies of Mild steel in 3.5 % NaCl and 1 M H₂SO₄ both in presence and absence of *Sclerocarya birrea* inhibitor.

Open circuit potential results for mild steel exposed to both 3.5 % NaCl and 1 M H₂SO₄ corrosive environments both in the absence and presence of varying concentrations of the *Sclerocarya birrea* inhibitors are depicted in Figure 4.46 a and b respectively. For samples exposed to simulated saltwater, as shown in Figure 4.46 a, the blank exposed sample OCP began at a relatively high value of -552 mv, dropped to -700 mv after 1500s, and remained stable. The initial high potential suggests that mild steel was in a passive condition, still generating a corrosion film, or that it had impurities, which most likely delayed the corrosion process for a short time (Eliaz, 2019b). When chloride ions strongly attacked the metal, the surface remained active, resulting in the observed rapid reduction of potential from -552 mv after 100 s to -700 mv after 1500 s. This indicates the breakdown in any protective or early passivation. The pronounced decline suggests that this harsh chloride-rich environment is beyond the steel's ability to withstand corrosion. A dynamic equilibrium between the metal degradation process and the production of corrosion products, like iron oxides or hydroxides, has been obtained when the potential stabilizes at about -748 mV. As the steel corrodes at a comparatively constant rate, the potential stays stable, indicating a continuous corrosion process (Xu et al., 2021). The OCP changed to a less negative potential with 10 g/L of the inhibitor. It began at -600 mV and stabilized at -224 mV after 250 seconds, showing less corrosion. The OCP showed even better corrosion protection at 20 g/L, peaking at -198 mV and stabilizing at -162 mV after 250 seconds. The mild steel is kept in a more passive state for the duration of the test, demonstrating better performance at the higher concentration of 20 g/L. According to these findings, *Sclerocarya birrea* leaf extract is a potent green inhibitor, and in conditions containing chloride, higher quantities of the extract provide superior corrosion protection.

The OCP results show complex electrochemical behaviour impacted by the hostile acidic environment and the inhibitor's variable efficiency for mild steel in 1 M H₂SO₄, both in the presence and absence of the *S. birrea* inhibitor as depicted by Figure 46 b. In the case of the blank sample, the OCP began at -392 mV and increased gradually to -288 mV over the course of 2120 seconds before stabilizing. This suggests the creation of a layer of corrosion product that somewhat passivates the surface while permitting continued corrosion (Feliu et al., 2011). The potential rapidly plummeted to -797 mV at the introduction of 10 g/L of the inhibitor, indicating fast adsorption. After just 200 seconds, the potential quickly rose to 10 mV, most

likely because of the production of a protective film. The sharp decline down to -314 mV, however, followed by a steady state at about 3600 seconds, points to a potential partial instability or disintegration of the protective layer, perhaps because of localized corrosion or inhibitor desorption. The OCP showed a similar pattern with 20 g/L of the inhibitor; it began at -721 mV and increased to a significantly more positive 270 mV after 460 seconds, indicating more effective surface protection. However, a significant decline to just below the potential of the 10 g/L sample at 3000 seconds suggests considerable inhibitor instability with extended exposure. The OCP rose once more and stabilized at a higher potential between 3400 and 3600 seconds, showing that the system eventually recovered, and the greater inhibitor concentration created a more resilient protective coating. Similarly like in simulated seawater media, the findings demonstrate that although the steel is initially protected by both concentrations of the inhibitor, the 20 g/L concentration offers longer-lasting protection that is more effective and stable, even though there are some fluctuations in the intermediate stages, which are probably caused by interactions between the inhibitor and the acidic medium. In conclusion the inhibitor proved to give much better protection in 3.5 % NaCl environment than in 1 M H₂SO₄. Over time, in simulated seawater conditions, stable OCP values were attained; however, in samples exposed to an acidic medium, there were more potential fluctuations and less stable inhibitor performance. For both media high inhibitor concentration of 20 g/L offered a notable metal surface protection.

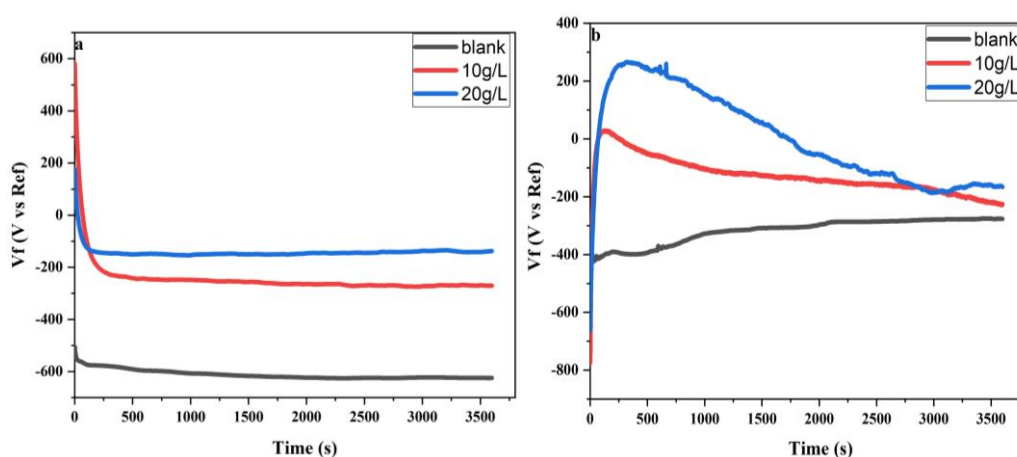


Figure 0.46: OCP of mild steel in a) 3.5 % NaCl and b) 1 M H₂SO₄ in the absence (blank) and presence of varying concentrations of *Sclerocarya birrea* inhibitor.

4.4.1.2 Open circuit potential (OCP) studies of API 5L X42 pipeline steel in 3.5 % NaCl and 1 M H₂SO₄ both in presence and absence of *Sclerocarya birrea* inhibitor.

Results for OCP of *Sclerocarya birrea* inhibited and uninhibited API 5L X42 pipeline steel samples submerged in 3.5 % NaCl show distinct behaviors as depicted in Figure 4.47 (a) and (b). A quick decline in potential from 906 mV to -200 mV was observed after 135 seconds for the uninhibited blank exposed sample, suggesting rapid corrosion onset. Following a period of minor fluctuations at about 1250 seconds, which were probably caused by localized disruptions of this layer, it stabilized, indicating the creation of a corrosion product layer (Valcarce & Vázquez, 2008). The initial potential of the sample exposed to 10 g/L of leaf extract was more positive (780 mV), suggesting partial surface protection. The potential then decreased to -30 mV in 100 seconds, and reached equilibrium remaining stable thereafter, suggesting the inhibitor effectively reduced corrosion activity by creating a barrier to shield steel from degradation. The sample immersed in corrosive solution containing 20 g/L of the inhibitor outperformed the rest, stabilizing at almost -5 mV after 88 seconds, having started at a substantially higher potential (410 mV). This implies that the inhibitor forms a strong, protective barrier, hence safeguarding the metal against corrosion (Shwetha et al., 2024). Though minor fluctuations in each case indicate transient instabilities in the surface coating, the inhibited sample's overall stabilization shows that the *S. birrea* ethanolic extract is effective at safeguarding API 5L X42 pipeline steel from seawater corrosive environments.

For samples exposed to acidic medium as displayed in Figure 4.47 b, the outcome is much different from observations gathered for samples in seawater. The blank sample's initial potential was 805 mV, but it gradually dropped until it reached -1780 mV at the end of the experiment without reaching equilibrium, which is indicative that corrosion was continuing without a layer of protection building on the steel surface. For the sample immersed in 1 M H₂SO₄ in the presence of 10 g/L inhibitor had an initial potential of -500 mV and it increased to 303 mV in 100 seconds, indicating partial inhibition. However, by the end, it gradually decreased once more to -419 mV, indicating that although some protection was given, it was not enough for long-term stability. Lastly the sample immersed with 20 g/L of inhibitor responded better, starting with an initial potential of -140 mV and increasing to 488 mV in 100 seconds. After that, there was a slow decline, but the sample still ended up with a positive potential of 1200 mV, indicating strong corrosion resistance. The failure to reach equilibrium in all the samples shows that the pipeline steel surface and the acidic medium are continuously interacting dynamically (Xu et al., 2023), with the 20 g/L inhibitor offering the best corrosion

mitigation. This indicates that formation shielding layer and higher concentrations of the leaf extract considerably enhance corrosion resistance.

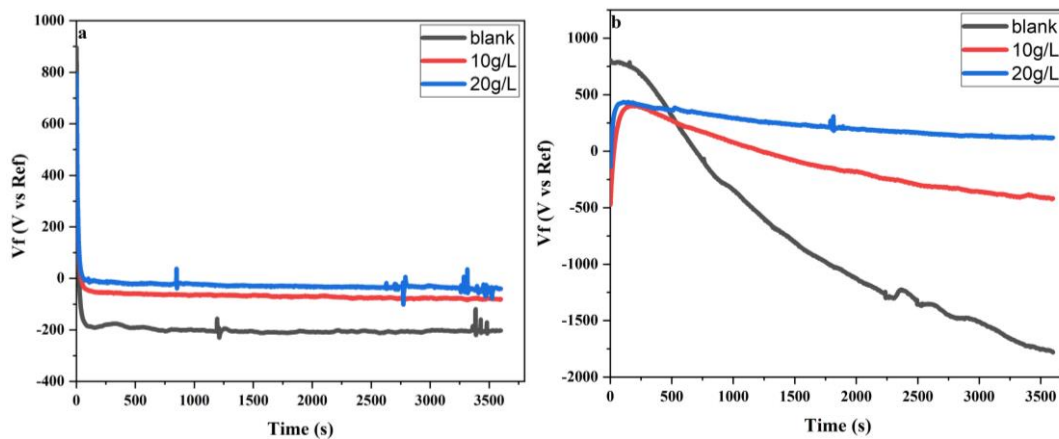


Figure 0.47: OCP of API 5L X42 pipeline steel in a) 3.5 % NaCl and b) 1 M H₂SO₄ in the absence (blank) and presence of varying concentrations of *Sclerocarya birrea* inhibitor.

4.4.1.3 Open circuit potential (OCP) studies of Aluminium (AA 1100) in 3.5 % NaCl and 1 M H₂SO₄ both in presence and absence of *Sclerocarya birrea* inhibitor.

The OCP results for the aluminium metal alloy immersed in the aggressive media of 3.5 % NaCl and 1 M H₂SO₄ both in the absence and presence of *Sclerocarya birrea* inhibitors are shown in Figure 4.48 a) and b). It is notable from the results in Figure 4.48 a that within the first 100 seconds, the potential for the blank sample rose sharply from -2000 mV to 12 mV, indicating a quick first response between the aluminium surface and the chloride ions. After that, there were variations, which included a peak at 1009 mV at 995 seconds, which was probably caused by surface passivation or a localized oxide layer breakdown. After that, the value settled close to equilibrium at -2 mV, which indicated instability in the surface shield. A more stable surface coating and lower corrosion activity were shown by the sample immersed in simulated sweater with 10 g/L of *S.birrea* inhibitor, which began at a milder potential of -493 mV, rose to 0 mV, and stabilized at 1 mV until 3600 s elapsed. The performance of the sample containing 20 g/L of the inhibitor was much better; it began at a potential of -1750 mV and increased gradually to 260 mV with very little fluctuation, indicating the creation of a robust barrier to protect the aluminium surface. It is evident that increased inhibitor concentration offered increased surface protection and overall metal stability (Kaya et al., 2023b).

Figure 4.48 b depicts observations for AA 1100 exposed to the 1 M H_2SO_4 in the absence and presence of *Sclerocarya birrea* inhibitor. In the absence of protective intervention, blank exposed sample showed a progressive decline in potential starting at 1000 mV and reaching equilibrium after 2500 seconds. The metal is actively dissolving in a harsh, acidic environment, as observed by this gradual fall. The sample containing 10 g/L of the inhibitor, on the other hand, began at a much lower potential (515 mV), dropping only slightly to 494 mV after 5 seconds. It then remained quite constant until 2000 seconds later, when it decreased slightly to 488 mV before reaching equilibrium. This indicates that by generating a layer of protection on the surface, the inhibitor reduced the corrosion rate. Even more noticeable surface protection was observed in the sample containing 20 g/L of inhibitor; it had an initial potential of 488 mV but dropped abruptly to -2 mV after 10 seconds and reached equilibrium until the end of the experiment. This abrupt decline, followed by stability, shows that a strong protective layer is quickly forming and significantly lowering corrosion. In both the corrosive media, *Sclerocarya birrea* proved to be much effective in 3.5 % NaCl even though notable protection was also observed in acidic medium at an inhibitor dosage of 20 g/L.

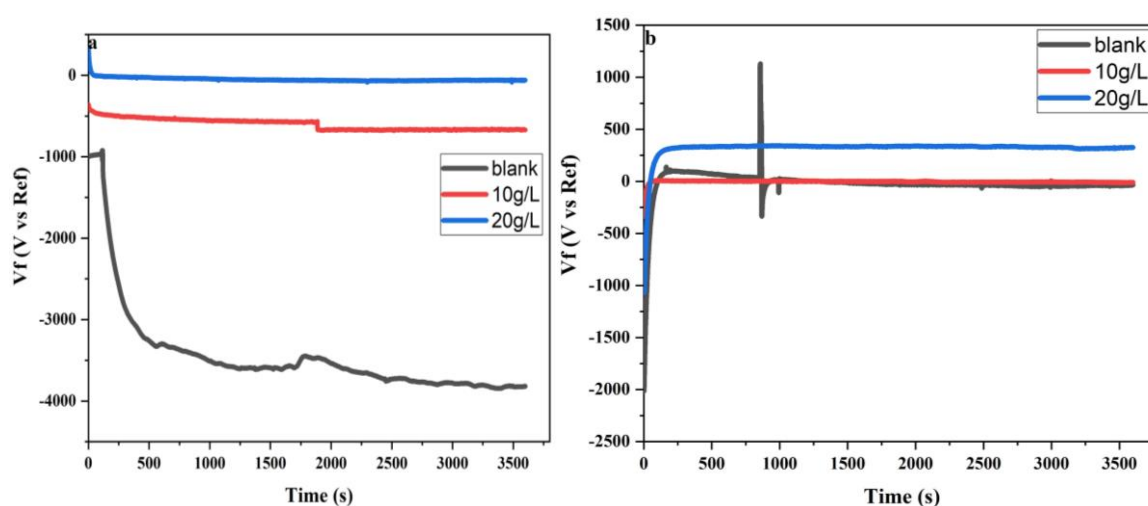


Figure 0.48: OCP of AA 1100 in a) 3.5 % NaCl and b) 1 M H_2SO_4 in the absence (blank) and presence of varying concentrations of *Sclerocarya birrea* inhibitor.

4.4.2 Potentiodynamic Polarization (PDP)

Potentiodynamic Polarization technique was carried out to elucidate the influence of *Sclerocarya birrea* ethanolic extract inhibitor on the kinetics of the anodic and cathodic reactions of mild steel, API 5L X42 pipeline steel and AA 1100 in both 3.5 % NaCl and 1 M H_2SO_4 aggressive environments. The polarization curves give some insights on the mechanism

of surface protection by the leaf extract. The calculated polarization kinetic parameters for all metals such as corrosion potential (E_{corr}), inhibition efficiency (I.E %), corrosion current (I_{corr}), and Tafel slope constants (β_a and β_c) are presented in Tables 4.18 – 4.20 and discussed below. Figures 4.49 – 4.51 show the polarisation curves for all three metals exposed to blank and *Sclerocarya birrea* inhibitor-containing solutions of 3.5 % NaCl and 1 M H_2SO_4 conditions.

4.4.2.1 Potentiodynamic polarization studies of Mild steel in 3.5 % NaCl and 1 M H_2SO_4 both in presence and absence of *Sclerocarya birrea* inhibitor.

Figure 4.49 a and b illustrate the changes in polarization curves following the addition of *Sclerocarya birrea* inhibitor to the corrosive media demonstrating the effect of the inhibitor on mild steel degradation. The corresponding electrochemical polarization parameters being Tafel slope constants (β_a and β_c), corrosion current (I_{corr}), inhibition efficiency (I.E %) and corrosion potential (E_{corr}) are displayed in Tables 4.18.

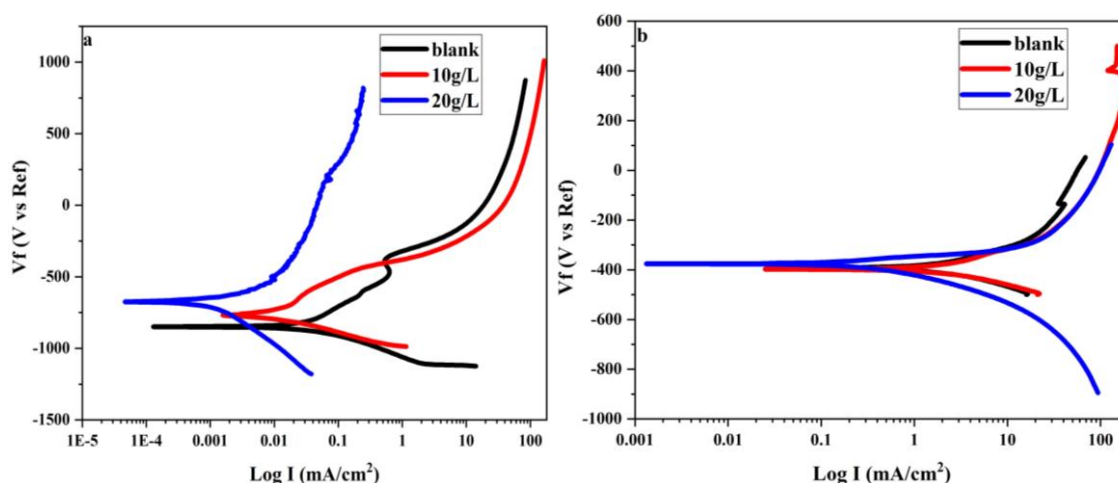


Figure 0.49: The Tafel plot for mild steel in a) 3.5 % NaCl and b) 1 M H_2SO_4 in the presence and absence of different concentrations of *Sclerocarya birrea* inhibitor.

Table 0.18: Potentiodynamic polarization parameters for corrosion of mild steel in 3.5 % NaCl and 1 M H_2SO_4 in the presence and absence of *Sclerocarya birrea* inhibitor

3.5 % NaCl

S.no	Conc (g/L)	- E_{corr} (mv/Ref)	I_{corr} ($\mu A/cm^2$)	β_a (mv/decade)	β_c (mv/decade)	I.E %	Surface coverage (θ)
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1.	Blank	833	844	597	26	-	-
	(0)						
2.	10.0	770	96.7	282	59	88.6	0.886
3.	20.0	670	18.3	198	348	97.8	0.978

1 M H₂SO₄

1.	Blank	393	3701	186	123	-	-
	(0)						
2.	10.0	398	1682	108	83	54.6	0.546
3.	20.0	371	1024	88	172	72.3	0.723

4.4.2.2 Potentiodynamic polarization studies of API X42 pipeline steel in 3.5 % NaCl and 1 M H₂SO₄ both in presence and absence of *Sclerocarya birrea* inhibitor.

The effects of the *Sclerocarya birrea* inhibitor on the degradation of mild steel are shown in Figure 4.50 a and b, which show the changes in polarisation curves when the inhibitor is added to 3.5 % NaCl and 1 M H₂SO₄ corrosive media. Tables 4.19 show the associated electrochemical polarisation characteristics, which are inhibition efficiency (I.E %), corrosion potential (E_{corr}), Tafel slope constants (ba and bc), and corrosion current (I_{corr}).

The findings shown in Table 4.18 show that the anodic and cathodic potentiodynamic polarisation constants, ba and bc, for both 3.5% NaCl and 1 M H₂SO₄ were considerably altered by the addition of *Sclerocarya birrea* inhibitor. Potentiodynamic polarization results depict that *Sclerocarya birrea* extract is an effective corrosion of mild steel in both acidic and seawater conditions. For samples exposed to 3.5 % NaCl, when the inhibitor concentration is raised from 0 to 20 g/L the corrosion potential (-E_{corr}) decreases from -833 mv at 0 g/L to -371 mv at 20 g/L shifting towards more noble potential which is indicative of reduction in metal degradation. A notable inhibitory effect is also observed in the corrosion current density (I_{corr}), which decreases significantly from 844 μA/cm² at 0 g/L to 18.7 μA/cm² at 20 g/L. The calculated inhibition efficiencies increase with concentration from 88.6 % at 10.0 g/L to a high of 97.8 % which is indicative of the inhibitor's efficacy in combating mild steel dissolution. Lastly the anodic Tafel slope (Ba) decreases as the inhibitor concentration is increased, indicating the inhibitor hinders anodic reactions whilst the cathodic Tafel slope (Bc) rises in proportion to each increase in inhibitor concentration which is a reflection that *Sclerocarya birrea* act as a mixed type of inhibitor. Due to the *Sclerocarya birrea*'s high rich profile of phytochemical

chemical compounds they tend to adsorb onto the steel surface, thereby obstructing active sites and hindering both cathodic and anodic reactions.

Mild steel samples immersed in 1 M H_2SO_4 in the absence and presence of *S. birrea* inhibitors, a close trend similar for specimens immersed in 3.5 % NaCl was observed. The corrosion potential (E_{corr}) shifted towards positive value with an increase in the inhibitor from -393 mV at 0 g/L to -371 mV, with corrosion current (I_{corr}) also decreasing with each rise in inhibitor concentration. Anodic metal dissolution diminishes with increasing extract concentration, as evidenced by the anodic Tafel slope (B_a), which gradually drops from 186 mV/decade at 0 g/L to 88 mV/decade at 20 g/L. This shows that the inhibitor effectively inhibits iron oxidation, probably by adsorbing organic molecules to the metal surface and blocking active anodic sites (Mechbal et al., 2021). The cathodic Tafel slope (B_c), which decreases from 123 mV/decade at 0 g/L to 83 mV/decade at 10 g/L, has a more complex behaviour. This suggests that the inhibitor is efficient at delaying the hydrogen evolution at moderate doses. However, at 20 g/L, the B_c rises to 172 mV/decade, which may indicate that the cathodic reaction mechanism has changed or that the inhibitor has saturated the steel surface, resulting in altered kinetics (Mechbal et al., 2021). These results implies that *Sclerocarya birrea* in 1M H_2SO_4 provides a mixed-mode inhibition influencing both the cathodic and anodic reactions. The inhibition efficiency also increases with an increase in inhibitor concentration with 54.6 % achieved at 10.0 g/L and 72.3 % achieved at inhibitor concentration of 20.0 g/L. Lower inhibition efficiencies were attained in acidic environment compared to seawater environments owing to aggressive nature of the acidic settings.

Sclerocarya birrea inhibitor performance in slowing API 5L X42 pipeline steel dissolution in acidic and seawater water conditions is demonstrated by the potentiodynamic polarization results displayed in Figure 4.50 a and b as well as Table 4.19. For simulated seawater environment (3.5 % NaCl), the inhibitor mainly impacts the cathodic process at lower concentrations but stabilizes at higher concentrations, as evidenced by the corrosion potential (E_{corr}), which varied from -410 mV at 0 g/L to -653 mV at 10 g/L and back to -381 mV at 20 g/L. The significant decrease in corrosion current density (I_{corr}) from 1490 $\mu\text{A}/\text{cm}^2$ at 0 g/L to 515 $\mu\text{A}/\text{cm}^2$ at 20 g/L indicates effectiveness of the *Sclerocarya birrea* inhibitor is reducing metal dissolution. This is also supported by the achieved inhibition efficiencies which increased with inhibitor dosage, with 59.2 % inhibition efficiency achieved at 10.0 g/L concentration and a high of 65.4 % attained at 20.0 g/L inhibitor concentration. When concentration of the inhibitor was raised, anodic Tafel slope (B_a) decreased from 579 mV/decade to 242 mV/decade, indicating restriction of pipeline substrate dissolution by the

inhibitor. A growing influence on the hydrogen evolution process was indicated by the increasing cathodic Tafel slope (B_c), which increases from 103 mV/decade to 171 mV/decade. This observation is probably due to inhibitor molecules adhering to the metal and lowering the number of active sites available for the corrosion process. The inconsistency of Tafel slopes with varying inhibitor concentrations indicates that the inhibitor's action results from meddling with the mechanisms underlying the corrosion processes at both the cathode and the anode (Jayanthi et al., 2012; Maheswari et al., 2015; Matheswaran & Ramasamy, 2010).

When compared to its performance in 3.5 % NaCl, *Sclerocarya birrea* inhibitor exhibits a moderate level of inhibitory efficacy in 1 M H_2SO_4 environment. A tendency towards increased anodic protection with increasing inhibitor concentration is indicated by the corrosion potential (E_{corr}), which shifts from -352 mV at 0 g/L to -160 mV at 20 g/L. However, the shift is not as strong as observed in simulated seawater environment. At 20 g/L inhibitor concentration, the corrosion current density (I_{corr}) dropped from 1886 $\mu A/cm^2$ to 902 $\mu A/cm^2$, indicating a maximum inhibition efficiency of 52.2% which was lower than the 65.4 % attained in 3.5 % NaCl. The anodic Tafel slope (B_a) increased from 123 mV/decade at 0 g/L to 244 mV/decade at 20 g/L, suggesting that the inhibitor, but not as effectively as in 3.5 % NaCl, slowed the anodic metal dissolution. In 3.5 % NaCl medium, the B_a consistently decreased with inhibitor concentration. Likewise, the cathodic Tafel slope (B_c) increased from 138 mV/decade at 0 g/L to 319 mV/decade at 20 g/L, indicating that the inhibitor had some effect on the cathodic reaction. However, this effect on the evolution of hydrogen in sulphuric acid is not as strong as it was in seawater environment, where it was more consistent. Generally, *Sclerocarya birrea* inhibitor has proved to be more effective in chloride rich environment compared to acidic medium as indicated by computed inhibition efficiencies. The decreased inhibitory efficacy in comparison to simulated sweater environment may be explained by the more intricate mechanisms of corrosion in sulphuric acid as well as its capacity to protonate or break down organic molecules (Alahiane et al., 2023).

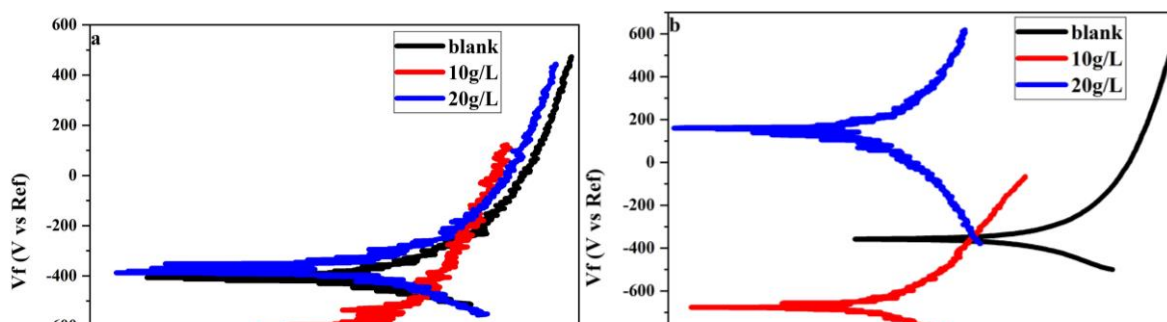


Figure 0.50: The Tafel plot for API 5L X42 pipeline steel in a) 3.5 % NaCl and b) 1 M H₂SO₄ in the presence and absence of different concentrations of *Sclerocarya birrea* inhibitor.

Table 0.19: Potentiodynamic polarization parameters for corrosion of API 5L X42 pipeline steel in 3.5 % NaCl and 1 M H₂SO₄ in the presence and absence of *Sclerocarya birrea* inhibitor.

3.5 % NaCl

S.no	Conc (g/L)	-Ecorr (mv/Ref)	Icorr (μ A/cm ²)	β_a (mv/decade)	β_c (mv/decade)	I.E %	Surface coverage (θ)
1.	Blank (0)	410	1490	579	103	-	-
2.	10.0	653	608	388	126	59.2	0.592
3.	20.0	381	515	242	171	65.4	0.654

1 M H₂SO₄

1.	Blank (0)	352	1886	123	138	-	-
2.	10.0	678	1275	279	346	32.4	0.324
3.	20.0	-160	902	244	319	52.2	0.522

4.4.2.3 Potentiodynamic polarization studies of Aluminium 1100 in 3.5 % NaCl and 1 M H₂SO₄ both in presence and absence of *Sclerocarya birrea* inhibitor.

Figure 4.51 shows the potentiodynamic polarisation results for aluminum specimens submerged in 3.5 % NaCl and 1 M H₂SO₄ media, both with and without a leaf inhibitor

safeguarding the metal against dissolution. The anodic Tafel slope (B_a), cathodic Tafel slope (B_c), corrosion potential (E_{corr}), corrosion current density (I_{corr}), and inhibition efficiency at different inhibitor concentrations (0, 10, and 20 g/L) were computed and tabulated in Table 4.20.

The potentiodynamic polarization corrosion inhibition results for aluminum 1100 specimens with *Sclerocarya birrea* inhibitor in 3.5 % NaCl and 1 M H_2SO_4 show distinctive behaviors, which are indicative of the different types of corrosive environments the samples are exposed to. The results are depicted in Figure 4.51 and Table 4.20. The corrosion potential (E_{corr}) in 3.5 % NaCl shifts more noticeably with increasing inhibitor concentration, going from -728 mV at 0 g/L to -334 mV at 20 g/L, suggesting strong anodic protection. An impressive 87.3 % inhibition efficiency is obtained by a sharp decrease in the corrosion current density (I_{corr}), which goes from 1573 $\mu\text{A}/\text{cm}^2$ at 0 g/L to 200 $\mu\text{A}/\text{cm}^2$ at 20 g/L. Whereas the cathodic Tafel slope (B_c) first rises but then sharply decreases at higher concentrations, suggesting improved inhibition of the cathodic hydrogen evolution process. The anodic Tafel slope (B_a) steadily decreases with increasing extract concentration, indicating effective control over the anodic dissolution process (Fouda et al., 2021).

A slightly different pattern of results is observed by the *Sclerocarya birrea* inhibitor in 1 M H_2SO_4 . At lower concentrations, the change in E_{corr} is less significant than that in 3.5 % NaCl, even though it still goes towards more noble values. In contrast to results observed in simulated seawater conditions, samples in 1 M H_2SO_4 exhibits a more marked decrease in corrosion current density, going from 3607 $\mu\text{A}/\text{cm}^2$ at 0 g/L to 313 $\mu\text{A}/\text{cm}^2$ at 20 g/L of inhibitor concentration. This results in a greater inhibition efficiency of 91.3 % at 20 g/L which is more than 87.9% achieved at the same concentration in 3.5 % NaCl. A more complex behaviour in acidic medium is shown by the anodic Tafel slope (B_a), which dips sharply at inhibitor concentration of 10 g/L but rises at 20 g/L, possibly due to modifications in the inhibitor's surface contact. In this harsh environment, it appears that the extract mostly affects the hydrogen evolution process because the cathodic Tafel slope (B_c) rises gradually. Similarly to mild steel and API 5L X42 pipeline, *Sclerocarya birrea* inhibitor exhibit mixed-type inhibition mechanism for aluminum (AA1100) in both corrosive media. In conclusion, while the inhibitor in 1 M H_2SO_4 medium is less effective at lower concentrations but offers superior overall protection at higher concentrations, the inhibitor in 3.5 % NaCl environment exhibits smoother and more consistent inhibition of both anodic and cathodic processes.

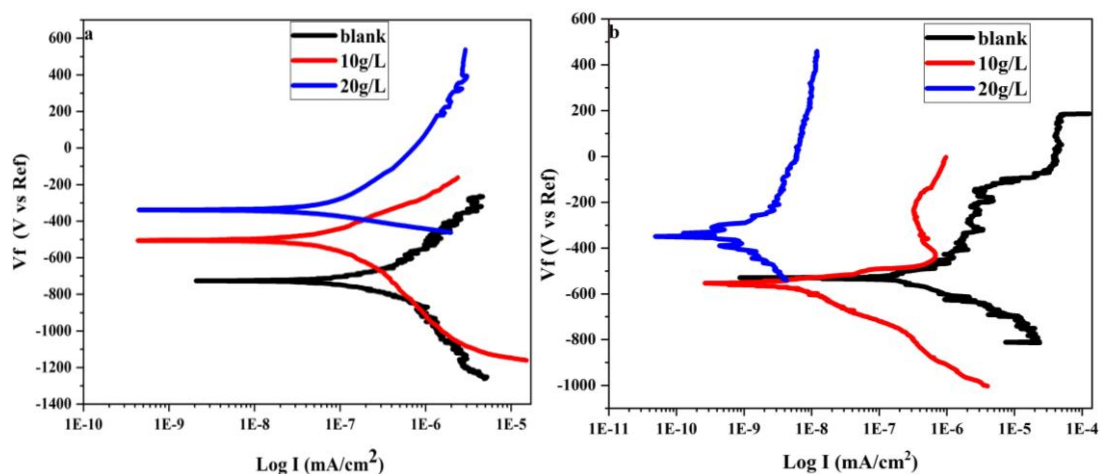


Figure 0.51: The Tafel plot for AA 1100 in a) 3.5 % NaCl and b) 1 M H₂SO₄ in the presence and absence of different concentrations of *Sclerocarya birrea* inhibitor.

Table 0.20: Potentiodynamic polarization parameters for corrosion of Aluminum (AA1100) in 3.5 % NaCl and 1 M H₂SO₄ in the presence and absence of *Sclerocarya birrea* inhibitor.

3.5 % NaCl

S.no	Conc (g/L)	-Ecorr (mv/Ref)	Icorr (μ A/cm ²)	β_a (mv/decade)	β_c (mv/decade)	I.E %	Surface coverage (θ)
1.	Blank (0)	728	1573	227	210	-	-
2.	10.0	506	496	193	221	68.5	0.685
3.	20.0	334	200	139	68	87.3	0.873

1 M H₂SO₄

1.	Blank (0)	525	3607	186	107	-	-
2.	10.0	555	2239	42	202	37.9	0.379
3.	20.0	356	313	634	303	91.3	0.913

4.4.3 Electrochemical Impedance Spectroscopy (EIS)

To determine fundamental mechanisms of *Sclerocarya birrea* inhibitor's corrosion inhibition and related metal dissociation kinetics, electrochemical impedance spectroscopy was used on all three metals (API 5L X42 pipeline steel, mild steel, and AA1100) exposed to environments containing 3.5 % NaCl and 1 M H₂SO₄. The resulting Nyquist and Bode plots together with all calculated values are displayed in Figures 4.52 to 4.57 as well as in Table 4.21 to 4.26. Figure 4.58 depicts the analogous electrical circuit used for modelling and fitting the charge transfer and metal/solution interfaces for all inhibited and uninhibited metal substrates.

4.4.3.1 Electrochemical impedance spectroscopy studies of Mild steel in 3.5 % NaCl and 1 M H₂SO₄ both in presence and absence of Sclerocarya birrea inhibitor.

The impedance spectrum for mild steel corrosion in 3.5 % NaCl and 1 M H₂SO₄ is displayed in Figure 4.52 a and b . Table 4.21 shows the charge transfer resistance (R_{ct}) and double layer capacitance (C_{d1}) impedance kinetics parameters that were computed after fitting with the equivalent circuit model displayed in Figure 4.58. For both corrosive conditions, mild steel exhibits depressed incomplete charge transfer semicircles, implying that charge transfer and/or the development of a protective film on the metallic surface are responsible for the mild steel inhibition process in acidic and simulated seawater settings.

The Nyquist plot for mild steel in both acidic and simulated seawater environments as displayed in Figure 4.53 depicts an inductive loop in the lower frequency zone and a dejected capacitive sphere in the higher frequency region instead of producing a flawless semicircle. The distortion from ideal semicircle is due to the surface inhomogeneity of structural or interfacial origin and mass transport resistance (Brugge et al., 2020). The charge-transfer resistance (R_{ct}) respite time invariable with double-layer capacitance (C_{dl}) at the electrode/solution interface is typically attributed to the increased frequency capacitive sphere (Marti & Huskens, 2022). From the attained results the diameter of the capacitive loop increases with each increase in the inhibitor concentration. The observed charge transfer capacitance (C_{d1}) values from table 4.21 decrease with each increase in inhibitor concentration for both samples exposed to 3.5 % NaCl and 1 M H₂SO₄ . The continuous decrease in the C_{d1} values is attributable to the constant decrease of local dielectric constant and/or the electric double layer becoming thicker (Al-Amiery et al., 2016; Ansari et al., 2013). The decrease in C_{d1} values symbolizes the reduction of active metal surface area due to the adsorption of *Sclerocarya birrea* inhibitor which actively blocked the active sites (Vranda Shenoy et al., 2021). The R_{ct} values increase with increase in inhibitor dosage for all aggressive media.

Observed higher (R_{ct}) values indicate greater coating system integrity and, hence, slower corrosion response development beneath the inhibitor adsorption layer (Al-Amiery et al., 2016). The computed inhibition efficiencies (I.E %) are consistent with results obtained from weight loss and potentiodynamic polarization with high efficiencies achieved at high inhibitor concentrations.

The bode plots in Figure 4.53 a and b depict high impedance at low frequencies which is indicative that mild steel is highly protected at high inhibitor concentrations of *S.birrea*. Higher phase angle values are attained with each increase in inhibitor concentration for both all the corrosive media. This observation is a resultant of a more capacitive behavior which could be due to increased charge transfer resistance that forces more current through the capacitor (A. Singh & Quraishi, 2015). The increase in phase angle with increase in inhibitor concentration promotes more capacitive electrochemical behaviour which enhances rapid adsorption of inhibitor molecules on the metal surface leading to improved overall metal protection.

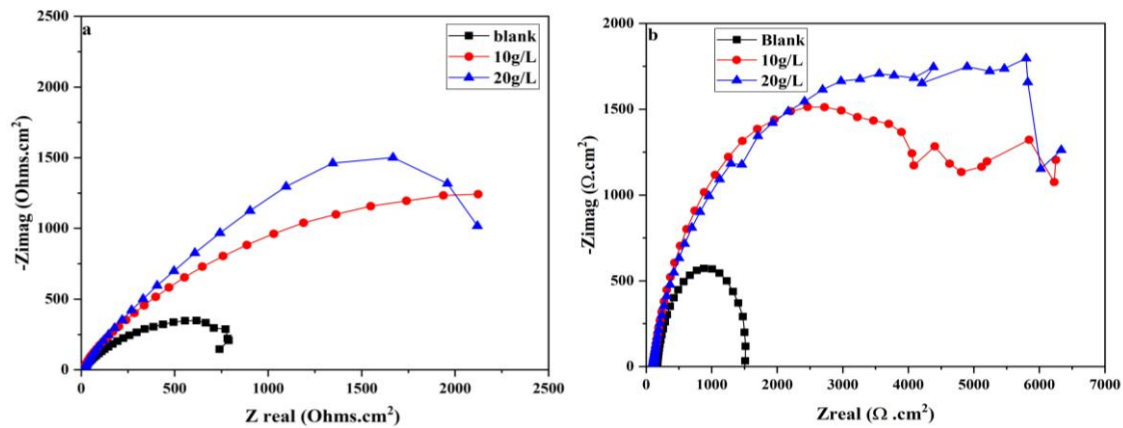


Figure 0.52: The Nyquist plot for mild steel in a) 3.5 % NaCl and b) 1 M H_2SO_4 corrosive solutions in the presence and absence of varying concentrations of *Sclerocarya birrea* inhibitor.

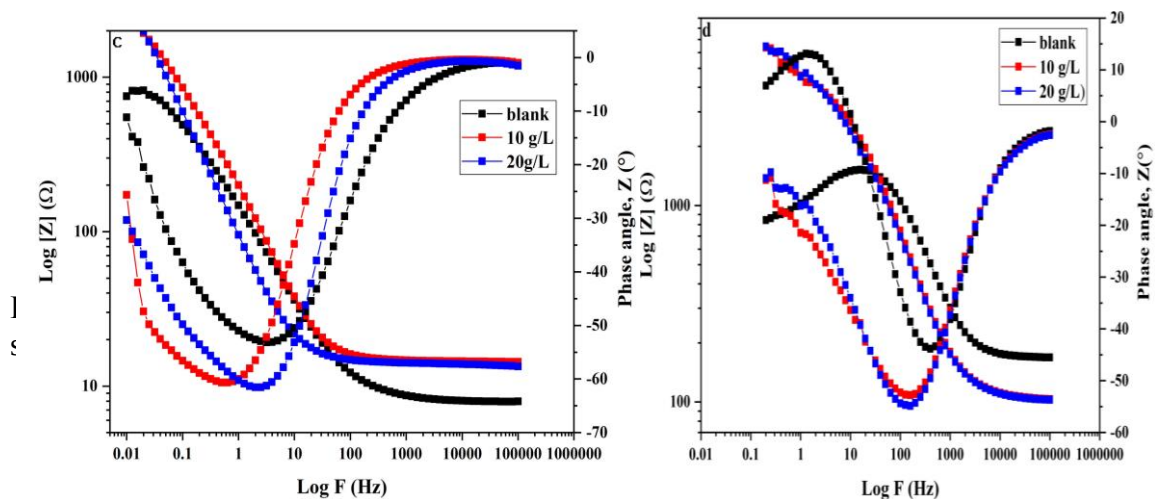


Table 0.21: EIS corrosion parameters for *Sclerocarya birrea* inhibited and uninhibited mild steel specimens immersed in both 3.5 % NaCl and 1 M H₂SO₄ corrosive environments.

Media	Concentration (g/L)	Rct (Ω cm ²)	Cd1 (nF/cm- ²)	fmax (Hz)	I.E (%)
3.5 % NaCl	Blank (0.0)	755	2.00	89450	-
	10.0	2131	1.00	65387	64.57
	20.0	2167	0.98	58129	65.16
1 M H ₂ SO ₄	Blank (0.0)	1489	0.99	77273	-
	10.0	6211	0.61	41921	76.03
	20.0	6359	0.59	41081	76.58

4.4.3.2 Electrochemical impedance spectroscopy studies of API 5L X42 Pipeline steel in 3.5 % NaCl and 1 M H₂SO₄ both in presence and absence of *Sclerocarya birrea* inhibitor.

The electrochemical impedance spectroscopy results for API 5L X42 Pipeline steel immersed in both 1 M H₂SO₄ and 3.5 % NaCl in the presence and absence of the inhibitor are presented in the form of Nyquist and bode plots in Figure 4.54 to 4.55. Corrosion alternating current (AC) impedance parameters are in Table 4.22.

A comparable depressed incomplete semicircle that was observed in mild steel is produced by the observed Nyquist plot results for pipeline steel in both corrosive media, and it grows as the inhibitor's concentration rises. Generally, corrosion is under charge transfer control with some surface inhomogeneity when the Nyquist plot displays a depressed, incomplete semicircle (Jawad et al., 2019). Several factors that affect the impedance response, such as surface roughness, flaws, or non-uniform inhibitor adsorption, might cause this inhomogeneity (Al-Amiery et al., 2016). The partial semicircle in the observed data suggests that the impedance response is not entirely dominated by the charge transfer mechanism, which is probably related to corrosion reactions at the metal-electrolyte interface within the frequency range that was measured. This could also point to the involvement of intricate interfacial phenomena or diffusion-controlled mechanisms (Prangnell, 2000). The capacitance (Cd1) values in both the aggressive solutions decrease with each increase in the *Sclerocarya birrea* inhibitor which confirmed the adsorption of the inhibiting molecules on the metal surface. Adsorbed inhibitor molecules on the metal's surface impedes the charge transfer by increasing the protected surface area. This behaviour suggests that by increasing the charge transfer distance, which is

demonstrated by a decreased capacitance, the inhibitor molecules are changing the electrochemical interface in addition to blocking active sites.

In simulated seawater environment the C_{dl} value for blank exposed sample was $1.00 \times 10^{-9} \text{ F / cm}^2$ which dropped to a low of $0.83 \times 10^{-9} \text{ F / cm}^2$ at the highest inhibitor concentration of 20.0 g/L. Similarly for samples exposed to acidic medium in blank solution had a high C_{dl} value of $4.00 \times 10^{-9} \text{ F / cm}^2$ which dropped to $0.96 \times 10^{-9} \text{ F / cm}^2$ at 20.0 g/L inhibitor concentration. Inhibition efficiencies also increased with each increase in inhibitor concentration as expected, with high efficacy achieved at 20.0 g/L in both media. The charge transfer resistance (R_{ct}) increased with increase in inhibitor concentration. An increase in the R_{ct} value as inhibitor concentration rises indicates that the inhibitor is successfully adhering to the steel surface and creating a barrier that slows down electrochemical reactions. This barrier hinders the corrosion process by keeping hostile ions such as chloride ions in a saline environment from getting to the steel surface (Román et al., 2014).

The Bode plot for pipeline steel in both the corrosive solutions in the presence and absence of the inhibitor produce a similar fit which is predominated by odd values in Bode (Phase angle vs Log Frequency) graphs. These fluctuations may be attributed to presence of localized corrosion sites, non-uniform adsorption of inhibitor molecules at the metal-solution interface and impedance drift due to surface inhomogeneity (Vračar & Dražić, 2002). Generally, the bode plot results depict high impedance values attained at lower frequencies and high phase angle shifts attained at high inhibition frequencies affirm the metal's protection.

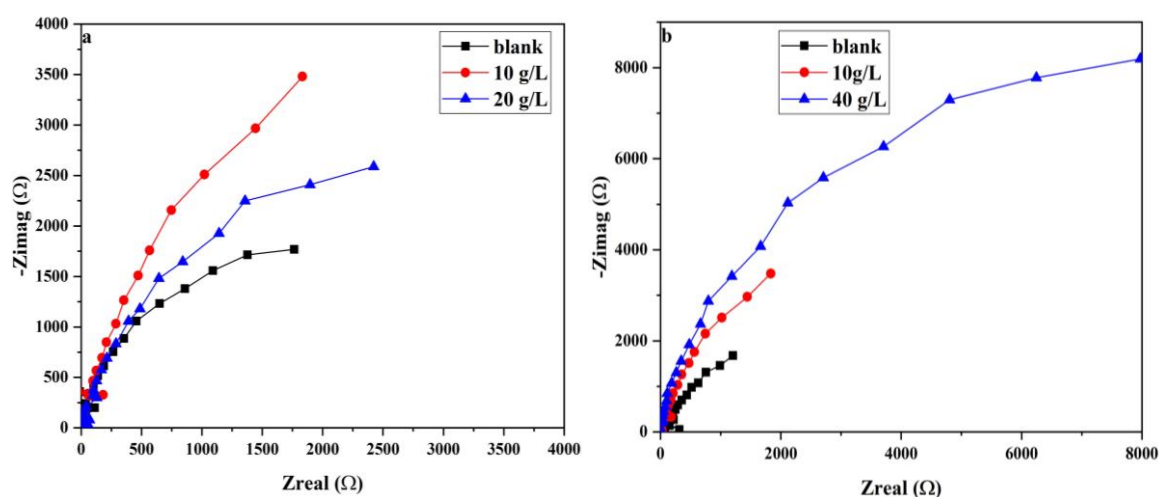


Figure 0.54: The Nyquist plot for API 5L X42 pipeline steel in a) 3.5 % NaCl and b) 1 M H₂SO₄ corrosive solutions in the presence and absence of varying concentrations of *Sclerocarya birrea* inhibitor.

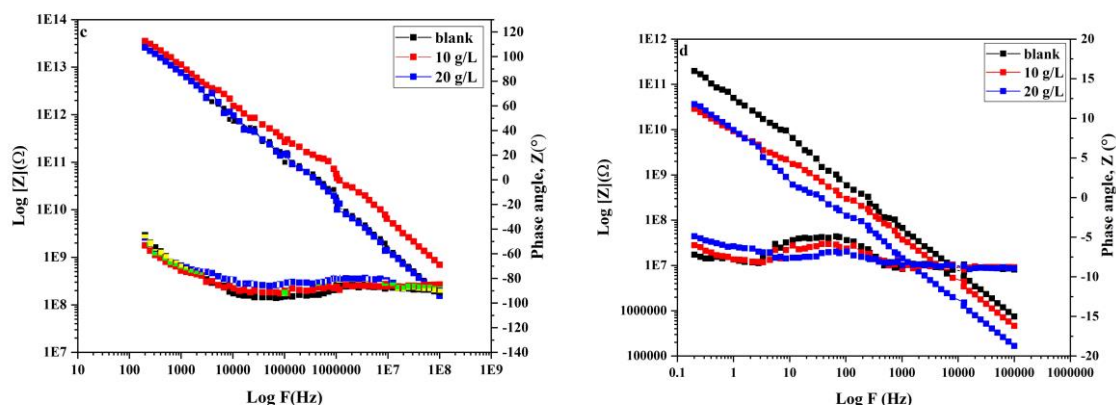


Figure 0.55: The Bode plot for API 5L X42 pipeline steel in c) 3.5 % NaCl and d) 1 M H₂SO₄ corrosive solutions in the presence and absence of varying concentrations of *Sclerocarya birrea* inhibitor.

Table 0.22: EIS corrosion parameters for API 5L X42 pipeline steel immersed in both 3.5 % NaCl and 1 M H₂SO₄ in the presence and absence of different concentrations of *Sclerocarya birrea* inhibitor.

Media	Concentration (g/L)	Rct (Ω cm ²)	Cd1 (nF/cm ⁻²)	fmax (Hz)	I.E (%)
3.5 % NaCl	Blank (0.0)	1370	1.00	63574	-
	10.0	1838	0.95	58214	25.46
	20.0	2458	0.83	77945	44.26
1 M H ₂ SO ₄	Blank (0.0)	1203	4.00	32145	-
	10.0	1884	2.98	27412	36.15
	20.0	7981	0.96	20677	84.93

4.4.3.3 Electrochemical impedance spectroscopy studies of Aluminium (AA 1100) in 3.5 % NaCl and 1 M H₂SO₄ both in presence and absence of *Sclerocarya birrea* inhibitor.

The Nyquist and bode plots for (AA1100) immersed in 3.5 % NaCl and 1 M H₂SO₄ in the presence and absence of varying concentrations of the inhibitor are shown in Figures 4.56 to 4.57. The subsequent AC impedance data is displayed in Table 4.23.

Like the mild steel and API 5L X42 pipeline, the trend of results observed for AA 1100 is the same for both the corrosive environment. The Nyquist plot (Figure 4.56) is characterized by depressed incomplete semicircles with its diameters increasing with increase in the inhibitor concentration. An increase in the capacitive loop's diameter, which signifies the ongoing development of a passive film containing *S. birrea* extract on the sample surface, is a characteristic of the inhibitory effect of *Sclerocarya birrea*. The capacitive and inductive loops in the Nyquist plots indicate the establishment of a metal inhibitor complex at the interface between the metal and the solution (Kissi et al., 2006). The thick coating of adsorbed inhibitor molecules minimized corrosion of the Aluminium metal alloy by reducing the area of contact between the electrolyte and substrate. Charge transfer resistance (R_{ct}) values in samples exposed to a 3.5 % NaCl environment rose from 1269 Ω in blank solution to 1669 Ω at an inhibitor concentration of 20.0 g/L, while samples submerged in 1 M H_2SO_4 in blank solution showed a R_{ct} value of 1077 Ω , which rose to 1505 Ω at a 20.0 inhibitor concentration. Increased resistance and inhibitor molecule adsorption on the Aluminium surface are responsible for the rise in R_{ct} values as the inhibitor concentration is raised, indicating that charge transfer mechanism governs much of the corrosion response (Abdel Hameed et al., 2022).

For both corrosive solutions, the CdI values dropped as the inhibitor concentration was raised, confirming water molecules substitution by the inhibitory molecules, hence lowering the degree of metal dissolution (Luo et al., 2021; Shahini et al., 2021). The effectiveness of the inhibition is closely correlated with the inhibitor dosage applied, increasing as the inhibitor's concentration is increased.

The bode plots of aluminium showed some inconsistencies just like for the API 5L X42 pipeline steel in both the aggressive media. The bode plot shows a rise in the absolute impedance value $[Z]$ at low frequencies following initial *Sclerocarya birrea* inhibitor treatment of aluminium coupons. This outcome demonstrates how the adsorption of *S. birrea* on the aluminium surface results in increased metal protection as the inhibitor's concentration rises (Xhanari & Finšgar, 2019). A less stable barrier of protection at higher frequencies is indicated by the continuous, non-consistent, noticeable phase angle shift at advanced frequencies shown by the Log F vs. Phase angle plot (Figure 4.57).

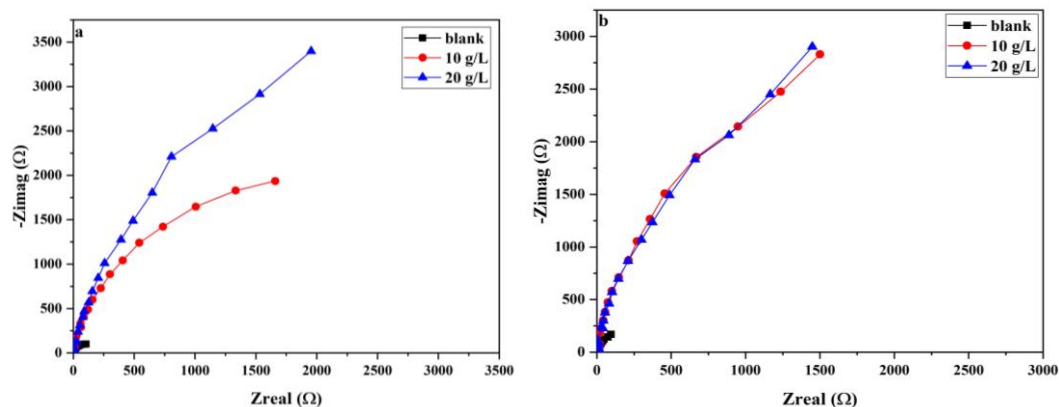


Figure 0.56: The Nyquist plot for Aluminium (AA 1100) in a) 3.5 % NaCl and b) 1 M H₂SO₄ corrosive solutions in the presence and absence of varying concentrations of *Sclerocarya birrea* inhibitor.

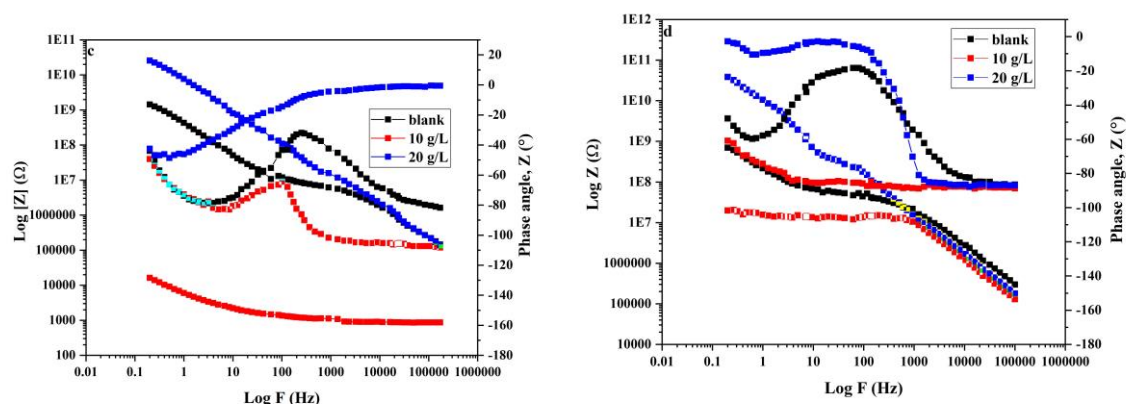


Figure 0.57: The Bode plot for Aluminium (AA 1100) in c) 3.5 % NaCl and d) 1 M H₂SO₄ corrosive solutions in the presence and absence of varying concentrations of *Sclerocarya birrea* inhibitor.

Table 0.23: EIS corrosion parameters for AA 1100 immersed in both 3.5 % NaCl and 1 M H₂SO₄ in the presence and absence of different concentrations of *Sclerocarya birrea* inhibitor.

Media	Concentration (g/L)	R _{ct} (Ω cm ²)	Cd1 (nF/cm ⁻²)	f _{max} (Hz)	I.E (%)
3.5 % NaCl	Blank (0.0)	1269	2.00	45874	-
	10.0	1669	0.99	48712	23.97
	20.0	1996	0.89	88784	36.42

1 M H ₂ SO ₄	Blank (0.0)	1077	3.00	39466	-
	10.0	1474	2.00	43569	26.93
	20.0	1505	1.00	95207	28.43

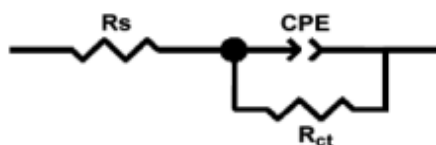
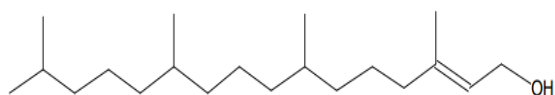


Figure 0.58: Equivalent electrical circuit employed for modelling the interfaces of mild steel, API 5L X42 pipeline steel, and AA1100 in 3.5 % NaCl and 1 M H₂SO₄ solutions, both with and without the *Sclerocarya birrea* inhibitor.

4.5 Quantum Chemical Calculations – Density Functional Theory and Monte Carlo Simulations

Quantum chemical computations were conducted to elucidate and validate the experimental results as well as to gain additional understanding of the donor–acceptor interactions between the mild steel, API 5L X42 pipeline steel and aluminium (AA 1100) surfaces and the investigated *Sclerocarya birrea* extract derivatives in both acidic and simulated seawater environments. The 3,7,11, 15 Tetramethyl-2-hexadecen-1-ol (T1), ethanol,2-(octadecyloxy) (T2), hexadecanoic acid, ethyl ester (T3), octadecanoid acid, ethyl ester (T4), and octadecanoid acid (T5) organic derivatives of *Sclerocarya birrea* leaf ethanolic extract were utilized in the investigation. These derivatives are displayed in Figure 4.59 as derived from the GC-MS analysis. To verify the experimental findings, quantum chemical calculations were utilized to examine the corrosion inhibition efficiency of the five compounds (T1, T2, T3, T4, and T5), and Monte Carlo simulations were applied to evaluate their adsorption behaviour on Fe(1100 and Al(111) surfaces.



a) 3,7,11,15-Tetramethyl-2-hexadecen-1-ol (T1)

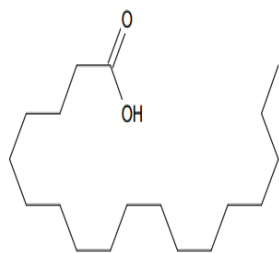


b) Ethanol, 2-(octadecyloxy) (T2)



c) Hexadecanoic acid, ethyl ester (T3)

d) octadecanoic acid, ethyl ester (T4)



e) Octadecanoic acid (T5)

Figure 0.59 (a – e): Chemical structures of the four derivatives of *Sclerocarya birrea* ethanolic leaf extract.

4.5.1 Density Functional Computations for *Sclerocarya birrea* derivatives on mild steel and API 5L X42 pipeline steel.

To obtain substantial information regarding the reactivity of the derivatives of *Sclerocarya birrea*, local descriptors of the reactivity were identified in aqueous phase and presented in Table 4.24. The descriptors evaluated were the density distributions of the electrostatic potential maps (ESP), lowest unoccupied molecular orbital (LUMO), and highest occupied molecular orbital (HOMO). The distribution of the reactive portions of the inhibitors under study, which represent the most interaction sites, is depicted by the electrostatic potential maps (ESP) in Table 4.24 (Alahiane et al., 2020). To be more specific, the inhibitor compound's HOMO density distributions in Table 4.24 reveal which locations are most likely to give electrons to an electron-deficient structure (Roque et al., 2008) in which for this project it will be Fe and Al surfaces that need to be safeguarded against degradation. Additionally, the LUMOs distribution in the same figure indicates which areas of a potential reactive material have the most capacity to take electrons from a donor electron (Cruz et al., 2005). The more strongly an organic derivative is bound to the metal, the larger the electron donor, which is indicated by a larger E_{HOMO} or a smaller E_{LUMO} (Hadisaputra et al., 2020b). Quantum chemical parameters of *Sclerocarya birrea* derivatives such as E_{HOMO} , E_{LUMO} , Gap energy ΔE , ionization potential (I), electron affinity (A), electronegativity (χ), hardness (η) and number of electron transfers (ΔN), dipole moment (μ) were calculated based on DFT and ab initio methods then presented in Table 4.25.

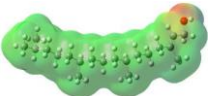
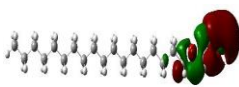
The density distributions in frontier molecular orbitals as displayed in Table 4.24 for all derivatives exhibit disparity in the HOMO and LUMO distributions. It is apparent from these

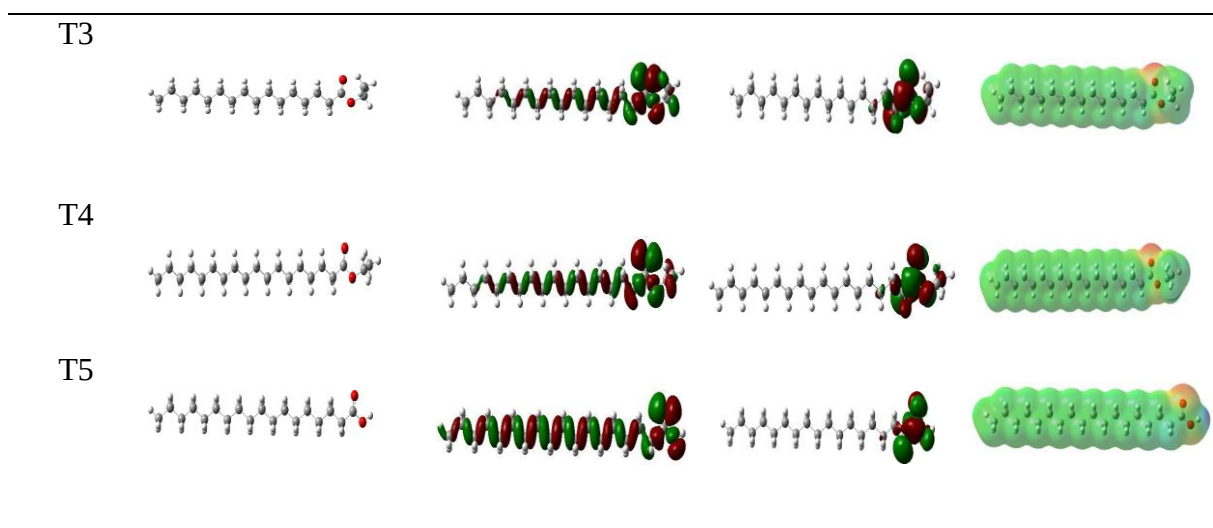
results that *Sclerocarya birrea* derivatives interact with the metallic surface through active sites they possess (Oukhrib et al., 2021). Although these five derivatives were present in multiple locations, it is also clear from the HOMO and LUMO that they were localized preferentially inside the structure around the hydroxyl (OH) atoms to a comparable extent also around the oxygen (O) atoms. The observation suggests that the constituents of the *Sclerocarya birrea* derivative structure that contain hydroxyl and oxygen atoms, such as (O, O-H, C=O, and C–O), are probably the regions where these molecule’s reactions with the Fe (110) surface occur.

The inhibition efficiency of the inhibitors as derived from E_{HOMO} values were displayed in table 4.25. The table indicates prominently that the inhibition efficiency for mild steel and X42 pipeline steel is correlated with the highest EHOMO value by T1>T2>T4>T5.

The nucleophilic and electrophilic active spots in the derivatives are shown on the ESP maps in Table 4.24; the negative region is indicated by red, and the positive region is depicted by green and blue (Oukhrib et al., 2021). As illustrated in Table 4.24, every red to yellow zone was dispersed among negatively charged groups including heteroatoms, including O atoms, as well as couple of carbon atoms on their side or rings of O and N heterocyclic atoms (Qiang et al., 2016). The reactive sites of inhibitors are represented by the ESP maps as displayed in Table 4.24; for *Sclerocarya birrea* derivatives, the primary adsorption sites are hydroxyl (OH) and oxygen atoms. Thus, it is plausible to assume that the *S.birrea* inhibitors have many adsorption sites that are primarily differentiated from one another by the OH, C-H, and O atoms.

Table 0.24: Visualization of the 2D structure, HOMO, LUMO, and ESP orbitals of T1, T2, T3, T4 and T5.

Inhibitor	Optimized molecular structures	HOMO	LUMO	ESP
T1				
T2				



Key

- | | |
|----|--|
| T1 | : 3,7,11,15-Tetramethyl-2-hexadecen-1-ol |
| T2 | : Ethanol,2-(octadecyloxy) |
| T3 | : Hexadecanoic acid, ethyl ester |
| T4 | : Octadecanoid acid, ethyl ester |
| T5 | : Octadecanoid acid |

The inhibition efficiency for mild steel and API X42 pipeline steel clearly correlates with the highest E_{HOMO} value in the order; $T1 > T2 > T4 > T5$, as shown in table 4.25. It is evident from the data that T1 is higher than T2, T3, T4 and T5 with its E_{HOMO} of -6.0333 eV. According to the E_{HOMO} comparison, T1 is expected to contribute the most to corrosion inhibition efficiency. E_{HOMO} is directly related to the ionization potential value (Sastri & Perumareddi, 1997). When evaluating a compound's reactivity, especially its capacity to take electrons, its E_{LUMO} (Energy of the Lowest Unoccupied Molecular Orbital) values are crucial. Since inhibitors frequently work by absorbing electrons from the metal surface to create a durable protective layer, lower E_{LUMO} values signify better electron-accepting ability, which is significant in corrosion inhibition investigations. From Table 4.25, T5 inhibitor has shown to be the greatest electron acceptor among all the derivatives of *Sclerocarya birrea* explored for this study.

The least amount of energy needed for electrons to be released and get attached to the metal surface to shield them from corrosive substances is known as the ionization potential value (Harsimran et al., 2021). Thus, a low value of the ionization potential can boost the effectiveness of inhibition (Sastri & Perumareddi, 1997). The ionization potential value at T1 (6.0333 eV) is lower than the values at T2 (6.7114 eV), T3 (7.2214 eV), T4 (7.2216 eV) and T5 (7.3509), as shown in Table 4.25. This ionization potential value suggests that T2 exerts a more inhibitory effect than the other derivatives. Electronegativity (χ) is the greatest influence in chemical reactivity theory. To balance

the chemical potential, electrons will move from lower electronegativity values (organic inhibitors) to higher electronegativity values (Au) when they contact with Fe metal (Mollaamin, 2023; Sastri & Perumareddi, 1997). T5 ($\chi = 3.5420$ eV) has the highest electronegativity of all the derivatives, suggesting a strong propensity to attract electrons that may improve physisorption. The somewhat lower but equivalent electronegativities of T3 ($\chi = 3.4138$ eV) and T4 ($\chi = 3.4118$ eV) indicate similar inhibition efficiencies dominated by electron-accepting interactions. Stronger electron-donating tendencies are highlighted by the noticeably lower electronegativities of T1 ($\chi = 2.6308$ eV) and T2 ($\chi = 2.459$ eV), which may favor chemisorption mechanisms. Based on electron reception mechanisms, the T1 inhibitor produced the highest inhibition efficacy followed by T2.

Table 0.25: Quantum chemical parameters of T1, T2, T3, T4 and T5 with B3LYP/6-311(d).

Parameter	Inhibitor				
	T1	T2	T3	T4	T5
E_{HOMO} (eV)	-6.0333	-6.7114	-7.2241	-7.2216	-7.3509
E_{LUMO} (eV)	0.7717	1.7921	0.3965	0.3981	0.2669
ΔE_{gap} (eV)	-6.8050	-8.5036	-7.6206	-7.6197	-7.6178
I (eV)	6.0333	6.7114	7.2241	7.2216	7.3509
A (eV)	-0.7717	-1.7921	-0.3965	-0.3981	-0.2669
μ (Debye)	1.7345	0.5015	1.4571	1.4536	1.4844
χ (eV)	2.6308	2.4596	3.4138	3.4118	3.5420
η (eV)	3.4025	4.2518	3.8103	3.8099	3.8089
σ (eV ⁻¹)	0.2939	0.2352	0.2624	0.2625	0.2625

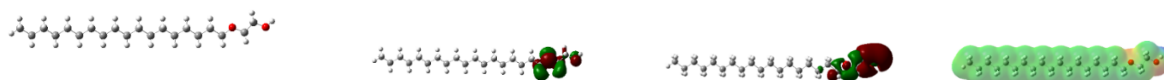
4.5.2 Density Functional Computations for *Sclerocarya birrea* derivatives on Aluminium (AA 1100).

Table 4.26 depicts the electron distribution in T1, T2, T3, and T4 molecular orbitals. There is a discernible variation in the electron distribution of the five compounds, with T1 having a more substantial electron distribution. T5 results for aluminium continuously detached from the studio software and the results could be presented. This outcome strengthens the expected E_{HOMO} -related sequence, which enhances performance of the inhibitor.

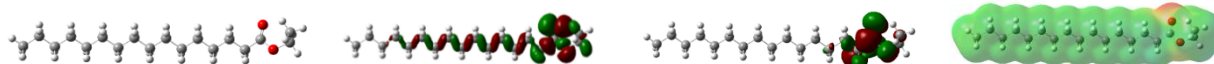
Table 0.26: Visualization of the 2D structure, HOMO, LUMO, and ESP orbitals of T1, T2, T3, and T4.

Inhibitor	Optimized molecular structure	HOMO	LUMO	ESP
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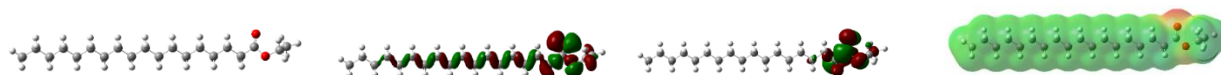
T1



T2



T3



T4

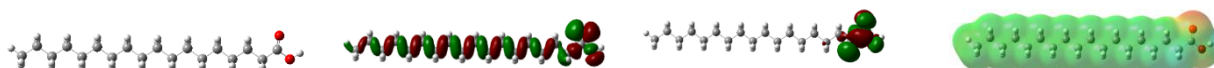


Table 0.27: Quantum chemical parameters of T1, T2, T3, and T4 with B3LYP/6-311(d).

Parameter	Inhibitor			
	T1	T2	T3	T4
E_{HOMO} (eV)	-6.7114	-7.2241	-7.2216	-7.3509
E_{LUMO} (eV)	1.7921	0.3965	0.3981	0.2669
ΔE_{gab} (eV)	-8.5036	-7.6205	-7.6197	-7.6178
I (eV)	6.7114	7.2241	7.2216	7.3509
A (eV)	-1.7921	-0.3965	-0.3981	-0.2669
μ (Debye)	0.5015	1.4571	1.4536	1.4844
χ (eV)	2.4596	3.4138	3.4117	3.5419

η (eV)	4.2518	3.8103	3.8099	3.8089
σ (eV ⁻¹)	0.2352	0.2624	0.2625	0.2625

The tendency of molecules to transfer electrons to metals is known as E_{HOMO} . The likelihood that the molecule will transfer electrons to the acceptor molecule is indicated by a high E_{HOMO} value (Islam & Chandra Ghosh, 2011). Consequently, the organic inhibitor molecule's adherence to the metal surface increases with the E_{HOMO} value. Thus, the E_{HOMO} value can be used to anticipate which organic inhibitors will have the highest corrosion inhibition effectiveness values. Table 4.27 demonstrates that for aluminium metal, the sequence of corrosion inhibition efficiency values corresponds to the highest E_{HOMO} value, namely $T1 > T3 > T2 > T4$. From the results it's apparent that T1 has an E_{HOMO} of -6.7114 eV and is greater than T2, T3 and T4. It is anticipated that T1 makes the most contribution to corrosion inhibition efficiency based on the E_{HOMO} comparison. The electron distribution in the four inhibitors' HOMO orbitals is displayed in Table 4.26.

According to Table 4.27 the ionization potential value is lower at T1 at 6.7114 eV, compared to the ionization potential value T2 (7.2241 eV), T3 (7.2216 eV) and T4 (7.3509 eV). It may be inferred from this ionization potential value that T2 contributes more to inhibitory efficacy than the other derivatives. This result may be due to the stability factor of the organic inhibitor in the solution. Table 4.27 shows the lowest electronegativity at T1 of 2.4596 eV. The electronegativity values of other molecules T2, T3 and T4 are 3.4138 eV, 3.4117 eV and 3.5419 eV, respectively. T1 is anticipated to have the highest corrosion inhibition effectiveness value among the three inhibitors based on the electronegativity value.

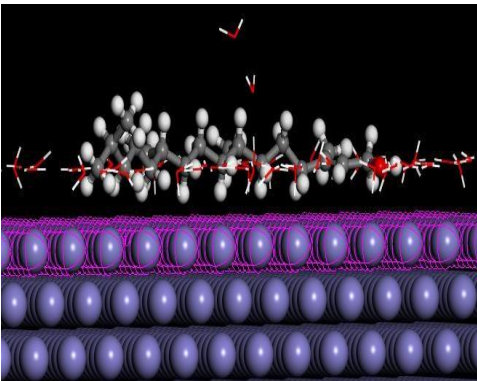
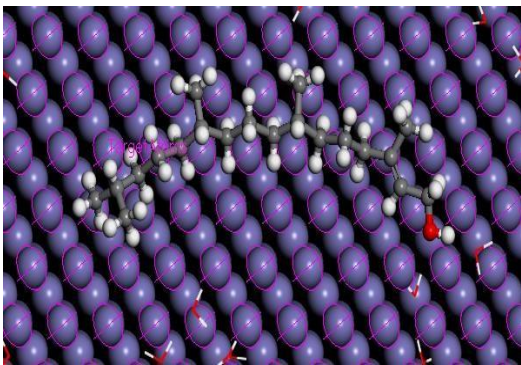
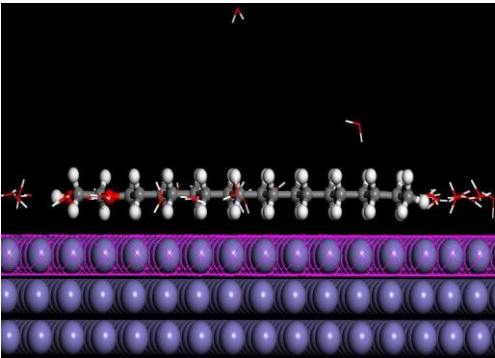
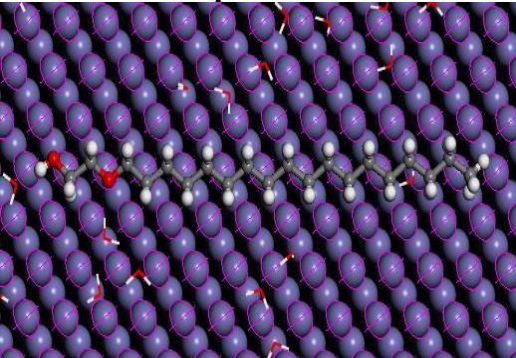
The electron transfer value shows that the efficiency of the inhibitor is an electron donor, whereas aluminium metal acts as an acceptor, creating a corrosion-resistant adsorption layer. More electrons will cover the Al surface due to the growing capacity to contribute electrons to the Al metal surface. Therefore, the value of electron transfer that can occur in the corrosion process is inhibited (Sastri & Perumareddi, 1997). The high to low electron transfer ability values are $T1 > T3 > T2 > T1 > T4$. The magnitude of this electron donor accounts for T1's highest corrosion inhibition efficacy.

4.5.3 Monte Carlo Simulations for *Sclerocarya birrea* derivatives on mild steel and API 5L X42 pipeline steel.

Monte Carlo simulations of the selected *Sclerocarya birrea* derivatives (T1 to T5) were studied on the Fe(110) surfaces. The Fe (110) surface is particularly interesting due to its high atomic

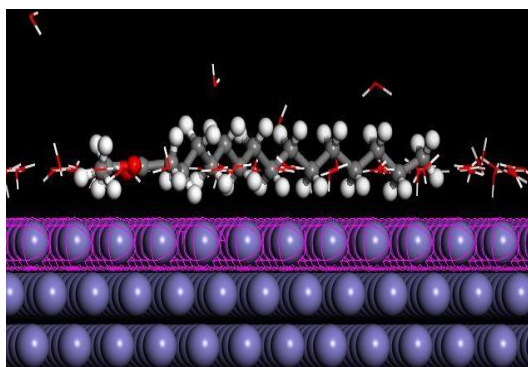
density and reactivity, making it an ideal model for researching adsorption processes (Guo et al., 2017). These simulations were performed on metal surfaces, H₂O molecules, and organic inhibitor complexes. The notably enduring adsorption pattern on the Fe(110) surface with 100 water molecules and organic inhibitors is illustrated in Table 4.28 (T1, T2, T3, T4, and T5). Table 4.28 depicts all the interactions between *Sclerocarya birrea* derivatives, Fe(110), and water molecules viewed from the top and side. It can be observed in Table 4.28 that the derivatives are adsorbed parallel to the Fe(110) surface. This horizontal adsorption of inhibitor molecules on metal surfaces improves corrosion inhibition by covering a larger surface area and generating higher binding energy (Elsa et al., 2024). *Sclerocarya birrea* derivatives exhibit planar adsorption due to free oxygen electrons and the aromatic ring's π electrons. This orientation leads to a large adsorption surface area and high inhibitory efficacy (Laihemdi et al., 2024) .

Table 0.28: Adsorption of T1, T2, T3, and T4 on the surface of Al in Monte Carlo Fe(110) /inhibitor/100 H₂O system.

T1	Side View	Top View
		
	Fe(110)/ 3,7,11,15-Tetramethyl-2-hexadecen-1-ol /100 H ₂ O	Fe(110)/ 3,7,11,15-Tetramethyl-2-hexadecen-1-ol /100 H ₂ O
T2	Side View	Top View
		
	Fe(110)/ Ethanol,2-(octadecyloxy)/100 H ₂ O	Fe(110)/ Ethanol,2-(octadecyloxy)/100 H ₂ O

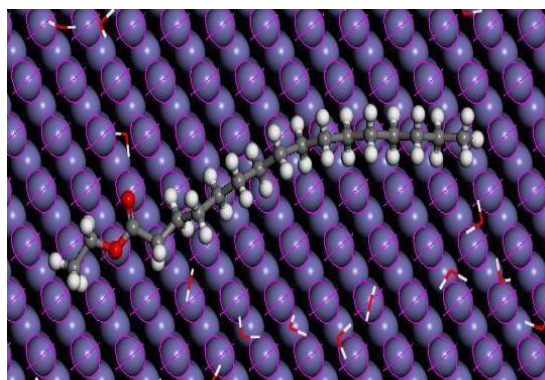
T3

Side View



Fe(110)/ Hexadecanoic acid, ethyl ester
/100 H₂O

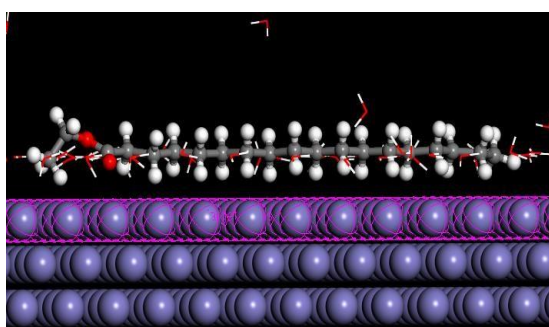
Top View



Fe(110)/ Hexadecanoic acid, ethyl ester /100
H₂O

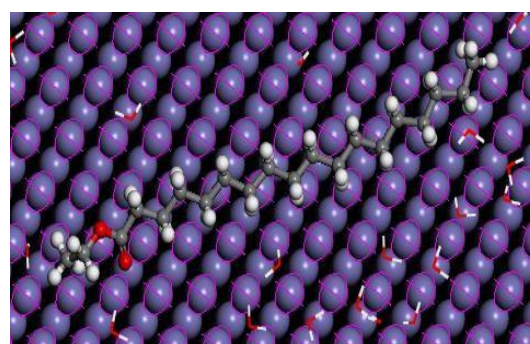
T4

Side View



Fe(110)/ Octadecanoic acid, ethyl ester
/100 H₂O

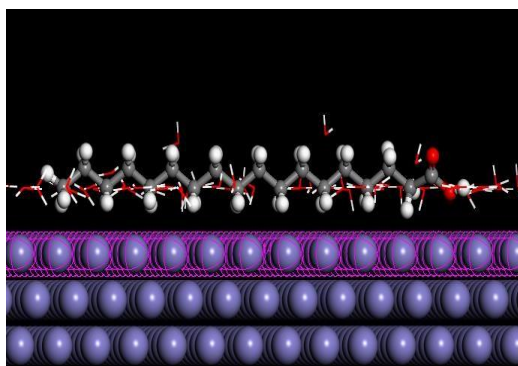
Top View



Fe(110)/ Octadecanoic acid, ethyl ester /100
H₂O

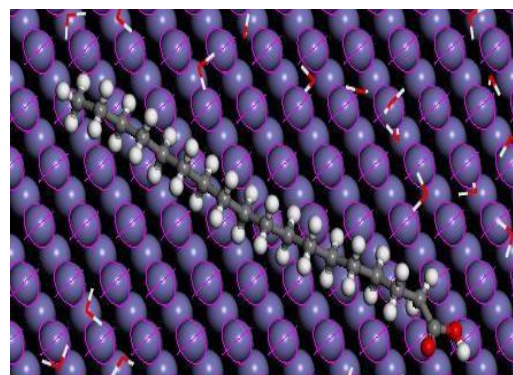
T5

Side View



Fe(110)/ Octadecanoic acid/100 H₂O

Top View



Fe(110)/ Octadecanoic acid/100 H₂O

Several important parameters, including the adsorption energy (E_{ads}), rigid adsorption energy, deformation energy of inhibitors, and water molecules, were calculated and are presented in Table 4.29. These parameters collectively offer an extensive perspective on the adsorption kinetics, facilitating the evaluation of each derivative's efficacy as a corrosion inhibitor for Fe (110). All derivatives (T1 to T5) as noted from Table 4.29 demonstrate substantial negative adsorption energies, indicating robust adsorption on the Fe (110) surface. Consequently, the adsorption of these inhibitor molecules is feasible and spontaneous (Laihemdi et al., 2024). They could safeguard against steel corrosion by forming a barrier which will block all active metal sites. Among all the derivatives, T2 exhibits the most significant absolute E_{ads} (-5202.014 kcal/mol), indicating it forms the most persistent adsorbed layer and presumably provides the highest inhibitory efficiency. T4 as observed in Table 4.29 has the most negative rigid adsorption energy (-1533.229 kcal/mol), implying the strongest primary interaction with the Fe surface in its unaltered state. T1, T2, T3 and T5 show comparable rigid adsorption energies, slightly lower than T4.

The derivatives studied exhibit comparable deformation energies (-2704 to -2717 kcal/mol), indicating significant structural alterations following adsorption. T2 and T3 have the greatest deformation energies, indicating they undergo more substantial structural alterations when interacting with the Fe(110) surface (He et al., 2023; Tian et al., 2018). For inhibitor's change in adsorption energy per molecule (dE_{ads}/dN_i) T2 exhibits the largest negative value (-242.864 kcal/mol), suggesting its high adsorption strength and efficiency as a corrosion inhibitor (Raisemche et al., 2024). T4 and T5 similarly demonstrate significant adsorption per inhibitor molecule. Water molecules adsorption energy per molecule (dE_{ads}/dN_i) is less negative (-29 to -35 kcal/mol), indicating lesser adsorption compared to inhibitors. The rivalry between inhibitors and water adsorption favors the inhibitor since its adsorption energy is substantially lower. According to the adsorption character, the order of performance is as follows: $T2 > T4 \approx T5 > T3 > T1$. The experimental results from Mass loss and electrochemical testing techniques agree with these observations, where the inhibitor forms a barrier layer and absorbs to prevent degradation.

Table 0.29: The energy of T1, T2, T3, and T4 adsorption and Fe(110)/inhibitor/100 H₂O system derivatives based on Monte Carlo simulation.

Inhibitor	Adsorption Energy (Kcal mol ⁻¹)	Rigid Adsorption Energy (Kcal mol ⁻¹)	Deformation Energy (Kcal mol ⁻¹)	Inh: dE_{ads}/dN_i (Kcal mol ⁻¹)	H ₂ O: dE_{ads}/dN_i (Kcal mol ⁻¹)
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T1	-4153.311	-1448.626	-2704.685	-194.257	-29.286
T2	-5202.014	-1485.299	-2716.786	-242.864	-35.073
T3	-4169.796	-1453.307	-2716.489	-206.792	-29.373
T4	-4247.115	-1533.229	-2713.886	-224.096	-33.985
T5	-4199.628	-1483.867	-2715.761	-220.254	-34.456

The adsorption energy distributions for all the five derivatives are displayed in Figures 4.60 to 4.64.

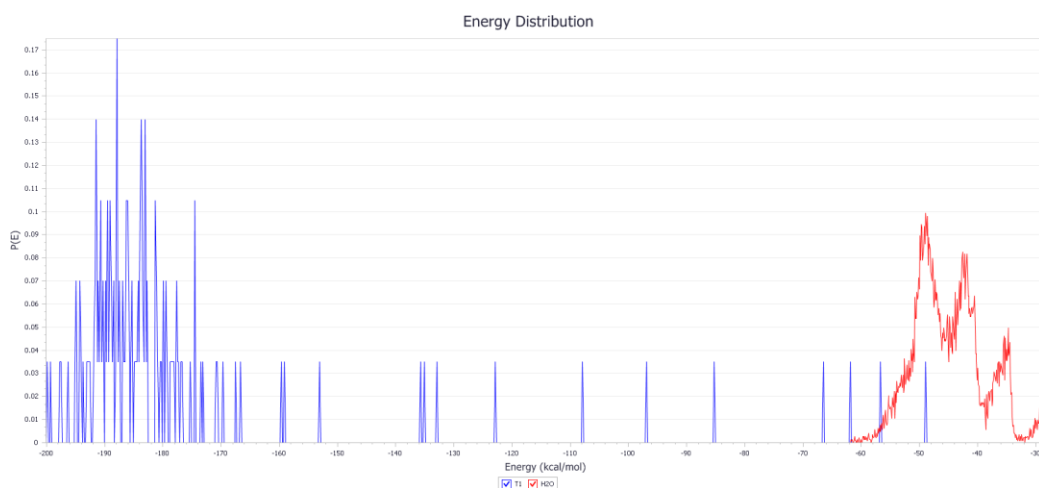


Figure 0.60: Adsorption energy distribution for 3,7,11,15-Tetramethyl-2-hexadecen-1-ol /100 H₂O in Fe(110).

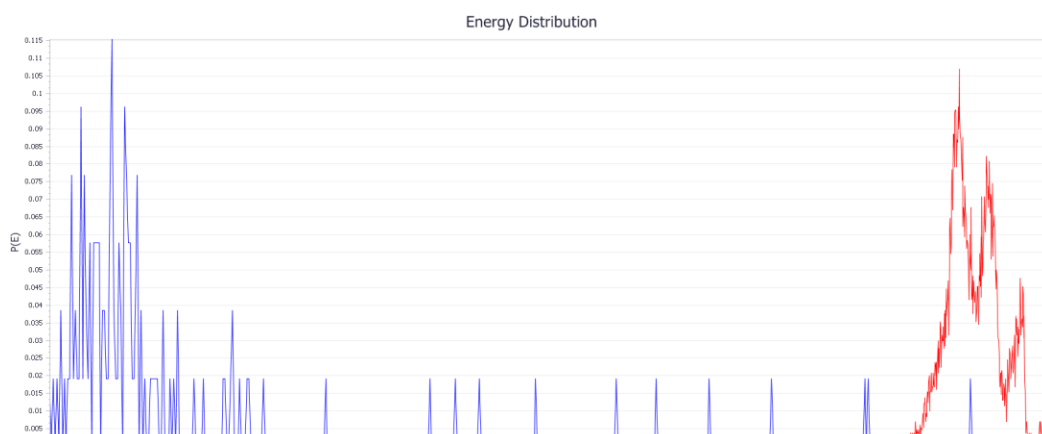


Figure 0.61: Adsorption energy distribution for Ethanol,2-(octadecyloxy)/100 H₂O in Fe(110)

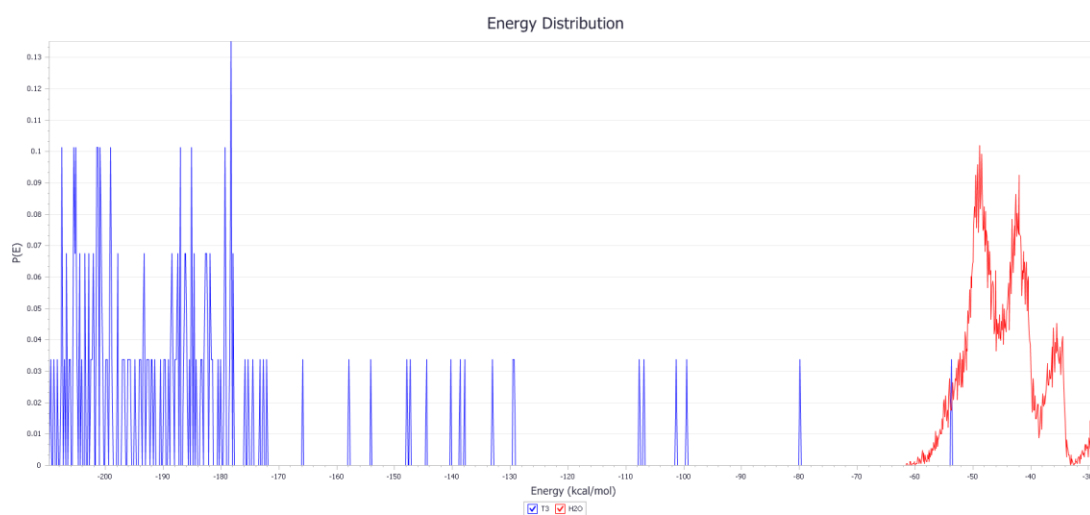


Figure 0.62: Adsorption energy distribution for Hexadecanoic acid, ethyl ester/100 H₂O in Fe(110).

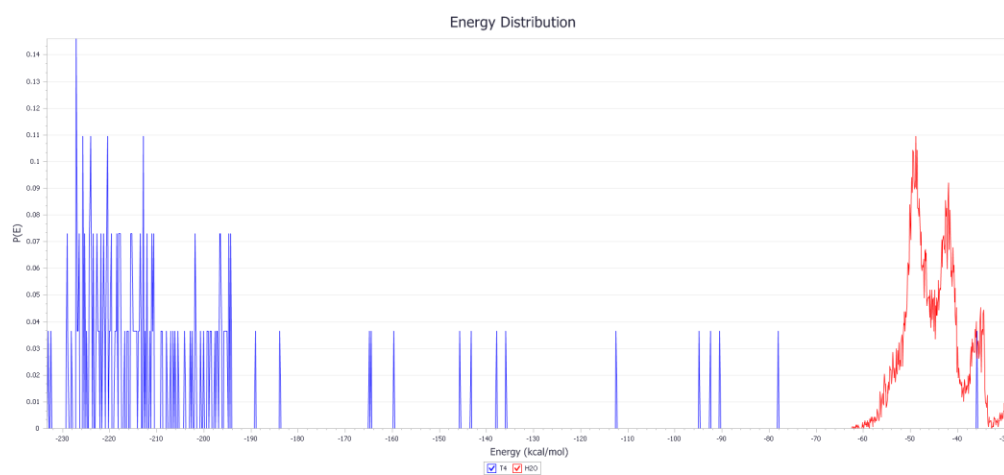


Figure 4.63: Adsorption energy distribution for Octadecanoic acid, ethyl ester 100 H₂O in Fe(110).

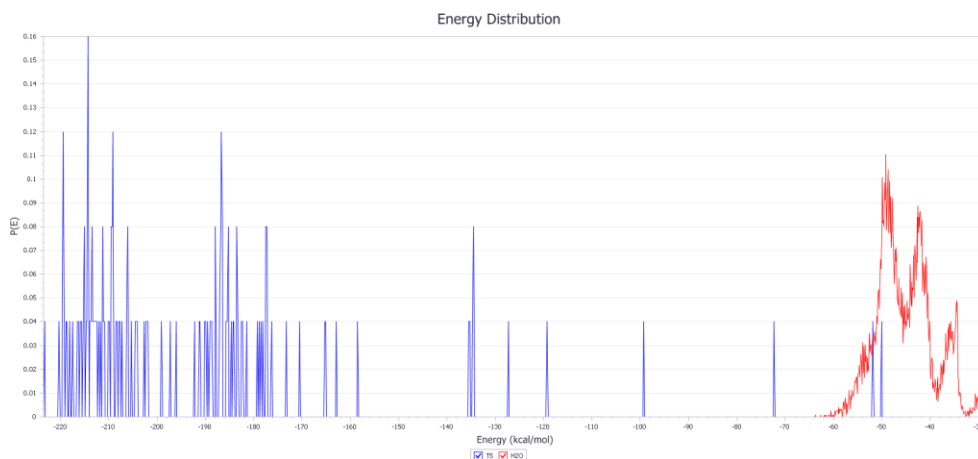


Figure 0.63: Adsorption energy distribution for Octadecanoic acid 100 H₂O in Fe(110)

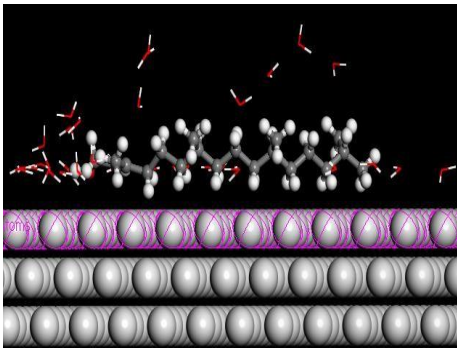
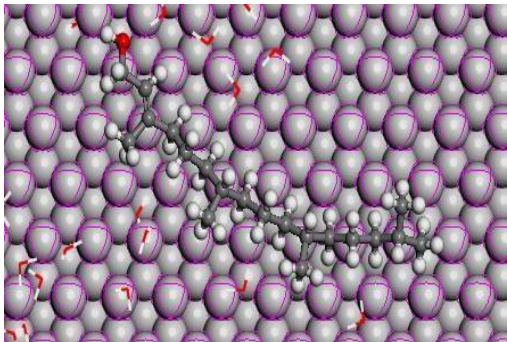
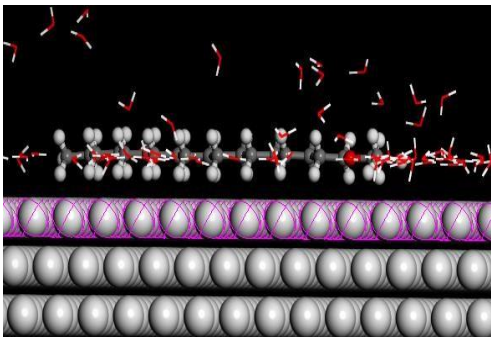
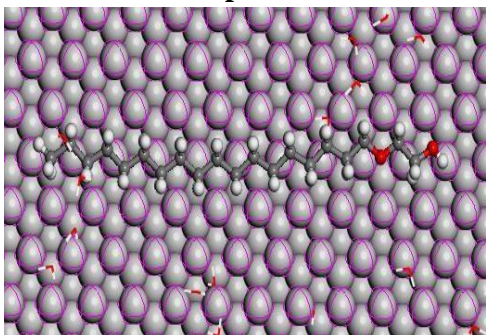
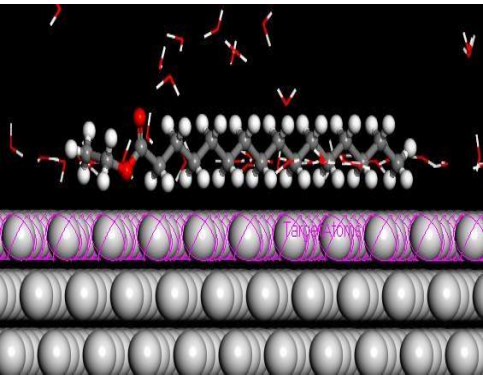
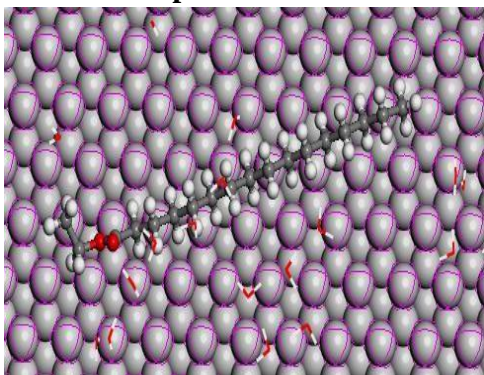
4.5.4 Monte Carlo Simulations for *Sclerocarya birrea* derivatives on Aluminium (AA 1100) surface.

Monte Carlo simulations were carried out on organic inhibitor systems, H₂O molecules, and metal surfaces. Monte Carlo simulation was used to explore the adsorption properties of inhibitor molecules and 100 water molecules on the Al (111) metal surface. The Monte Carlo simulation procedure utilizes the Al (111) surface given that it has the most stable surface (Chiter et al., 2015). The remarkably persistent adsorption pattern on the Al (111) surface with 100 water molecules and organic inhibitors is depicted in Table 4.30 (T1, T2, T3 and T4). The type of adsorption process can be defined by the distance between the Al (111) surface and the organic corrosion inhibitor (Huong et al., 2020). Table 4.30 depicts how the strong layer on the Al (111) surface and the chemisorption (chemical) adsorption characteristics may safeguard aluminium metal from corrosion attacks if the distance value is less than 3.5 Å. Additionally, this system reaches normalcy, allowing the anticipated organic inhibitor to be adsorbed on the surface of Al (111). Table 4.31 shows that the adsorption energy for the most stable configuration is for the system Ethanol,2-(octadecyloxy)/100 H₂O, 3,7,11,15- Tetramethyl-2-hexadecen-1-ol /100 H₂O, and Hexadecanoic acid, ethyl ester /100 H₂O. Compared to 100 water molecules, the inhibitor's adsorption energy is substantially higher.

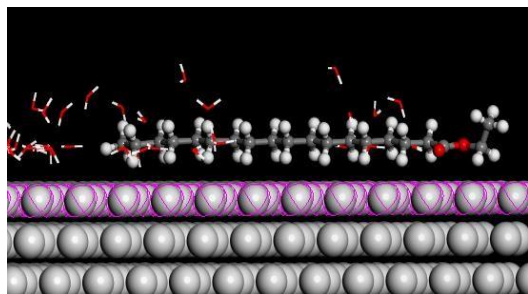
Figures 4.66 to 4.69 exhibits the distribution of adsorption energies for both water and the organic inhibitor. It is feasible to segregate the adsorption energy distribution of each organic inhibitor from that of water. T1 works well as a corrosion inhibitor on aluminium metal surfaces because it can generate an extremely strong coating layer (Chiter et al., 2015; Huong et al., 2020). The order of adsorption energy of organic inhibitors on the Al(111) surface in the presence of 100 water molecules is T1 > T3 > T2 > T4. The highest adsorption energy value for the T1 adsorbate was obtained at -3738.108 kcal/mol on the Al(111) surface in a medium

of 100 water molecules. Stronger adsorption is prevalent when the adsorption energy has a larger negative value (Hadisaputra et al., 2021; Huong et al., 2020).

Table 0.30: Adsorption of T1, T2, T3, and T4 on the surface of Al in Monte Carlo Al(111)/inhibitor/100 H₂O system.

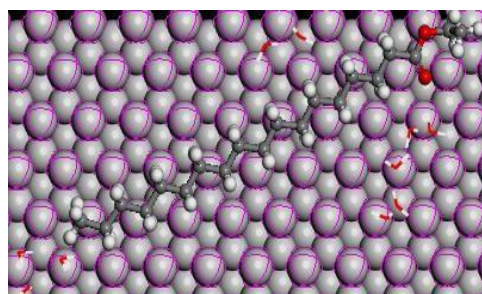
T1	Side View  Al(111)/3,7,11,15-Tetramethyl-2-hexadecen-1-ol /100 H ₂ O	Top View  Al(111)/3,7,11,15-Tetramethyl-2-hexadecen-1-ol /100 H ₂ O
T2	Side View  Al(111)/Ethanol,2-(octadecyloxy)/100H ₂ O	Top View  Al(111)/ Ethanol,2-(octadecyloxy)/100 H ₂ O
T3	Side View  Al(111)/Hexadecanoic acid, ethyl ester /100 H ₂ O	Top View  Al(111)/Hexadecanoic acid, ethyl ester /100 H ₂ O

T4Side View



Al(111)/Octadecanoic acid, ethyl ester
/100 H₂O

Top View



Al(111)/Octadecanoic acid, ethyl ester /100 H₂O

Table 0.31: The energy of T1, T2, T3, and T4 adsorption and Al(111)/inhibitor/100 H₂O system derivatives based on Monte Carlo simulation.

Inh	Adsorption Energy (Kcal mol ⁻¹)	Rigid Adsorption Energy (Kcal mol ⁻¹)	Deformation Energy (Kcal mol ⁻¹)	Inh: dEad/dNi (Kcal mol ⁻¹)	H ₂ O: dEad/dNi (Kcal mol ⁻¹)
T1	-3738.992	-1024.431	-2714.56	-103.041	-28.637
T2	-3738.108	-1018.808	-2719.299	-121.182	-28.416
T3	-3702.752	-984.786	-2717.966	-102.512	-28.501
T4	-3717.256	-1000.809	-2716.466	-114.550	-28.765
T5	-3702.308	-986.295	-2716.013	-111.655	-28.498

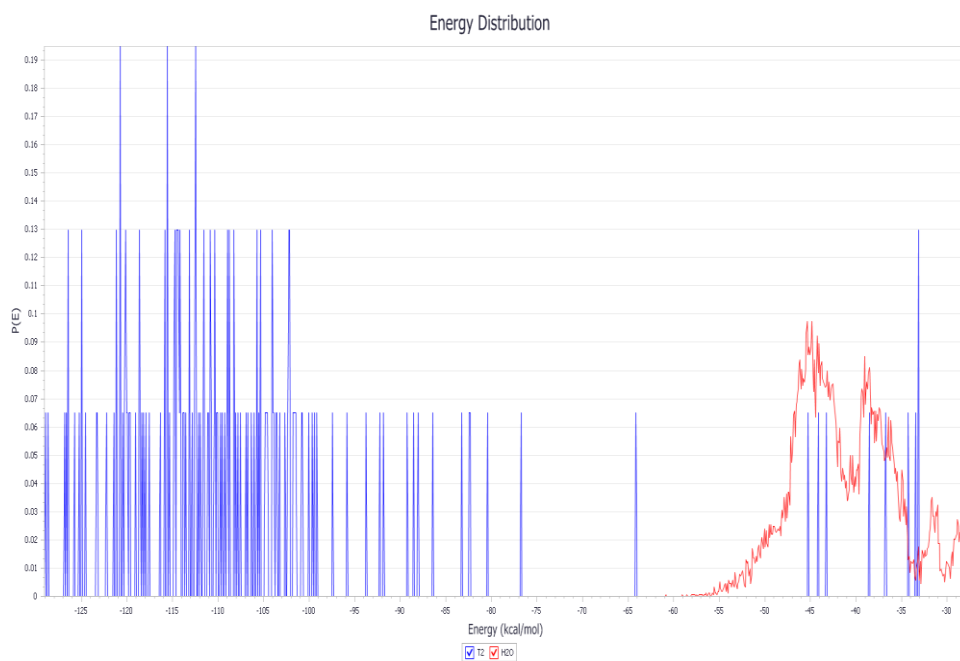


Figure 0.64: Adsorption energy distribution for 3,7,11,15-Tetramethyl-2-hexadecen-1-ol /100 H₂O.

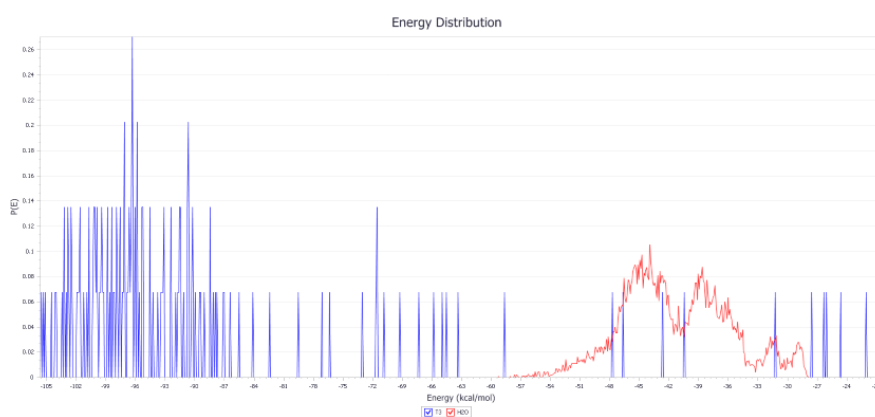


Figure 0.65: Adsorption energy distribution for Ethanol,2-(octadecyloxy)/100 /100 H₂O.

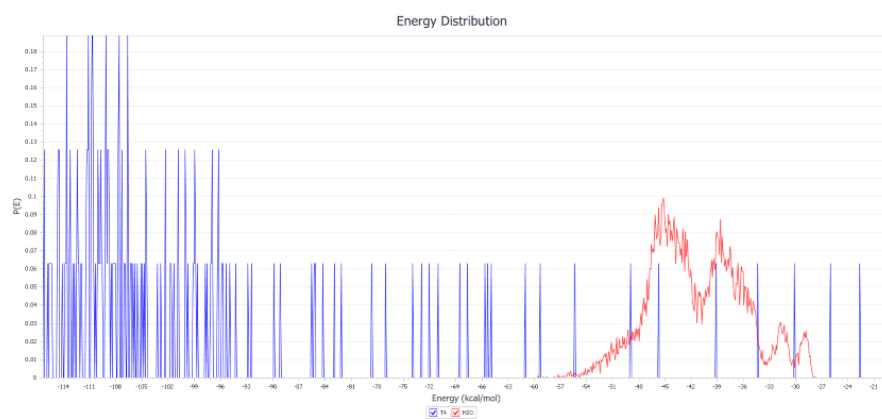


Figure 0.66: Adsorption energy distribution for Hexadecanoic acid, ethyl ester /100 H₂O.

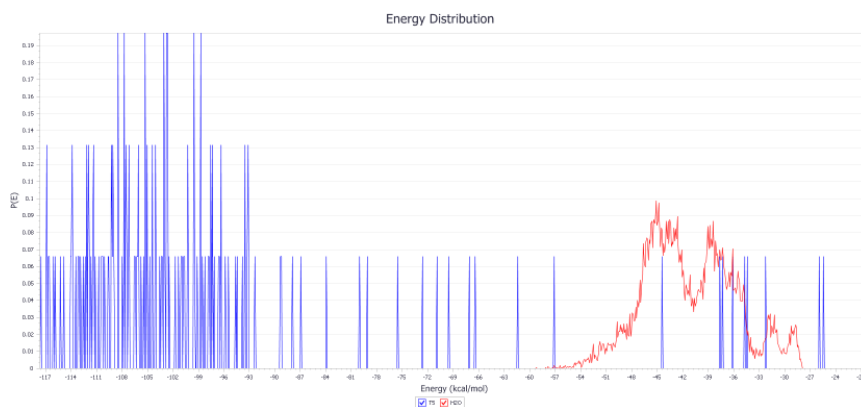


Figure 0.67: Adsorption energy distribution for Octadecanoid acid, ethyl ester /100 H₂O.

4.6 Surface analysis using X-Ray Diffraction (XRD) and Raman Spectroscopy

The superficial analysis for inhibited and non-inhibited mild steel, API 5L X42 pipeline steel and aluminum (AA 1100) was studied using XRD and Raman spectroscopy instruments. These studies were carried out to determine the protective film formation, presence of oxides as well as surface modifications in the presence or absence of ethanolic *Sclerocarya birrea* inhibitors in 1 M H₂SO₄ and 3.5 % NaCl. The two techniques have been used to identify phase transitions and understand the underlying process of corrosion inhibition (Moloto et al., 2020). These findings may be helpful in developing more effective corrosion management and prevention strategies.

4.6.1 XRD results analysis

X-ray diffraction tests were conducted to detect presence of film formation and oxides on metal surfaces exposed to 1 M H₂SO₄ and simulated seawater conditions. Surface variations due to the formation or disappearance of peaks were used to discuss the performance of the inhibitor in corrosive environments. The XRD technique is widely known for material characterization, identification of crystalline phases and quantitative phases, therefore its use to elucidate surface interactions is extremely important (Chugh et al., 2020). Figures 4.68 to 4.70 show XRD plots of mild steel, API 5L X42 pipeline steel, and aluminum exposed to corrosive environments containing 3.5 % NaCl and 1 M H₂SO₄ with *Sclerocarya birrea* inhibitor presence and absence.

Figure 4.68 a and b shows large peaks of metallic iron (Fe) at $2\theta = 44.65^\circ$, 64.98° and 82.28° in polished mild steel before exposure to hostile conditions. Chugh et al., (2020) reported similar peaks in their mild steel corrosion tests in the presence and absence of an inhibitor in 1 M HCl. For simulated seawater environment, there was no significant difference in the peaks for uninhibited polished and inhibited polished mild steel (exposed to 3.5 % NaCl plus

Sclerocarya birrea inhibitor), as the Fe peaks at $2\theta = 44.65^\circ$, 64.98° , and 82.28° remained. The decrease in Fe peak intensity for blank exposed samples in 1 M H_2SO_4 and 3.5 % NaCl can be attributed to metal decay.

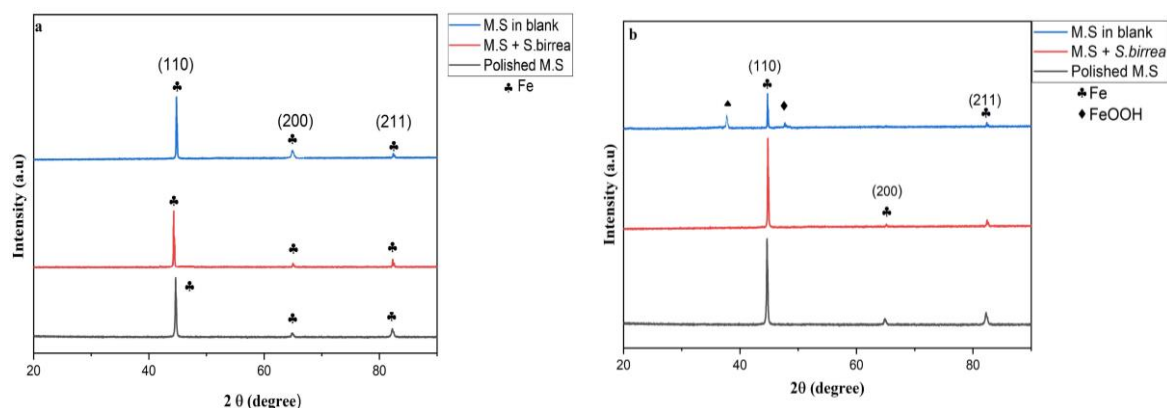


Figure 0.68: The XRD plots for polished mild steel prior to and post exposure to a) 3.5 % NaCl and b) 1 M H_2SO_4 media in the absence and presence of *Sclerocarya birrea* inhibitor.

Blank samples in acidic environment showed minor diffraction peaks at $2\theta = 37.71^\circ$ and 48.67° , indicating the existence of $\alpha\text{-FeOOH}$ (goethite) (Muthukrishnan et al., 2015; Popescu et al., 2022). Inhibited samples in seawater showed a significant increase in peak intensity, indicating the generation of a robust safeguarding film to prevent corrosives from degrading the metal and forming oxides (Kamaruzzaman et al., 2021). The removal of Fe peaks in a blank sample immersed in 1 M H_2SO_4 can be attributed to a phase change caused by the corrosion process as well as the development of amorphous phases from corrosion products that lack a well-defined crystal structure. Weak diffuse scattering at $2\theta = 30^\circ$ to 45° may indicate the existence of oxides and hydroxides, although their small number makes determining their composition difficult. Hematite (Fe_2O_3) and magnetite (Fe_3O_4), which are typically found in corrosion products, were not detected. This could be due to the sample handling process, which involved washing and cleaning the samples between weight loss experiments, destroying the brown rust that formed on the metal surfaces.

Meanwhile, the XRD graphs for the API 5L X42 pipeline in 3.5 % NaCl and 1 M H_2SO_4 aggressive media were also derived (Figure 4.69 a, and b). The API X42 XRD peaks were matched to those in the International Center for Diffraction Data (ICDD) and classified as carbon steel (reference code 00-037-0474) with a BCC crystal structure (Aminul Islam &

Farhat, 2015). Polished API 5L X42 pipeline steel exhibited large metallic iron (Fe) peaks at $2\theta = 44.75^\circ$, 65.11° , and 82.45° , with corresponding planes 110, 200, and 211.

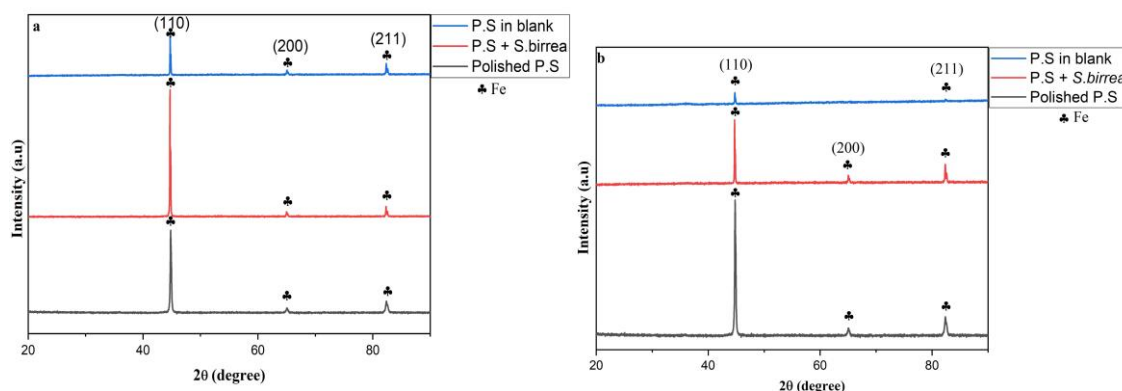


Figure 0.69: The XRD plots for polished API 5L X42 pipeline steel prior and post exposure to 3.5 % NaCl and 1 M H₂SO₄ aggressive media in the absence and presence of *Sclerocarya birrea* inhibitor.

The same peaks were identified in the inhibited samples, albeit with reduced intensity, indicating the formation of metal complexes between the steel and *Sclerocarya birrea* inhibitor molecules. The peaks at $2\theta = 65.11^\circ$ and 82.45° confirm the adsorption of *S. birrea* phytochemicals and inhibitors. The sample exposed to an empty environment of 1 M H₂SO₄ showed new peaks at $2\theta = 28.83^\circ$ and 35.37° , which can be attributed to FeOOH and Fe₂O₃, respectively (Kartsonakis et al., 2020). Under both corrosive conditions, inhibited samples showed no additional peaks, while polished samples showed repeated peaks, indicating the amorphous nature of the organic coating protected on the metal surface (Fathabadi et al., 2021). From these findings, it can be deduced that the adsorption of *Sclerocarya birrea* molecules on API 5L X42 pipeline steel is physical adsorption, this was also validated by the Langmuir adsorption isotherm and other calculated thermodynamic properties.

Five unique peaks at $2\theta = 38.48^\circ$, 44.72° , 65.10° , 78.23° and 82.44° were observed in polished, inhibited and non-inhibited Aluminium (AA 1100) metal samples exposed to both corrosive conditions, with different signal strengths (Figure 4.70). The corresponding planes were (111) for 38.48° , (200) 44.72° , (220) 65.10° , (311) 78.23° and (222) 82.44° (ICSD 01-085-1327). The aluminium metal is classified as FCC structure (Fiquet et al., 2018; Ning & Zhang, 2023).

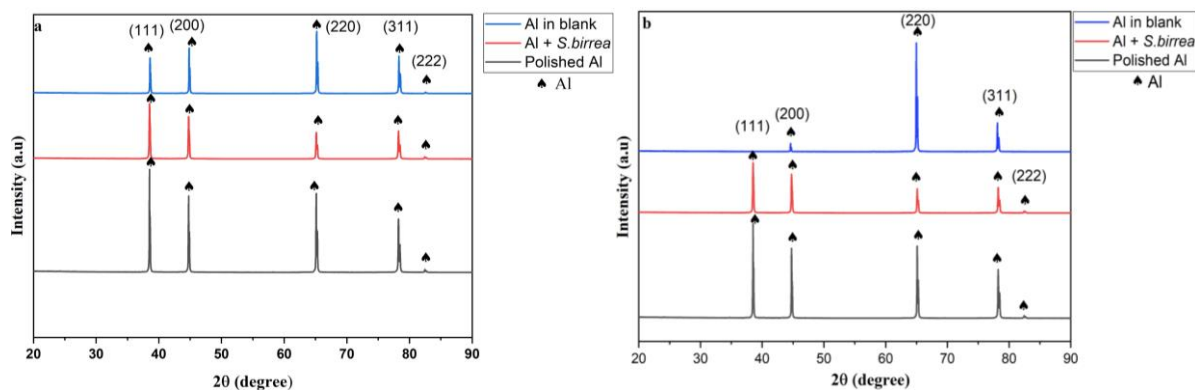


Figure 0.70: The XRD plots for polished aluminium prior and post exposure to 3.5 % NaCl and 1 M H₂SO₄ aggressive media in the absence and presence of *Sclerocarya birrea* inhibitor.

There was no significant difference between polished and inhibited samples in simulated seawater. The inhibited samples showed reduced intensities due to the adsorption of *Sclerocarya birrea* inhibitory molecules on the aluminum surface, which formed a complex compound in addition to the oxide film layer, protecting the metal integrity and limiting corrosion (Prabakaran et al., 2016). In a 1 M H₂SO₄ environment, inhibited Al produced the same peaks as polished Al but at lower intensities, indicating the development of a metal complex with the metal. The uninhibited sample showed only three distinct peaks, indicating a phase shift caused by corrosion on the metal surface. Without inhibitors, the aggressive nature of the acid could lead to a greater change in the crystal structure of the material (Nnaji et al., 2019). The formation of new corrosion products and peak broadening can lead to the disappearance of peaks. These data suggest that the ethanolic extract of *Sclerocarya birrea* can effectively protect aluminum samples from harsh saltwater and acidic environments.

Overall, the XRD data for pipeline steel showed that blank exposed sample to acidic conditions formed FeOOH at $2\theta = 28.83^\circ$ and Fe₂O₃ at $2\theta = 35.37^\circ$. However, the peaks disappeared when an inhibitor was applied. Similarly, mild steel exposed to acidic environments showed the formation of new peaks at $2\theta = 37.71^\circ$ and 48.67° , indicating FeOOH production. Aluminum samples did not show the development of new peaks in any of the corrosive media. In general, for all metals, the peak intensity decreased in inhibited samples, indicating physisorption and the development of a metal complex to protect the metal in aggressive environments. The *Sclerocarya birrea* is therefore an effective corrosion inhibitor for structural steel, API 5L X42 pipeline steel and aluminum in a medium containing 3.5 % NaCl and 1 M H₂SO₄. Its physical

properties are absorbed by the metal substrate and its inhibitory molecules form a safeguarding film that prevents corrosive chemicals from damaging the metal.

4.6.2 Raman Spectroscopy results analysis

Raman spectroscopy was used to study and characterize the film components on metal surfaces after and before exposure to 1 M H_2SO_4 and 3.5 % NaCl in the absence and presence of *Sclerocarya birrea* extract inhibitor. Analysis of the Raman spectrum is crucial for understanding corrosion, inhibition mechanisms and change in phenomena over time in saline and acidic environments (Bleij et al., 2022a). It enables peak identification of corrosion products, including oxides and hydroxides, as well as organic functional groups that aid in safeguarding metals against degradation.

The Raman spectrum for polished mild steel specimens immersed in 3.5 % NaCl and 1 M H_2SO_4 in the absence and the presence of *S. birrea* inhibitors are displayed in Figure 4.71 below. Before being exposed to corrosive conditions, a polished mild steel specimen shows just three noticeable peaks: 103 cm^{-1} , 240 cm^{-1} , and a higher intensity peak at 248 cm^{-1} . These peaks correspond to the lattice vibrations of iron oxides or hydroxides, specifically magnetite (Fe_3O_4) for mild steel (Speidel et al., 2016). In contrast, when mild steel was immersed in simulated saltwater containing *S. birrea* inhibitor, multiple peaks were identified, as shown in Figure 72 c and peak 220 cm^{-1} indicated the presence of $\alpha\text{-Fe}_2\text{O}_3$ (Sheikh, 2023), peak 389 cm^{-1} is attributed to lepidocrocite ($\gamma\text{-FeOOH}$) (Colomban et al., 2008). The observed bands in the peak ranges from 500 to 800 cm^{-1} are largely ascribed to aliphatic chains and C-C rings (Govindammal et al., 2021).

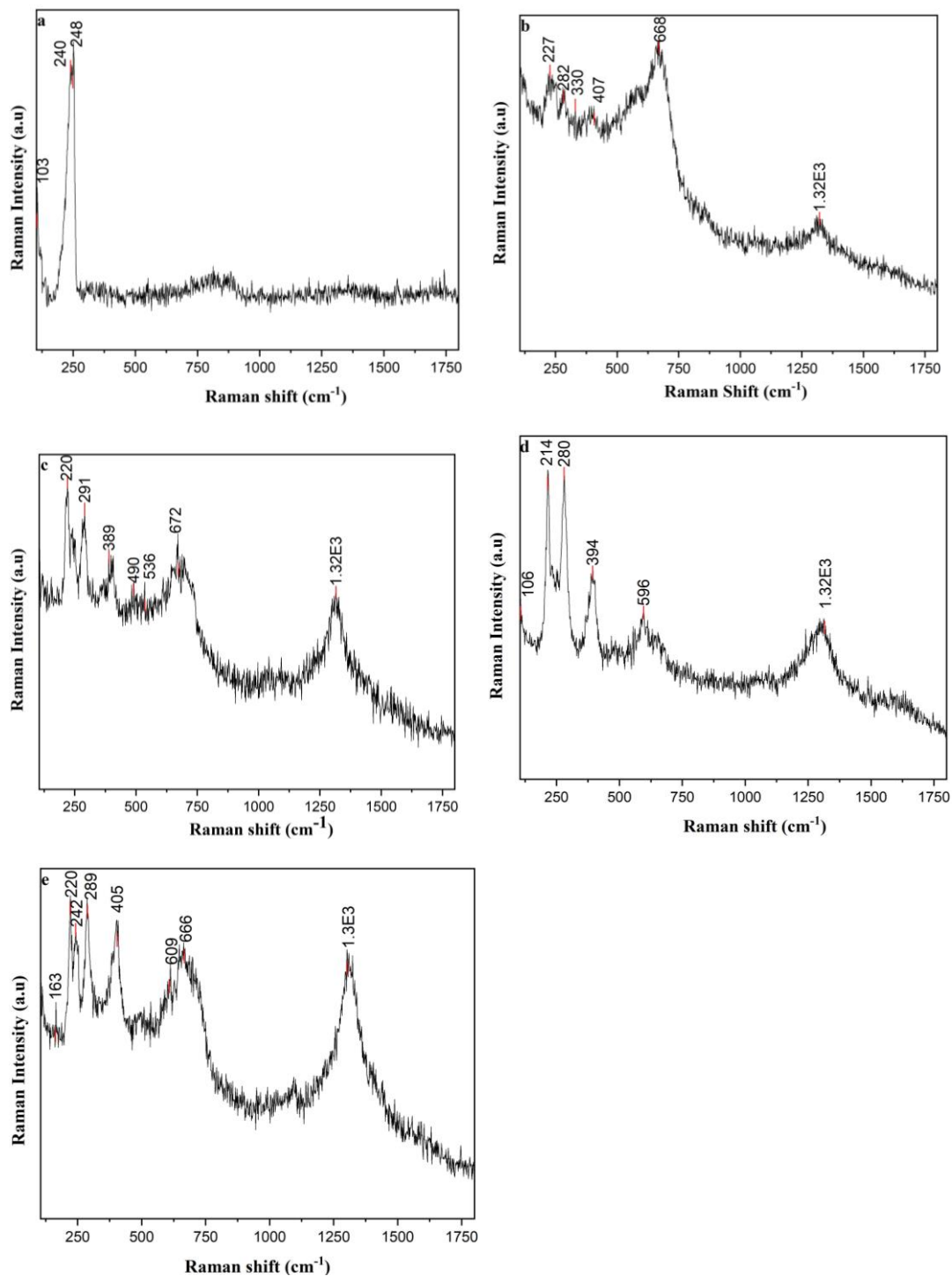


Figure 0.71: The Raman plots for a) polished, b) 3.5 % NaCl, c) 3.5 % NaCl + *Sclerocarya birrea* inhibitor, d) 1 M H₂SO₄ and e) 1 M H₂SO₄ + *Sclerocarya birrea* inhibitor exposed mild steel

Raman peaks between 200-450 cm⁻¹ can be attributed to α , β , and γ -crystalline iron oxides and oxyhydroxides, as well as amorphous products, for specimens subjected to a blank simulated seawater hostile solution which is shown in Figure 4.71 b (Kartsonakis et al., 2019). The

distinctive peaks at 227 cm^{-1} , 282 cm^{-1} , 303 cm^{-1} , and 407 cm^{-1} corresponds to hematite ($\alpha\text{-Fe}_2\text{O}_3$) (Saura et al., 2022). The band at 282 cm^{-1} represents the presence of lepidocrocite ($\gamma\text{-FeOOH}$) (Colomban et al., 2008; Faivre, 2016). Although the peaks in the spectrum resemble hematite, they are slightly offset from one other, presumably due to the employment of laser beams with variable potentials, as described by de Faria et al. (1997). The band at 668 cm^{-1} corresponds to Fe_3O_4 whereas the distinctive peak at 668 cm^{-1} indicates the presence of $\alpha\text{-Fe}_2\text{O}_3$ (Baek et al., 2001; Lai et al., 2021). Most of the peaks found in the simulated seawater were still detectable in samples exposed to $1\text{ M H}_2\text{SO}_4$, with very few new peaks discovered. Figure 4.71 (e) shows new peaks at 163 cm^{-1} and 242 cm^{-1} in the presence of the inhibitor, while in Figure 4.71 d, peaks at 106 cm^{-1} , 214 cm^{-1} , and 394 cm^{-1} in blank $1\text{ M H}_2\text{SO}_4$ are all ascribed to the Fe_2O_3 oxide (Manh et al., 2022). The presence of C-O functional groups on the mild steel surface is indicated by vibration stretching exhibited in Figure 4.71 (e) in the inhibited sample in the $1000\text{-}1300\text{ cm}^{-1}$ range (Nam et al., 2013). Peak 405 cm^{-1} , commonly associated with metal-ligand complexes, indicates metal complex development at the metal's surface (Wang et al., 2020). In this study, it can be attributed to Fe atoms interacting with *Sclerocarya birrea* inhibitor molecules at the metal contact. The C-H aromatic groups and vibrations are seen in the bands at 596 cm^{-1} and 666 cm^{-1} , which may also mimic out of plane vibrations (Umoren et al., 2016). Peak 596 cm^{-1} in blank sample resembles Fe_3O_4 as previously reported by Raja & Sethuraman (2008).

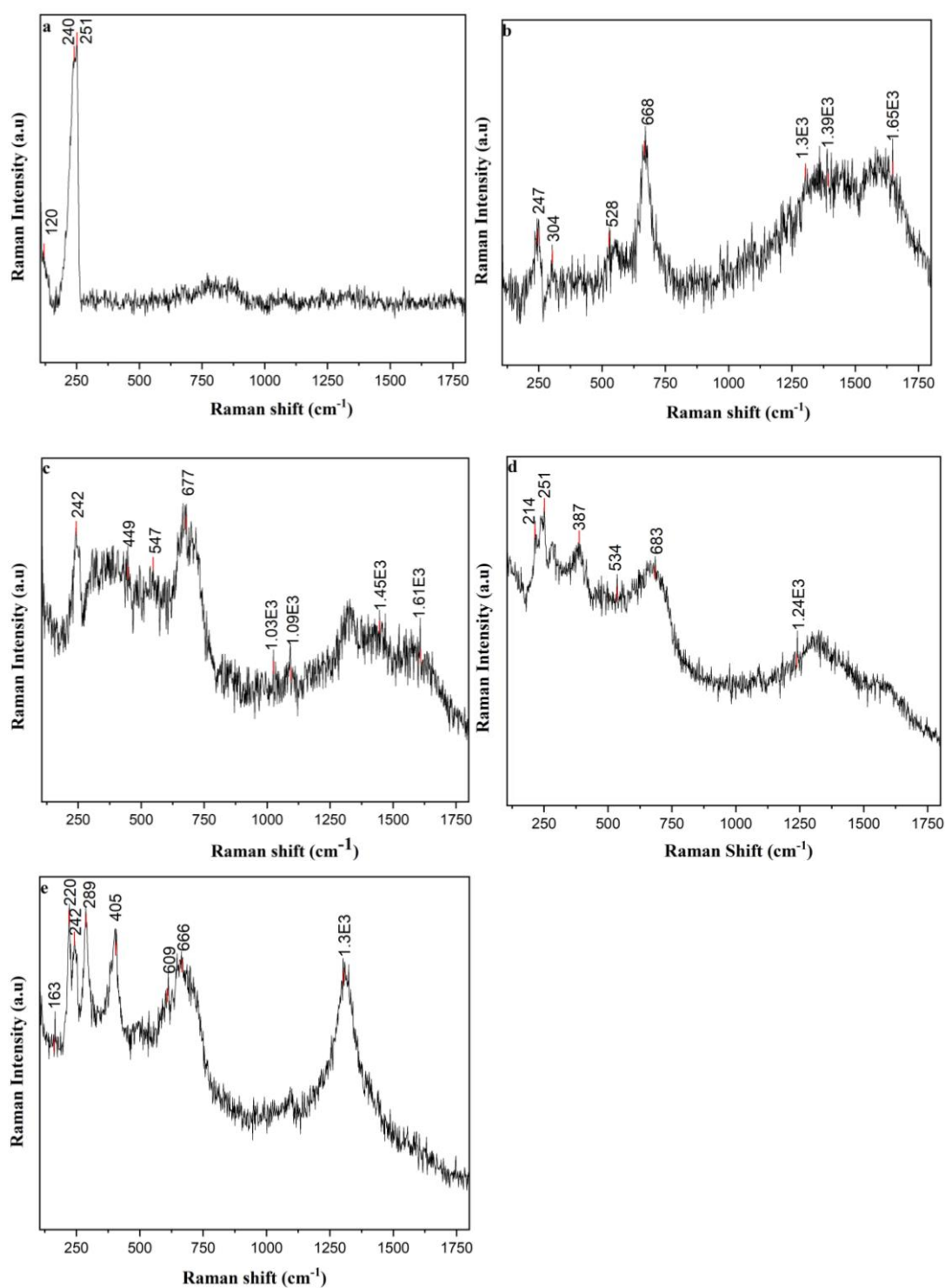


Figure 0.72: The Raman plots for a) polished, b) 3.5 % NaCl, c) 3.5 % NaCl + *Sclerocarya birrea* inhibitor, d) 1 M H₂SO₄ and e) 1 M H₂SO₄ + *Sclerocarya birrea* inhibitor exposed API 5L X42 pipeline steel.

Similarly to mild steel analysis, the API 5L X42 pipeline steel specimens were also subjected to Raman spectroscopy before and after exposure to 3.5 % NaCl and 1 M H₂SO₄ solutions. The

spectroscopic data obtained in simulated seawater, in the presence and absence of *S.birrea* inhibitor, revealed the formation of significant corrosion products, predominantly iron oxides and hydroxides as shown in Figure 4.72 (a – e). For polished pipeline steel, as shown in Figure 4.72 a, only three significant peaks were found. Low vibrational modes of hematite (Fe_2O_3) caused by corrosion during steel processing or possibly from handling during polishing phase are linked to peak at 120 cm^{-1} (Thinaharan et al., 2020). Residual impurities, lattice vibrations, or phonon modes in the iron matrix are reflected by peaks 240 and 251 cm^{-1} (Bleij et al., 2022a). Simulated seawater blank samples showed the presence of iron oxides in several peaks. The magnetite (Fe_3O_4) peaks at 247 cm^{-1} and 304 cm^{-1} indicates early-stage corrosion in chloride environments (Nakamura et al., 2006). Hematite ($\alpha\text{-FeO}_3$), a more stable oxide that forms later in the corrosion process, is most likely associated with the peak at 528 cm^{-1} (Thinaharan et al., 2020). Furthermore, the existence of lepidocrocite ($\gamma\text{-FeOOH}$), an iron oxyhydroxide found in corroded steel, is suggested by peaks at 668 cm^{-1} , 1304 cm^{-1} and 1392 cm^{-1} (Datta et al., 2021). Finally, the peak at 1648 cm^{-1} could represent surface hydration due to adsorbed water or hydroxyl groups in ferrihydrite ($\text{Fe}(\text{OH})_3$) (Islam & Farhat, 2015). Unique Raman peaks formed at 242 , 449 , 547 , 1030 , 1090 , 1450 and 1610 cm^{-1} when a leaf extract inhibitor was added to API 5L X42 pipeline steel immersed in a 3.5 % NaCl solution as in Figure 4.72 c. These new peaks are related to the formation of film from the organic components of the extract. For example, under chloride conditions, peak 242 cm^{-1} is generally linked to the magnetite (Fe_3O_4) formation, a common corrosion product on steel surfaces that is modified by the presence of organic inhibitors (Islam & Farhat, 2015). The peak at 449 cm^{-1} is associated with goethite ($\alpha\text{-FeOOH}$) and the peak at 547 cm^{-1} with hematite ($\alpha\text{-Fe}_2\text{O}_3$), which can still be detected in the presence of an inhibitor, but due to the Fe interactions with inhibitor surfaces (Nakamura et al., 2006).

For the peaks of 1030 cm^{-1} and 1090 cm^{-1} , they can be associated with the presence of C-O stretching vibrations of organic functional groups contained in the *Sclerocarya birrea* leaf extract (de Souza Morais et al., 2023). The peak 1450 cm^{-1} is associated with C=C stretching in aromatic rings, while the peak 1610 cm^{-1} is probably due to C-O stretching vibrations of the carbonyl groups due to *Sclerocarya birrea*, the phytochemical compounds such as flavonoids present on the steel surface the inhibitors of API 5L X42 pipeline are adsorbed (de Souza Morais et al., 2023; Feng et al., 2022). In the acidic medium, as shown in Figure 4.72 d, the peak represents 214 cm^{-1} Fe_3O_4 and 387 cm^{-1} Fe_2O_3 (T. Xu et al., 2024). At 534 cm^{-1} , vibrational modes of goethite ($\alpha\text{-FeOOH}$) are detected, while peaks at 683 cm^{-1} and 1240 cm^{-1}

are associated with lepidocrocite (γ -FeOOH) (Dwivedi et al., 2017). After introducing the inhibitor into the acidic medium, significant peaks were observed at 225 cm^{-1} and 289 cm^{-1} (Bleij et al., 2022b), indicating α -Fe₂O₃, and 400 cm^{-1} indicating Fe₃O₄ (Fan et al., 2020; Li & Hihara, 2015). The peak observed at 631 cm^{-1} is associated with the presence of lepidocrocite (γ -FeO(OH)) (Umoren et al., 2016). In general, C=C stretching vibrations or other vibrational modes in organic molecules are associated with peaks at 1290 cm^{-1} and 1570 cm^{-1} (Heuer & Luttge, 2018). This shows that the organic functional groups of the inhibitor have been absorbed on the steel surface, forming a barrier that allows further interaction between the metal and aggressive media.

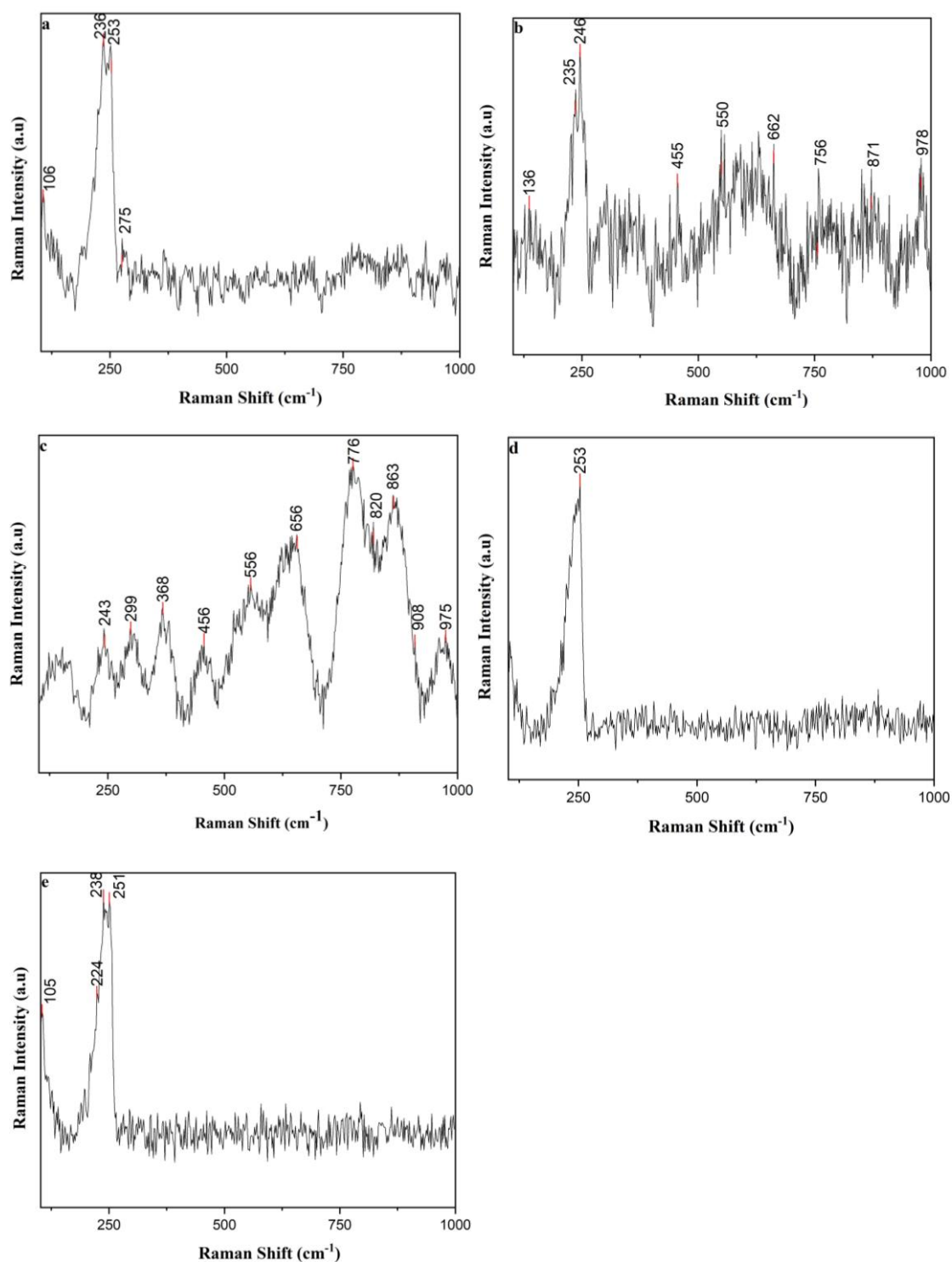


Figure 0.73: The Raman plots for a) polished, b) 3.5 % NaCl, c) 3.5 % NaCl + *Sclerocarya birrea* inhibitor, d) 1 M H₂SO₄ and, e) 1 M H₂SO₄ + *Sclerocarya birrea* inhibitor exposed aluminium (AA 1100).

Finally, the surface composition of polished aluminum before and after exposure to corrosive 3.5 % NaCl and 1 M H₂SO₄ in both the presence and absence of a corrosion inhibitor was also examined using Raman spectroscopy, like mild steel and pipeline steel. The Raman diagrams were recorded from 102 cm⁻¹ to 1000 cm⁻¹ as the noise increased and no significant peaks were observed at higher Raman shifts. To provide information about the protective or reactive properties of the aluminum surface, the study determined the chemical changes and surface species that occur under these circumstances. The effectiveness of the *Sclerocarya birrea* leaf inhibitor against aluminum degradation in aggressive media can be determined from the surface analysis of the inhibited and non-inhibited surfaces of the samples. In addition, the components of the protective layer formed can be clarified. The inhomogeneity and unevenness of the corrosion products formed on the aluminum surface resulted in uneven light distribution on the surface, resulting in fluctuations in the spectral baseline. Polished aluminum before exposure to corrosive solutions showed four distinct peaks, as shown in Figure 4.73 a, of which the peak at 106 cm⁻¹ indicated only low-frequency vibrational modes or defects in the aluminum crystal structure and could not be assigned to oxide or hydroxide (Mogensen et al., 2014) .

The peaks 236 cm⁻¹ and 253 cm⁻¹ resemble the formation of aluminum oxide (Al₂O₃) during corrosion processes (M. O. A. Ferreira et al., 2023a). Although the sample was not exposed to harsh conditions, aluminum is known to oxidize quickly when exposed to air alone, forming a protective oxide film layer. The observed peak at 275 cm⁻¹ is related to vibrational modes of aluminum oxides or other compounds that may form on the surface. For the blank sample exposed to simulated seawater, as shown in Figure 4.73 b, peaks 246, 662 and 455 cm⁻¹ indicate the presence of Al₂O₃ (Sampedro et al., 2014). Peaks at 235, 871 and 978 cm⁻¹ indicate the presence of Al (OH)₃ (Laha et al., 2005; Mindivan et al., 2008). The peak 550 cm⁻¹ is related to the stretching vibrations of the Al-O bond formed during the corrosion process of aluminum in a saline environment to form aluminum oxide (M. O. A. Ferreira et al., 2023b; Lekatou et al., 2013). The peak at 978 cm⁻¹ corresponds to the substrate as reported by Cava et al. (2007). Figure 4.73 (c) shows the peaks observed when an inhibitor was introduced into the sample exposed in 3.5 % NaCl. Several peaks were detected at 243, 299, 368, 456, 556, 656, 776, 820, 863, 908 and 975 cm⁻¹ respectively. In general, the peak indicates the presence of Al₂O₃ at 243 cm⁻¹ (Sampedro et al., 2014), α -Al₂O₃ at peaks at 368 and 456 cm⁻¹, peak areas from 365 to 369 cm⁻¹ indicate boehmite (γ -AlOOH) (Lekatou et al., 2013). The Raman shifts observed after a peak of 700 to 1000 cm⁻¹ are largely attributed to vibrations of functional groups adsorbed

on the aluminum surface. Peaks at 456, 776 and 908 cm^{-1} indicate vibrational modes associated with complexes or Al-O bonds which arise during the corrosion process (Lekatou et al., 2013; Wang et al., 2021). The presence of C=O functional groups on the aluminum surface is attributed to peaks 863 and 975 cm^{-1} (Assad & Kumar, 2021b; Joseph & Joseph, 2021). The peak 820 cm^{-1} is associated with the presence of hydroxyl groups (OH) on the metal surface (Prakashaiah et al., 2018).

Raman spectroscopy results for aluminum exposed to 1 M H_2SO_4 showed only a single significant peak at 253 cm^{-1} , as shown in Figure 4.73 d. It is usually attributed to the Al-O stretching mode of gamma-phase alumina ($\gamma\text{-Al}_2\text{O}_3$) (Y. Liu et al., 2014). Because aluminum corrodes in acidic environments, this aluminum oxide phase is often formed. A deformed cubic spinel structure in the γ phase leads to Raman active modes in the range of 200–300 cm^{-1} (Deb et al., 2000). The absence of other significant peaks could indicate that a single phase or a specific type of corrosion product, such as aluminum oxide, is dominant on the aluminum surface, without the presence of other contaminants or complicated multiphase corrosion products. Four notable peaks appear at 105, 224, 238 and 251 cm^{-1} when an inhibitor is added to the acidic medium, as shown in Figure 4.73 (e). The initial peak observed at 105 cm^{-1} indicates the metal inhibitor complex formed between the Al atoms and the inhibitor molecules of *Sclerocarya birrea* adsorbed on the surface, which may lead to new active Raman modes (Guo et al., 2022). Aluminum hydroxide ($\text{Al}(\text{OH})_3$), which is formed due to the passivation effect of the inhibitor, which reduces the direct corrosion rate, can be represented by the peak at 224 cm^{-1} (Misra, 2003). The peak 238 cm^{-1} can be attributed to Al-S or Al-N bonds formed by the adsorption of inhibitor molecules containing sulfur or nitrogen (Xhanari & Finšgar, 2019). These interactions change the surface chemistry of the aluminum, which can be seen in the low-frequency Raman region (Figure 4.73 e). This peak is likely due to $\gamma\text{-Al}_3\text{O}_4$ (gamma alumina), as is the peak at 253 cm^{-1} in the absence of an inhibitor. The presence of *Sclerocarya birrea* inhibitory molecules on the Al surface is responsible for the peak's shift.

Chapter 5 Summary, Conclusions and Scope for future work

5.1 Summary and conclusions

The major findings of this study dubbed “ **Corrosion mechanism and inhibition performance of *Sclerocarya birrea* (marula) leaf inhibitor in acidic and simulated seawater environments**” are summarized in this chapter. Descent work has been carried out to examine the performance of *Sclerocarya birrea* inhibitor in 3.5 % NaCl and 1 M H₂SO₄ corrosive environments for mild steel, API 5L X42 pipeline steel and Aluminium (AA 1100) alloy.

The study started off with phytochemical characterization of the *Sclerocarya birrea* ethanolic extract to identify phytochemical compounds , functional groups and other bioactive compounds that would aid in corrosion inhibition using phytochemical screening, FTIR, UV-Vis and GC-MS techniques. The initial phytochemical analysis indicated the existence of glycosides, phenols, flavonoids, terpenoids and alkaloids. The UV-Vis analysis detected characteristic peaks resembling chromophores within the wavelength spectrum from 200 to 800 nm. Meanwhile, the presence of alkanes, alkenes, phenols, esters, amines, aromatic rings, carboxylic acids etc. were confirmed using FTIR. Using GC-MS analysis 17 phytochemical and bioactive compounds were also discovered, including major phytochemical constituents such as phytol, pagicerine, octadecanoic acid, γ -Sitosterol and Hexadecanoic acid, ethyl ester which exhibited the highest peaks in the chromatograph. Due to this rich profile, *Sclerocarya birrea* qualified to be used as a potential corrosion inhibitor, taking into consideration various factors which may affect the extract’s performance such as media, type of material used and operating conditions.

Mass loss method was then implored to measure the inhibitor efficacy at room temperature over long duration and at various temperatures at shorter time durations . The corrosion rates, effectiveness of inhibition and surface coverage were calculated from the mass loss data. The outcomes validated the leaf extract's competence in decreasing corrosion in all tested metals, since the unconstrained (blank) samples showed considerably higher corrosion rates than those treated with the inhibitor. Moreover, metals exposed to 1 M H₂SO₄ corroded more severely than those in 3.5 % NaCl, demonstrating the harshness of the acidic environment. Among the metals studied, aluminum alloy had a negligible corrosion rate in a simulated seawater environment and low corrosion rates in 1 M H₂SO₄. Aluminum's protective mechanism was attributed to the creation of persistent oxide layer, enhanced further by the inhibitor particle adsorption, which served as an efficient barrier against further corrosion. The observed decline

in inhibitory efficacy with time is consistent with the physical properties of inhibitor particle adsorption on metal surfaces. This decrease in efficacy with greater exposure length suggests the need for periodic reapplication or adjustment of the inhibitor for long-term protection. In contrast, inhibition efficacy improved with increasing inhibitor dosage, indicating that *Sclerocarya birrea* phytochemical and bio-active chemicals play a critical role in strengthening corrosion resistance when present in higher amounts. For the weight loss with varying temperatures, thermodynamics and adsorption studies were computed to deduce inhibition mechanisms.

Electrochemical measurements techniques among others open circuit potential (OCP), Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) were employed to determine inhibitor efficiency, deduce its mechanism of inhibition and evaluate impact of charge resistance on inhibitor performance. According to the results of these electrochemical experiments, in both the 3.5 % NaCl and the 1 M H₂SO₄ corrosive environments, corrosion inhibition efficiency rises as the inhibitor concentration does. In comparison to uninhibited samples, the OCP measurements showed a shift towards more noble potential when the inhibitor is present, indicating inhibitor stabilization of the metallic surface against degradation. The shifts provide partial protection because of the creation of an inhibitive layer that prevents anodic breakdown, even if they are not significant enough to signify full passivation. Depressed partial semicircles were visible in the Nyquist plots for the electrochemical impedance spectroscopy data, indicating that charged transfer dominated the reactions with some surface inhomogeneity evident. Increases in inhibitor concentration were shown to slow down metal degradation by increasing the charge transfer resistance (R_{ct}) and decreasing the double layer capacitance (C_{dl}). This was achieved owing to the inhibitor molecules absorption on the metal surface and hence inhibiting active metal sites. The inhibitor reduces anodic metal dissolution as well as cathodic processes, acting as a mixed-type inhibitor as reflected by potentiodynamic polarisation curves. The reduced corrosion current densities (I_{corr}) observed with increased inhibitor concentration, which is directly correlated with improved inhibition efficiency, are indicative of this mixed inhibition behaviour. The change in the anodic and cathodic branches provides additional evidence that the inhibitor blocks active sites, lowering the metal surface's reactivity.

As for the quantum chemical calculations, Density Functional Theory (DFT) and Monte Carlo (MC) simulations were implored to predict the performance of five derivatives of *Sclerocarya birrea* ethanolic leaf extract. The inhibition efficacy of *Sclerocarya birrea* inhibitor derivatives

was evaluated using the density functional theory (DFT) at B3LYP function and ab initio MP2 while adsorption mechanism of these derivatives was studied by monte Carlo simulations. According to the quantum chemical calculations obtained from this study, 3,7,11,15-Tetramethyl-2-hexadecen-1-ol (T1), ethanol, 2- (Octadecyloxy) (T2), hexadecanoic acid, ethyl ester (T3), octadecanoic acid, ethyl ester (T4) and Octadecanoic acid (T5), will be effective in prevention of aluminum degradation in aqueous environments. From the DFT and monte Carlo simulation studies the inhibition performance of the derivatives are this order $T1 > T3 > T2 > T4$. Based on adsorption energy, the results show that T1 is the most effective inhibitor among the four derivatives which means it is the one which gives the strongest adsorption of the four.

The formation of corrosion products, inhibitor-metal complexes, and thin films on samples subjected to 3.5 % NaCl and 1 M H_2SO_4 with and without *Sclerocarya birrea* inhibitors were identified by surface analysis using XRD and Ramman spectroscopy techniques. To monitor any surface changes, the samples were analyzed both before and after being exposed to hostile settings. The XRD results for pipeline steel showed that blank exposed sample to acidic conditions formed FeOOH at $2\theta = 28.83^\circ$ and Fe_2O_3 at $2\theta = 35.37^\circ$. However, the peaks disappeared when an inhibitor was applied. Similarly, mild steel exposed to acidic environments showed the formation of new peaks at $2\theta = 37.71^\circ$ and 48.67° , indicating FeOOH production. Aluminum samples did not show the development of new peaks in any of the corrosive media. In general, for all metals, the peak intensity decreased in inhibited samples, indicating physisorption and the development of a metal complex to protect the metal in aggressive environments. It was clear from the findings of the Raman spectroscopic investigation that mild steel and pipeline had hematite and lepidocrocite as the predominant oxides, whereas aluminium (AA 1100) had aluminium oxide (Al_2O_3), boehmite ($\gamma-AlOOH$) and aluminium oxide (Al-O) bonds. Functional groups such C-O, C-H, and C=C were found on the surface and formed metal complexes for mild steel and pipeline steel following the injection of the inhibitor. Additionally, to the functional groups detected in mild steel and pipeline steel samples, OH functional groups were detected after the inhibitor was introduced for aluminium exposed to both 3.5 % NaCl and 1 M H_2SO_4 .

In summary, *Sclerocarya birrea* inhibitors have shown green potential to be used as an alternative to synthetic corrosion inhibitors for API 5L X42 pipeline steel, mild steel and aluminium (AA1100). The inhibitor works by adsorbing on the metal surface to form a thin coating and blocking the active metal sites. It functions as a hybrid inhibitor, decelerating both

cathodic and anodic processes. *S. birrea* retards metal degradation through physisorption, as the inhibitor concentration rises, its inhibition efficacy rises as well. The Langmuir and Temkin adsorption isotherms are primarily responsible for the adsorption. For these three metals different corrosion monitoring techniques have shown that aluminium (AA 1100) is the least corrosive, followed by mild steel and pipeline being the most corrosive in all the examined corrosive environments.

5.2 Scope for future study

Despite the excellent outcomes of the investigation into *Sclerocarya birrea* leaf inhibitor as a potential eco-friendly inhibitor for aluminium (AA 1100), API 5L X42 pipeline and mild steel in both acidic and simulated seawater environments, much more work needs to be done to expand this study. These are as follows:

- i) Isolation of *Sclerocarya birrea* inhibitor phytochemicals like pagicerine, octadecanoic acid ethyl ester, ethanol, 2 (octadecyloxy) and phytol to use them individually for corrosion inhibition.
- ii) Implore machine learning and artificial intelligence algorithms to develop predictive models for *Sclerocarya birrea* inhibitor derivatives inhibition performance for various metals in diverse corrosive environments.
- iii) Carry out the same corrosion inhibition analysis using different parts of marula tree (*Sclerocarya birrea*) like fruit peels, roots and bark to compare their efficiencies.
- iv) To conduct surface analysis on metal samples both pre and post exposure to corrosive media using Scanning Electron Microscopy (SEM-EDS), Auger Electron Spectroscopy (AES), Atomic Force Microscopy (AFM) and X-Ray Photoelectron Spectroscopy (XPS).
- v) Further utilization of electrochemical techniques like Chronoamperometry and cyclic voltametric tests to determine effect of exposure duration on metal corrosion as well as the underlying corrosion mechanism by the inhibitor.
- vi) To test the produced green corrosion inhibitors in electroplating and wastewater transmission industries to compare their performance against the synthetic inhibitors.
- vii) To commercialize *Sclerocarya birrea* inhibitor as an alternative to synthetic corrosion inhibitors after optimization and industrial application trials.

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Appendices

Sample Calculations

Preparation of 3.5 % NaCl

The calculations are as follows.

$$\frac{x}{300ml} \times 100 \% = 3.5 \% NaCl ; x = \frac{3.5 \times 300}{100} = 10.5 g \dots\dots\dots(1)$$

Preparation of 1 M H₂SO₄

To calculate the volume of sulfuric acid needed to produce a 300 mL solution of 1 M (molar) concentration, using these formulas:

$$Molarity = \frac{\text{moles of solute}}{\text{volume of solution in litres}} \dots\dots\dots(2)$$

$$Volume \text{ of solution} = \frac{\text{no.of moles}}{Molarity} \dots\dots\dots(3)$$

Molarity = 1 mol/L ; Volume of solution = 300 mL = 0.3 L

$$Moles \text{ of solute} = \left(1 \frac{mol}{L}\right) \times (0.3 L) = 0.3 mols \dots\dots\dots(4)$$

Molar weight of H₂SO₄ = (2 × 1.00784) + (32.065) + (4×15.999) = 98.07668 ml/mol

$$Volume \text{ of solute (ml)} = (0.3 mol) \times \left(98.07668 \frac{ml}{mol}\right) = 29.423004 ml = 29ml \dots\dots(5)$$

Preparation of the inhibitor concentrations

To make 5 g/L: C₁ = 200 g/L, V₁ = 3 ml, C₂ = 5 g/L, V₂ = ?

$$C_1V_1 = C_2V_2 ; \left(200 \frac{g}{L}\right) \times (0.003 L) = \left(5 \frac{g}{L}\right) \times V_2 \dots\dots\dots(6)$$

$$\text{Therefore, } V_2 = \frac{0.6}{5} = 0.12 L = 120 ml \dots\dots\dots(7)$$

For 20 g/L: C₁ = 200 g/L, V₁ = 3 ml, C₂ = 20 g/L, V₂ = ?

$$C_1V_1 = C_2V_2 ; \left(200 \frac{g}{L}\right) \times (0.003 L) = \left(20 \frac{g}{L}\right) \times V_2 \dots\dots\dots(8)$$

$$\text{Therefore, } V_2 = \frac{0.6}{20} = 0.03 L = 30 ml \dots\dots\dots(9)$$