INHIBITION OF MILD STEEL CORROSION USING *CARICA PAPAYA* AND BITTER-LEAF EXTRACTS IN 1.5M H_2SO_4 ENVIRONMENT

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CERTIFICATION

This is to certify that this work "**Inhibition of Mild Steel Corrosion in H_2SO_4 by *Vernonia Amygdalina* and *Carica Papaya* Leaf-Extracts**" was carried out by **Nwadike, Chikezie Obioma Magnus (20194197908)** in partial fulfilment of the requirements for the award of Master of Engineering Degree in Materials Engineering in the Department of Materials and Metallurgical Engineering, Federal University of Technology, Owerri.

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DEDICATION

This work is dedicated to Almighty God for his provisions in the course of carrying out this study. I also wish to humbly mention my parents: Late Mr. & Mrs. Philip & Bernadine Nwadike whom God used to set up the foundation of my academics.

To God be the glory!

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ABSTRACT

This work concerns the corrosion inhibition of mild steel in 1.5M H_2SO_4 solution with and without the addition of plant-leaf extracts of *Vernonia amygdalina* (VA) and *Carica papaya* (CP). The inhibitor was obtained by filtering the juice from the ground fresh leaves of VA and CP. Weight loss technique was employed in the corrosion study while phytochemical analyses were conducted on the examined plant leaves to unravel the bioactive constituents. The duration of exposure time of specimens in the study environment spanned for 24, 48, 72, 96, and 120 hours. The concentrations of the inhibitors were added at 5ml, 10ml, 15ml, and 20ml respectively. On the other hand, the inhibitor concentrations of the synergetic admixture (SA) were added such that CP or VA had the constant concentration (2ml) and remaining concentrations were augmented by the other at 5mL (2ml + 3ml), 10mL (2ml + 8ml), 15mL (2ml + 13ml), and 20mL (2ml + 18ml) respectively. Results revealed that the corrosion of mild steel in a 1.5 M H2SO4 solution was inhibited by the addition of both *Vernonia amygdalina* and papaya leaf extracts. As the VA leaf extract concentration was raised, the corrosion rate reduced, with the maximum inhibition efficacy of 64.8% being attained with 20 mL of VA after 24 hours. However, from 24 to 120 hours, a gradual decline in the inhibitor's potency was observed, which suggests that 20 mL concentration of VA does not offer a tenacious covering of the mild steel in 1.5 M H_2SO_4 for a longer period. The inclusion of Carica papaya leaf extract prevented mild steel from corroding in 1.5M H_2SO_4. After 48 hours, 20 mL of CP leaf extract produced the maximum inhibitory efficacy of about 86.89%. When *Vernonia amygdalina* and *Carica papaya* leaf extracts were combined, they demonstrated superior corrosion inhibition when compared to VA alone. The mixture of 18 mL of VA and 2 mL of CP showed the greatest degree of inhibitory effectiveness. Comparing *Vernonia amygdalina* to *Carica papaya* leaf extract, the latter appeared to be more successful in preventing corrosion in 1.5 M H_2SO_4 due to better inhibitory efficiency. The phytochemical analyses of the examined leaves revealed the presence of tannin, phytate, phenol, hydrogen cyanide, and alkaloid. To predict the observed corrosion rates, multiple regression (MR) and artificial neural network (ANN) models were applied. In general, ANN predictions had less errors than MR predictions, indicating that ANN is better at predicting nonlinear corrosion inhibition relationships.

Keywords: Corrosion inhibition, *Vernonia amygdalina*, *Carica papaya*, leaf-extract, Artificial neural network, Multiple regression.

CHAPTER ONE

INTRODUCTION

1.1 Background of Study

The broad array of structural materials available to advanced and emerging technologies has expanded the series from which they are chosen, allowing engineers to select the most suited material for each application based on physical or mechanical characteristics. Metallic materials have an essential role in a nation's development and its long-term progress in the global economy. There is no application, however, where the consequence of a metal or alloy's interaction with its surroundings can be entirely ignored. Corrosion is a natural process in which metals and alloys attempt to return to their more stable thermodynamic state as a result of chemical attack or reactivity with their surroundings. In other words, metals, with the exception of platinum and gold, are found in nature in impure forms, mainly as oxides or sulfides, which are stable. In most processing techniques, energy is consumed to obtain pure metals, causing the pure metals to be in a higher energy state compared to their ore. As a result, metals corrosion is the simplest and fastest way to reach their most stable state. Corrosion can also be triggered by natural or man-made causes. In general, metals corrosion is described as the natural and inevitable loss of desired metal characteristics due to interaction with particular elements present in the environment. (Ali Zakeri, Elnaz Bahmani, Alireza Sabour Rouh Aghdam, Dept of Materials Science and Engineering Ontario University, Canada, April, 2022). It can affect various materials such as engineering materials (metals, alloys, plastics, paint, and rubber), covalent and ionic substances, aggregates (composite materials and concrete, (© 2021 American Chemical Society).

Corrosion which is also the degradative interaction between a metallic material and its environment is a problem in the industrial sector where there are loss of production time and waste of resources for maintenance, reduction of output capacity and service satisfaction for production and delivery, contamination of products and environment by corrosion products, and ultimately risk of equipment failure for service and production including loss of lives and other collateral damages.

The economic cost of corrosion includes direct and indirect losses, which can be subdivided into four main categories, namely capital (e.g., replacement of equipment), control (e.g., corrosion control, repair, and maintenance), design (e.g., corrosion allowance and materials of construction), and associated (e.g., insurance and technical support) costs. The estimated costs of corrosion in some countries around the world shows that corrosion costs have significant consequences on the national economies of countries, which can reach about 2–4% of gross national product, according to an investigation by the National Association of Corrosion Engineers. To minimize such economic losses and combat corrosion, research has been ongoing in different dimensions as scientists and Engineers are exploring the affordable and effective ways and means to curb this menace. There are many alternatives taken to prevent corrosion nowadays, like choosing anti-corrosive materials in the real environment, design modifications to the system or components, electrochemical control, conditioning the metal and modifying the environment either by removing the oxygen or adding inhibitors (Norzila Mohd & Anis Suhaina Ishak, 2015; Rahuma, Amer, & Alfergani, 2014). Among them, the use of inhibitors as corrosion control reagents has become popular and gained attention due to their practical applicability in many unit operation systems (Norzila Mohd & Anis Suhaina Ishak, 2015).

In order to minimize corrosion challenges in the Industrial and Engineering sector, research is ongoing to find a more eco-friendly approach and this has led to the discovery of green inhibitors as a better option than synthetic Inhibitors that are often toxic, expensive and highly technical in application while green inhibitors are ecofriendly, safe, affordable, and biocompatible.

This research is the study of the inhibition of mild steel corrosion in sulphuric acid through the use of bitter leaf and Pawpaw leaf extracts. It is focused on exploring ecofriendly and cost-effective methods for protecting metals with respect to corrosion efficiency of the synergy. Having determined their individualistic corrosion efficiency, this research investigates the effectiveness of these plant extracts as corrosion inhibitors, which are alternatives to synthetic options that are often toxic and harmful to the environment when applied together. This is because the extracts contain organic compounds responsible for this inhibitive ability, and their performance varies with temperature and concentration of the inhibitor. The adsorption of the inhibitor molecules on the metal surface is consistent with the Langmuir adsorption isotherm, indicating a spontaneous and physical adsorption process.

Similarly, other studies have found that the leaves extract of plants like Luffa aegyptiaca and Morinda tinctoria also demonstrate effective corrosion inhibition in sulphuric acid medium. The efficiency of these inhibitors generally increases with the concentration of the extract but decreases with rising temperature. The addition of halide ions has been reported to improve the efficiency synergistically.

These findings suggest that plant extracts, including those from bitter leaf and pawpaw, could serve as sustainable and environmentally benign alternatives to conventional corrosion inhibitors, offering a green approach to corrosion control in industrial applications involving mild steel and acidic environments.

These inhibitors slow down the corrosion rate and thus prevent monetary losses due to metallic corrosion on industrial vessels, equipment, or surfaces (Chigondo Marko & Chigondo Fidelis, 2016). Corrosion failures are minimized by appropriate design, proper material selection, and control of metallurgical structure through heat treatments and the use of inhibitors (Asogwa et al., 2020).

This research will go a long way in solving the menace of corrosion since Industries frequently perform acid cleaning, pickling, descaling, and oil well-acidizing operations on metallic materials in acidic media. Cleaning agents used in these operations include hydrochloric acid, sulphuric acid, phosphoric acid, nitric acid, and others (Goyal et al., 2018). Tanks, storage facilities, pipelines, marine constructions, autos, bridges, and other structures deteriorate due to corrosion, which causes material and economic losses. In the chemical or petrochemical industries, some materials or components are exposed to a particular environment (acidic environments), making them prone to corrosion. As a result, corrosion must be prevented or at the very least slowed down.

Phytochemical tests conducted by researchers have shown that plant leaf extracts are excellent corrosion inhibitors – acting as rich sources of natural organic inhibitors that can be extracted seamlessly. For instance, *Fenugreek* leaves (Noor, 2007), *Piper guineas* extract (Ebenso et al., 2008), Fagetes erecta (Mourya et al., 2014), *Gangronema latifolium* (Eddy & Ebenso, 2010), *Combretum bractcosum* extracts (Okafor et al., 2009), *Carica papaya* (Omotioma & Onukwuli, 2016), *Garcinia Kola* extract (Okafor et al., 2010), *Vernonia amygdalina* (Odiongenyi et al., 2009), to mention a few have all proven to be excellent inhibitors in acidic environments.

This study focuses on the individual and combined effect of *Vernonia amygdalina* and *Carica papaya* as corrosion inhibitors wherein the inhibition efficiency of these extracts was evaluated using the weight loss technique.

In the present condition of research laboratories in Nigeria where the needed facilities to conduct corrosion studies are not available, the modelling of experimental data with viable predictive protocols becomes desirable. Both Artificial Neural Networks (ANNs) and Multiple Regression (MR) were employed in the current study to forecast the experimental corrosion rate of mild steel in the study environment.

1.2 Problem Statement

Several effective corrosion inhibitors of steel and other alloys that are synthesized and chromate-based are either expensive or toxic. Recently, the use of chromate-based inhibitors is discontinued because of its adverse consequences of toxicity and high cost. Researchers are now seeking alternative inhibitors that would not only be effective but eco-friendly and economical. It is on this basis that this study seeks to study the effectiveness of *Vernonia amygdalina* and *Carica Papaya* as potential corrosion inhibitors for mild steel in 1.5M sulphuric acid.

1.3 Aims/Objectives of Study

The major aim of the study is to evaluate the effectiveness of the combination of *Vernonia amygdalina* and *Carica papaya* plant-leaf extracts as corrosion inhibitors for mild steel in a corrosive environment (1.5M H_2SO_4).

The specific objectives of the research are to study the:

1. effect of addition of leaf extract of *Vernonia amygdalina* plant on the corrosion of mild steel immersed in 1.5M H_2SO_4.

2. effect of addition of plant leaf extract of *Carica papaya* on the corrosion of mild steel immersed in 1.5M H_2SO_4.
3. influence of addition of the combination of *Vernonia amygdalina* (VA) and Carica papaya leaf-extracts on the corrosion of mild steel immersed in 1.5M H_2S0_4 (CP to be maintained at 2 mL while the remaining concentration is to be augmented by (VA) and vice versa.
4. the phytochemicals present in the examined plant-leaves, and to
5. employ predictive models driven by multiple regression (MR) and artificial neural network (ANN to predict the corrosion Inhibition behavior of the leafextracts of *Vernonia amygdalina* (VA) and *Carica papaya* (CP) plants in 1.5M H_2SO_4.

1.4 Justification of Study

The justification of this research lies on the fact that *Vernonia amygdalina* and *Carica papaya* plant leaf extracts used in this research to inhibit mild steel corrosion in 1.5M H_2SO_4, are natural, eco-friendly and sustainable, and so the research is both scientifically relevant and environmentally significant in real life industrial application because as H_2SO_4 is widely used in various industrial processes, including acid pickling, cleaning, descaling, and oil well acidizing, its aggressive nature toward mild steel leads to metal dissolution but the use of green inhibitors as in the case study will prevent this metal loss. The Eco-Friendly nature of these green inhibitors will be a comparative advantage to traditional synthetic inhibitors that are often toxic and pose risks to both humans and the environment. Exploring these leaves' inhibitory properties, will aid the development of sustainable solutions for protecting metals in aggressive environments. Also, examining the inhibitory efficiency's time-dependent behavior will provide important information about how long these plant extracts will protect against corrosion and such information will aid development of corrosion prevention measures. A quantitative knowledge of the interactions between several parameters impacting corrosion, such as period of exposure and inhibitor concentration, is provided by the predictive models powered by ANN and MR that are applied. This work gains more credibility from the comparison of ANN and MR models as well as the confirmation of predictions. This discovery will have important applications for companies that handle mild steel in acidic conditions.

1.5 Scope of Study

In this study, only extracts of *Vernonia amygdalina* and *Carica papaya* plant leaves were utilized as inhibitors. Also, this medium utilized was 1M H_2SO_4 containing different concentrations of the above plant leaves extracts. The study will explore how these extracts affect the corrosion rate of mild steel, also investigate the optimal concentration of the extracts for maximum inhibition efficiency. Different extract concentrations will be tested to determine the most effective dosage. Weight loss technique was employed in the study to quantify the corrosion rate. The extent of metal dissolution in the presence of the extracts will be compared to the control (without inhibitors). The study will delve into the adsorption behavior of the extracts on the mild steel surface in order to understand how the extracts form a protective layer on the metal surface and determine if it is in agreement with the Langmuir adsorption isotherm. Parameters that can affect the inhibition efficiency e.g., time of exposure, concentration will be determined. Phytochemical analysis of the plant leaf specimen will be carried out for the quantification of the active ingredients responsible for the inhibition. The results will have practical implications for corrosion control in acidic environments. Data analysis will be done using IBM® SPSS® software, multiple regression, and artificial neural networks to forecast corrosion rate depending on inhibitor concentrations and exposure times.

CHAPTER TWO

LITERATURE REVIEW

2.1 Corrosion

Corrosion is the irreversible and spontaneous degradation of materials (usually metals and alloys) due to its reaction with its environment. When corrosion occurs, metals tend to revert to their natural combined state as oxides, sulphates, suphides, carbonates, amongst others. Metals spontaneously corrode due to a drop in free energy, the original compounds (minerals and ores) are recovered. Hence, energy consumed for alloying or extracting metal from ore is released during corrosion reactions. (Popov, 2015).

A widely accepted definition from the International Union of Pure and Applied Chemistry (IUPAC), encompasses the degradation of non-metals in addition to metallic materials as follows: "Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, polymer, amongst others) with its environment which results in consumption of the material or dissolution into the material of a component of the environment. Often, but not necessarily, corrosion results in effects that are detrimental to the usage of the material considered. Exclusively, physical, or mechanical processes such as melting or evaporation, abrasion or mechanical fracture are not included in the term 'corrosion'.

2.2 Corrosion Control Techniques

A material or substance will gradually deteriorate through the process of corrosion because of chemical interactions with the environment. It is a big problem in many different industries, including manufacturing, infrastructure, transportation, and building. Here are several techniques for controlling corrosion:

2.2.1 Cathodic protection

It is a technique used to stop metal from corroding by applying an external electrical current to it. For infrastructure like pipelines, tanks, and offshore platforms, this technique is applied. The two methods of cathodic protection are impressed current and sacrificial anode. A highly reactive metal (anode) is connected to the metal to be protected (cathode) in sacrificial anode cathodic protection to stop corrosion. On the other hand, impressed current cathodic protection uses an external power source to deliver an electrical current to the metal that must be protected. (Institute of Corrosion, Northampton UK, 2023).

2.2.2 Coatings

To protect a metal's surface from the elements and stop corrosion, protective coatings are applied. Polymers, epoxies, and metals are just a few of the materials that can be used to create coatings. Coating quality, adherence, and thickness all affect how effective they are. Some coatings can shield metal against types of corrosion due to their unique chemical properties. For instance, galvanic corrosion can be prevented by coatings made of zinc or aluminum. (Corrosion Resistant Coatings for Steel – Types and Uses, Secoa publication, 2023).

2.2.3 Design Modification

A structure's design might be changed to lessen the chance of corrosion. For instance, corrosion-resistant materials can be utilized, and the structure's design can be altered to increase corrosion resistance. Improvements in drainage and ventilation can also be made to lessen the buildup of moisture and humidity, which can hasten corrosion (Institute of Corrosion, Northampton UK, 2023).

2.2.4 Environmental Control

The environment in which the metal is located can be managed to prevent corrosion. Temperature, humidity, and the presence of corrosive gases can all be managed to achieve this. For instance, stainless steel is utilized in the food sector because it resists corrosion in acidic situations (Sastri, 2011; Revie & Uhlig 2008; NACE International, 2006; Mansfeld, & Kendig, 2006; Lefèvre, 2008).

2.2.5 Corrosion Inhibitors

They are chemical substances (inorganic or organic; solid, liquid or gases) which when added in small concentrations reduce the rate at which an (engineering) material corrodes. Corrosion inhibitors provide a passive coating on the metal surface to prevent direct contact between the metal and the corrosive fluid.

They find applications in chemical and petrochemical industries, petroleum refineries, water treatment industries, heavy manufacturing, and product additive industries where they are considered as the primary line of defense. They are available in spray form with a lubricant and maybe a penetrating oil; they can be used in situ without significantly unsettling the process because they do not react with the fluid (Institute of Corrosion, Northampton UK, 2023).

2.3 Types of Corrosion Inhibitors

Corrosion inhibitors are compounds that are added to fluids, gases, or metals to prevent or reduce the rate of corrosion. These inhibitors work by forming a protective layer on the metal surface or by reacting with the metal to form a more stable compound (Sastri, 2011; Shukla, Quraish, & Singh, 2013; Raja & Sethurama, 2012; Tukur, 2013; El-Etre, 2010). Here are some types/classes of corrosion inhibitors:

2.3.1 Anodic Inhibitors

Anodic inhibitors work by preventing the anodic reaction of corrosion, which involves the oxidation of the metal. These inhibitors are usually applied to the anodic areas of the metal surface to prevent oxidation. Examples of anodic inhibitors include chromates, molybdates, and nitrites (Corrosionpedia publication, 2024).

2.3.2 Cathodic Inhibitors

Cathodic inhibitors work by preventing the cathodic reaction of corrosion, which involves the reduction of oxygen or hydrogen ions. These inhibitors are usually applied to the cathodic areas of the metal surface to prevent reduction. Examples of cathodic inhibitors include mercaptans, sulfides, and amines (Corrosionpedia publication, 2024).

2.3.3 Mixed Inhibitors

Mixed inhibitors are compounds that inhibit both the anodic and cathodic reactions of corrosion. These inhibitors are usually more effective than anodic or cathodic inhibitors alone. Examples of mixed inhibitors include benzotriazole, tolyltriazole, and imidazolines (Corrosionpedia publication, 2024).

2.3.4 Organic Inhibitors

Organic inhibitors are compounds that contain carbon and are usually derived from organic compounds such as amines, imines, or heterocyclic compounds. These inhibitors work by forming a protective film on the metal surface, which prevents corrosion. Examples of organic inhibitors include aliphatic amines, aldehydes, and ketones (Corrosionpedia publication, 2024).

2.3.5 Inorganic Inhibitors

Inorganic inhibitors are compounds that do not contain carbon and are usually derived from inorganic compounds such as phosphates, silicates, or chromates. These inhibitors work by forming a protective layer on the metal surface or by reacting with the metal to form a more stable compound. Examples of inorganic inhibitors include phosphates, silicates, and chromates (Corrosionpedia publication, 2024).

2.4 Factors to be Considered when Selecting Inhibitors

While selecting an inhibitor, there are numerous factors to consider:

1. The price of the inhibitor may occasionally be quite high if a costly material is used or if a large quantity is required.
2. The inhibitor's toxicity may have detrimental consequences on people and other living things.
3. The choice of inhibitor will depend on its availability, and if availability is poor, the inhibitor will likely become pricey.
4. Environmental- friendliness. (Raja & Sethuraman, 2008).

2.5 Green Inhibitors

Although synthetic inhibitors are frequently used to control corrosion, they are poisonous and harmful to the environment: Green inhibitors are being tried to replace these potentially dangerous chemicals (Rani & Bas, 2011) partially or completely.

Green inhibitors are cheap, bio-compatible, non-toxic, and eco-friendly inhibitors obtained from cheap, natural, and renewable sources providing high inhibition efficiency in corrosive media. Green inhibitors are divided into organic and inorganic categories. The natural substances obtained from organic green sources, such as plants, include flavonoids, alkaloids, and other natural compounds. Numerous studies prove that green inhibitors are particularly effective at delaying steel corrosion, including weight loss, electrochemical impedance, and potentiodynamic polarization approaches (Wei et al., 2020). The two plant leaves utilized in the present study are *Vernonia amygdalina* and *Carica Papaya*.

2.5.1 *Vernonia amygdalina* leaves

Vernonia amygdalina is popularly known as ‘Bitter leaf’. It is a tiny shrub with rough bark and dark green foliage that is primarily found in tropical Africa, though it has been domesticated in many regions of West Africa. The leaves of this plant are used as vegetables for preparing bitter leaf soup (Igile et al., 1994). The usual height of *Vernonia amygdalina* is between two and five meters (6.6–16.4 ft). Up to 20 cm (7.9 in) long, the leaves are elliptical (Ijeh & Ejike, 2011) [Plate 2.1].

Plate 2.1: *Vernonia amygdalina leaves*

A few of the bioactive substances found in *Vernonia amygdalina* that have been connected to both its ethnobotanical and industrial uses as a green inhibitor include alkaloids, saponins, terpenes, lignans, flavonoids, phenolic acids, steroids, anthraquinone, coumarins, sesquiterpenes, xanthones, and edotides (Cimanga et al., 2004; Muraina et al., 2010). The study investigated the effect of bitter leaf extract on mild steel corrosion in 1.5 M sulphuric acid solution. Techniques such as weight loss were employed to evaluate the inhibitory performance. Bitter leaf extract demonstrated inhibition efficiency in reducing mild steel corrosion, especially at specific concentrations and temperatures.

2.5.2 *Carica papaya* leaves

Carica papaya is commonly referred to as papaya or the "paw-paw plant - a herbaceous succulent plant from the Caricaceae family. It is utilized for a variety of purposes, including anti-inflammatory, antioxidant, diuretic, antibacterial, abortifacient, vermifuge, hypoglycemic, antifungal action, antihelmenthic, and immunomodulatory. There is scientific evidence for their adaptable biological role, which supports its utilization in several disorders traditionally.

Plate 2.2: *Carica papaya*

Carica papaya leaf extract has been explored as a natural eco-friendly corrosion inhibitor with a lot of comparative advantage because it is

a. Non-toxicity: They are safe for the environment and human health.
b. Biodegradability: They break down naturally without causing harm.

c. Cost-effectiveness: Obtained from natural sources, they are often affordable.
d. Renewability: These inhibitors can be sustainably sourced.
e. Safety of Application: They pose minimal risks during handling.

According to phytochemical investigations, the *Carica papaya* plant primarily contains bioactive compounds like the alkaloids carpaine and pseudocarpaine, as well as tannins, flavonoids, carcin, gamma terpine, glycoside carposides, sugars, and other compounds (Roshan et al., 2014).

2.6 Active Ingredients in Plant Leaves

2.6.1 Tannin

Tannin is a naturally occurring chemical found in leaves, wood, bark, rhizomes, roots, and fruits, among other parts of the plant kingdom. It belongs to the family of polyphenols. Fruits, vegetables, and many plants in general contain polyphenols, which are antioxidant compounds that protect tissues from cellular aging. Tannins are present in the majority of plant species across the kingdom; they serve to protect the plant from predators and may also aid in growth regulation (Das et al., 2020). The tannins that accumulate in tree bark shield the tree from bacterial and fungal infections. The tannins in this instance precipitate out the enzymes and other protein exudates from the fungus and bacteria, preventing the tree from becoming infected by them. In many woody plants, tannins are found in the bud scales that shield the inner leaf tissue from being eaten. In many seed plants, tannins are also found in the first set of leaves that emerge from a germination seed. The chemical structure of tannin is shown in Figure 2.1.

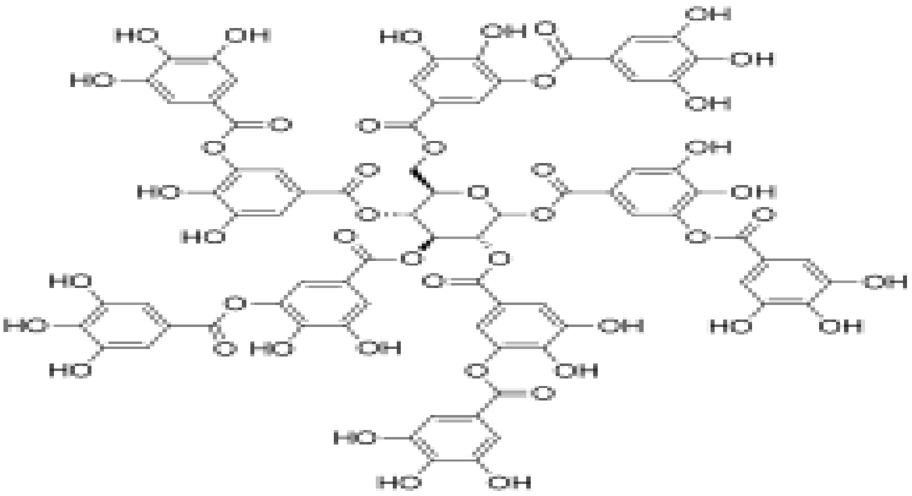


Figure 2.1: The chemical structure of tannin (In Wikipedia, 2023b)

2.6.2 Phenol

Plants generate phenolic chemicals primarily for growth, development, and protection. These molecules with an aromatic benzene ring are crucial for the plant's interactions with both biotic and abiotic stresses. They are an integral component of the secondary metabolites found in plants and are necessary for several physiological and mechanical processes. These varied plant phenolic chemicals have opposing effects on different environmental species, acting as both attractants and repellents (Pratyusha, 2022). They could serve as toxicants to drive away invasive diseases and pests as well as attract beneficial species. As the initial line of defense for plant disease resistance, these metabolite compounds frequently improve under a variety of stressful circumstances. Reactive oxygen species production and phytoalexin biosynthesis are two more plant metabolic processes that they are known to affect. These phenolic substances take part in the defensive mechanisms of plants both above and below ground. They are created as root exudates and have an impact on the variety of the nearby plants as well as the soil. The current article gives a general overview of the functions of plant phenolic compounds as defensive, antibacterial, pigment, and signaling molecules throughout the plant kingdom. The simple chemical structure of phenol is shown below.

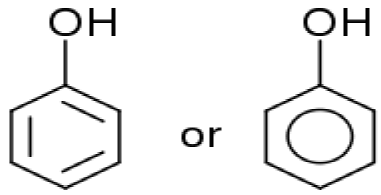


Figure 2.2: The simplest chemical structure of phenol (Naturally occurring phenols, 2023)

2.6.3 Alkaloid

Alkaloids are a broad class of chemical compounds that exist naturally and have one or more nitrogen atoms (sometimes amido or amino) in their structures. These compounds' alkalinity is a result of these nitrogen atoms. Usually, these nitrogen atoms are arranged in a ring-like (cyclic) structure. For instance, the nitrogen atom in the indole ring system is present in indole alkaloids. Alkaloids can be categorized into classes such as indoles, quinolines, isoquinolines, pyrrolidines, pyrrolizidines, tropanes, terpenoids, and steroids mostly based on their structures (Kurek, 2019).

Alkaloids' chemical structures differ greatly from one another. Alkaloids are often composed of at least one nitrogen atom in an amine-type structure, which is one that is produced from ammonia by substituting hydrogen atoms with groupings of hydrogen atoms known as hydrocarbons. In acid-base processes, this nitrogen atom or another one may be active as a base. Since the chemicals react with acids to generate salts, just like inorganic alkalis, they were initially given the label "alkaloid" (Britannica, The Editors of Encyclopaedia, 2023). The chemical structures of alkaloids are shown in Figure 2.3.

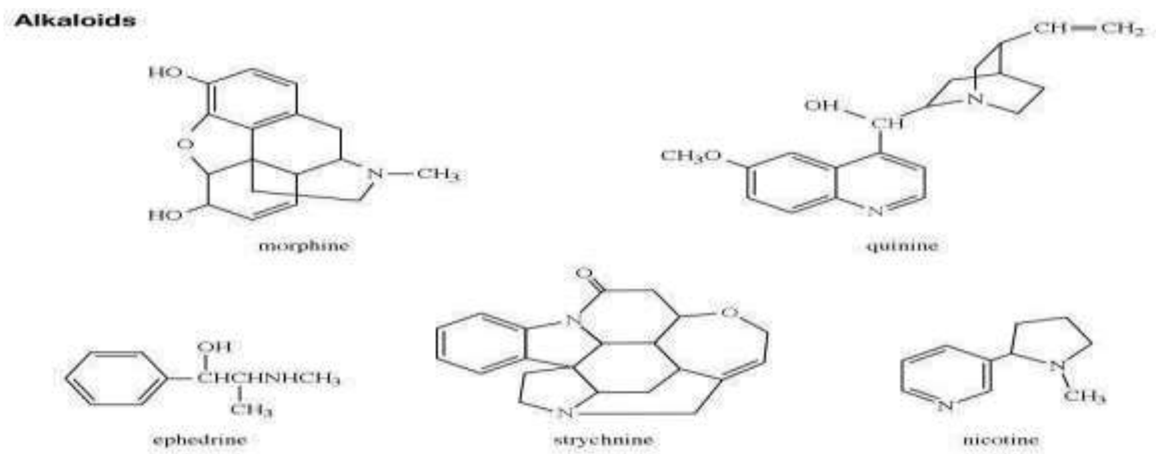


Figure 2.3: Chemical structures of Alkaloids (Britannica, The Editors of Encyclopaedia, 2023)

Most alkaloids have one or more nitrogen atoms arranged in a ring, sometimes referred to as a cyclic system. The suffix -ine often ends with alkaloid names, referring to their chemical categorization as amines. Most alkaloids are crystalline solids that are colorless and nonvolatile when they are pure. Their flavor is often bitter.

2.6.4 Phytates in plant leaves

Phytic acid is also known as inositol hexaphosphate, inositol hexakisphosphate (IP6), or inositol polyphosphate. It is a six-fold dihydrogenphosphate ester of inositol, more precisely the myo isomer. The phosphates partly ionize at physiological pH, producing the phytate anion (In Wikipedia, 2023a). A lot of seeds and fruits contain phytic acid, also known as phytate, which is the free-acid form of myo-inositolhexakiphosphate and is the main type of phosphorus stored there (Hadi Alkarawi & Zotz, 2014).

For the cation-Phytate interaction, complexes containing multiple divalent and trivalent cations are formed by phytotate.

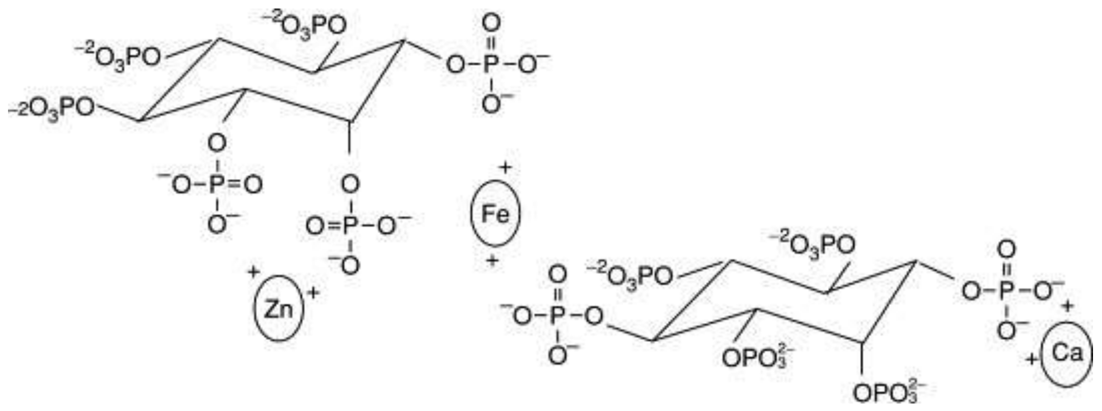


Figure 2.4: The diacylglycerol (DG)–phytate–cation interaction (Konietzny & Greiner, 2003).

The specific cation, pH level, phytate-to-cation molar ratio, and the existence of other substances in the solution all affect the stability and solubility of the cation–phytate complexes. Phytate satisfies the requirements for a chelating agent and contains six reactive phosphates. It is true that a cation can form a complex not just between two or more phosphate groups inside a single phytate, but also between two or more phytate molecules (Konietzny & Greiner, 2003).

2.7 Previous Studies on the Use of Plant Extracts to Reduce Corrosion Research has provided us with the record that there are several eco-friendly corrosion inhibitors that can effectively protect metals in sulphuric acid environments. Some of them are but not limited to

A. **Eucalyptus Leaf Extract:** Eucalyptus leaves have been studied as an ecofriendly corrosion inhibitor for mild steel in both sulphuric acid and phosphoric acid solutions. The extract from eucalyptus leaves demonstrates inhibitory properties, reducing the corrosion rate of mild steel.

B. **Biopolymers:** Biopolymers such as cellulose, starch, chitosan, pectin, alginate, and natural gums (guar, xanthan, acacia, etc.) are eco-friendly compounds with inhibitory properties. They form protective layers on metal surfaces, reducing corrosion rates.

C. **Multicomponent Reactions (MCRs) and Microwave/Ultrasound Irradiations:** Compounds derived through MCRs or using microwave and ultrasound techniques are considered eco-friendly alternatives. These methods allow the creation of novel inhibitors with reduced environmental impact.
D. **Ionic Liquids (ILs):** ILs possess low vapor pressure and are regarded as designer environment-friendly alternatives. They can be effective in inhibiting corrosion in acidic media.
E. **Polyethylene Glycol (PEG):** PEG is another eco-friendly option with low vapor pressure. It can be used as a corrosion inhibitor in sulphuric acid solutions.
F. **Green Solvents:** Chemicals synthesized using green solvents such as **water**, **ILs**, and **supercritical CO_2** are also considered eco-friendly. These solvents contribute to the development of environmentally conscious corrosion inhibitors.

Researchers in a bid to close the knowledge gaps in the use of green inhibitors to control corrosion have studied the effects of different plant extracts on metallic materials under varying and different conditions. Some of these studies focused on the use of a single inhibitor: Odiongeyi, Odoemelam, & Eddy (2009); Loto, Joseph, Loto, & Popoola (2013); Akinbulumo & Odejobi (2019); Abiola & James (2010); Eddy and Odoemelam (2009).

Odiongeyi, Odoemelam, & Eddy (2009) in the study titled 'Corrosion Inhibition and Adsorption Properties of Ethanol Extract of Vernonia amygdalina for the Corrosion of Mild Steel in H_2SO_4' inspected the effectiveness of Vernonia amygdalin as an inhibitor using weight loss, thermometric, gasometric, and IR methods. Results disclosed the inhibition efficiency of Vernonia amygdalin increased as concentration of extract increased. In addition, the Langmuir adsorption isotherm best described the metal-extract interaction and phytochemical studies confirmed the presence of tannin, saponnins, flavonoid, and anthraquinone in Vernonia amygdalina.

The inhibitive effect of Vernonia amygdalina extract on the corrosion of mild steel reinforcement of concrete in 3.5M NaCl media was investigated by Loto, Joseph, Loto, & Popoola (2013) using gravimetric, pH, electrochemical potential measurement techniques as well as a two-factor ANOVA test wherein results showed that varied concentration of *Vernonia amygdalina* and the test exposure time affected the corrosion potential of embedded steel bars in concrete with an inhibition efficiency of 90.08% at 25% concentration. ANOVA test showed that the concentration of V*ernonia amygdalina* had greater effect on potential measurement while exposure time had greater effect on pH measurement.

The weight loss technique was used to investigate the corrosion inhibition of *Euphorbia heterophylla* (L.) extract (below 343K) on mild steel in 1.5M H_2S0_4 medium by Akinbulumo & Odejobi (2019). They discovered that as inhibition efficiency increased, immersion time also increased; as corrosion rate decreased immersion time decreased also but increased with temperature. Flory-Hugins isotherm model of physical adsorption was detected.

Abiola and James (2010) checked the effect of Aloe Vera extract on the kinetics and corrosion process of zinc in 2M H_2S0_4 solution. They discovered that Langmuir adsorption isotherm best described the metal-extract interaction mechanism. Using the gasometric technique, Eddy and Odoemelam (2009) examined the corrosion of mild steel in sulphuric acid using ethanol extract of Aloe Vera at 303K and 333K. Results showed presence of a chemical adsorption isotherm.

Recently, Dehgani, Bahlakeh, & Ramezanzadeh (2019) investigated green Eucalyptus leaf extract (ELE) as green inhibitor for mild steel in HCl solution using electrochemical technique (EIS and polarization technique). EIS analysis result showed that as concentration increased, charge transfer resistance increased, and polarization test results indicated mixed inhibition effects of ELE with slight cathodic prevalence. A maximum inhibition efficiency of 88% was achieved after five hours at a concentration of 800 ppm.

Okewale & Olaitan (2017) employed gravimetric technique to investigate the effectiveness of rubber leaf extract as a green inhibitor for mild steel in 0.1M HCl solution. The maximum inhibition efficiency reached was 86% and inhibition efficiency decreased with time of exposure, as corrosion rate decreased with increase in various inhibitor concentration and exposure time. Metal- inhibitor interaction was spontaneous with Gibb's free energy of 18.07 KJ/mol and obeyed the Langmuir adsorption isotherm when compared with Temkin and Freundlich isotherm.

Ekanem, Umoren, Udoh, & Udousoro (2010) used weight loss technique and hydrogen evolution methods to ascertain the effectiveness and efficiency of pineapple leaves (Ananas comosus L.) extract at 30-60 degrees Celsius as corrosion inhibitor for mild steel in HCl. They discovered that inhibition efficiency increased with increase in concentration of extract and with increase in temperature. The metal-extract interaction was best explained by Langmuir adsorption isotherm at all temperatures and concentrations.

Loto, Popoola, & Loto (2011) in their work titled "Effect of Neem leaf (Azadirachta indica) extract on the corrosion inhibition of mild steel in dilute acids" used weight loss and potential measurements techniques to investigate the efficiency of the extract when immersed in 0.5M HCl and 0.5M H_2SO_4 acids at 30 degrees Celsius (ambient temperature) and 80 degrees Celsius (elevated temperature) respectively. The highest inhibition efficiency values were achieved at 0.5g/L for H_2SO_4 medium at 30 degrees Celsius and 0.25g/L for HCl medium. Inhibition efficiency was low in the two-test media after 10 days when the specimen was subjected to 80 degrees Celsius.

Odutose & Ajayi (2013) studied the corrosion inhibition of mild steel in 2M H_2SO_4 medium by Jathropa curcas leaves extract (JCLE) using weight loss and thermometric measurements. Results showed that inhibition efficiency increased with increasing inhibitor concentration. The interaction of the metal surface and JCLE phytochemicals was best explained using Langmuir adsorption model. An optimum inhibition efficiency of 93.33% was reached at 10mL concentration after 5 days.

Ishak et al. (2019) investigated the corrosion inhibition of mild steel in 1M HCl using Haematostaphis barteri leaves extract. Phytochemical analysis carried out disclosed the presence of alkaloids, flavonoids, tannins, phenolic compounds, saponins, among others and weight loss experiment conducted revealed a maximum inhibition efficiency of 74% at 301K at a concentration of 40g/L. The experimental data achieved fits both Langmuir and Temkin adsorption isotherm.

Njoku et al. (2013) studied the inhibitive effect of Nicotiana tabacum (NT) extract of mild steel in 0.1M HCl using weight loss and electrochemical technique. Results showed that NT was a good inhibitor and inhibition efficiency increased with increasing inhibitor concentration but decreased with time. Polarization data showed that NT is a mixed-type inhibitor whereas impedance results showed adsorption of organic species which followed the Langmuir adsorption isotherm model. UV spectrophotometry and gas chromatography mass analysis confirmed the presence of organic species in the extract – making NT a possible green inhibitor.

Gravimetric, depth of attack, and surface analysis techniques were used by Ogunleye et al. (2020) to inspect the corrosion inhibition of mild steel in 0.5M HCl solution using Luffa cylindrica leaf extracts. An optimum inhibition efficiency of 87.89% was obtained, and the extract-metal adsorption followed Langmuir adsorption model and pseudo-2nd order adsorption kinetics.

Arthur & Abechi (2019) investigated the corrosion inhibition of mild steel using Acalypha chamaedrifolia leaves extract in 1M HCl solution. This was achieved using the weight loss technique that showed a drop-in corrosion rate from 0.48mg cm^{-2} to $0.15mg.cm^{-2}$ at inhibitor concentration of 0.25g/L. Inhibition efficiency peaked at 85.11% at 1.25g/L. Furthermore, the experimental data followed Langmuir adsorption model with a correlation coefficient of 0.97.

Ji, Shukia, Ebenso, & Prakash (2013) evaluated the inhibitive effect of Agremone mexicana leaves extract on mild steel subjected to 0.5M H_2SO_4 environment. This was done using weight loss, tafel polarization, and electrochemical impedance spectroscopy technique. Optimum inhibition efficiency of 80% was reached at inhibitor concentration of $600mg.L^{-1}$. The adsorption behaviour followed the Langmuir isotherm, optical microscopy and fourier-transform infrared spectroscopy disclosed the presence of organic molecules responsible for the extract's inhibitive nature.

Anuchi and Ngobiri (2018) used the squeezed extracts of Piper guineense to evaluate the corrosion inhibition of mild steel in 2M H_2SO_4 via weight loss technique at 1%, 2%, 3%, 4%, and 5% v/v extract concentration plus the control solution at temperatures – 303K, 313K, and 323K. The upshot revealed that inhibition efficiency increased with increasing concentration and temperatures (313K and 323K). Maximum efficiency reached was approximately 43% at 5% v/v under 323K.

2.8 Combination of Green Inhibitors to Reduce Corrosion

Numerous studies focused on the use of multiple inhibitors as an effective method of controlling corrosion as well as increasing the usage of green inhibitors. Here, the synergistic inhibition effects of some of these plants were studied either by employing two different plant extracts or by utilizing different parts of a plant. Details of some of these works (and their findings) are evident in the subsequent paragraphs:

Obiukwu, Opara, & Oyinna (2013) analyzed the effectiveness of Vernonia amygdalina and Azadirachta indica extracts as inhibitor(s) for reducing corrosion of stainless steel when immersed in acidic environments and when exposed to the atmosphere. Azadirachta indica disclosed a better effect with an inhibition efficiency of 85% in contrast to 69% for Vernonia amygdalina in H_2SO_4 solution and Azadirachta indica showed superior inhibition efficiency – 83% - under atmospheric conditions (noticed after 35 days).

Ibisi, Okoroafor, & Amuta (2017) studied the inhibition effects of Piper guineense and Vernonia amygdalina leaves extracts in reducing mild steel corrosion when subjected to a concentrated corrosive medium (2.5M HCl) using gravimetric and gasometric methods. Results showed inhibition efficiency of almost 100% for both plant extracts which increased as the concentration of extracts increased but decreased when temperature is increased.

Okafor, Ebenso, and Ekpe (2010) investigated the inhibitive effects of leaves (LV), roots (RT), and seeds (SD) of Azadirachta indica on mild steel corrosion in H_2SO_4

solution using weight loss and hydrogen evolution techniques. Results showed that the extracts performed as a good inhibitor and followed the trend: SD > RT >LV with maximum inhibition efficiency of 60.04% for LV, 66.8% for RT and 81.8% SD at a concentration of 4.0g/L.

The combined effect of Tobacco and Kola tree extracts on the corrosion inhibition of mild steel in acid chloride was studied by Loto, Poppola, & Loto (2011). They employed gravimetric and potential monitoring methods. Maximum inhibition efficiency of 91.27% was evident when Kola leaf and Tobacco extracts were combined at 100% concentration whereas 82.78% was reached when Kola leaf, nut, and Tobacco extracts were combined at the same concentration.

Uwah, Okafor, and Ebiekpe (2010) investigated the inhibitive action of ethanol extracts from the leaf, bark, and root of Nauclealatifolia on the corrosion of mild steel in H_2SO_4 solution as well as their adsorption characteristic at temperature range - 30-60°C. Weight loss and gasometrical techniques were used: The extract inhibited corrosion of mild steel and the efficiencies of the inhibitor peaked in the root extract followed by leaf and bark extracts respectively. Inhibition efficiency increased with increasing extracts concentration and reduced with increasing temperature. Adsorption of the phytochemical components of the plant on the metal surface was proposed as a physical adsorption mechanism.

Okafor, Ebenso, and Ekpe (2010) utilized weight loss and gasometrical techniques to investigate the effect of leaves, root, and seeds extracts of Azadirachta indica on the corrosion behavior of mild steel in sulphuric acid solution. The results showed the extracts functioned as good inhibitors in acid solutions. The inhibition efficiency was found to increase with the concentration of extracts and was in the order: Seed > Root> Leaves. The corrosion inhibition was attributed to chemical adsorption of the phytochemical components of the plant on the surface of the mild steel and the Freundlich adsorption isotherm best described the adsorption isotherm.

Loto (2001) investigated the performance of bark and leaf solution extracts of mango (Mangifera indica) on corrosion inhibition of mild steel test specimen immersed in 0.2M dilute H_2SO_4 at ambient temperature. The experiment was performed using the weight loss method and potential measurement technique, a better result was produced when there was a combination of bark and leaf solution extracts at a concentration of 1.0mL/ 100mL of 0.2M dilute sulphuric acid in contrast with the result obtained from the bark and the leaves separately.

Uwah et al. (2013) evaluated the corrosion inhibition of mild steel using ethanol extracts of Andrographis paniculate (king bitters) - EEAP and Vernonia Amygdalina (Bitter leaf) - EEVA in 2.0M H_2S0_4 solution at 30°C, 40°C, 50°C, and 60°C. Results from weight loss and hydrogen evolution techniques indicated that both plant extracts inhibit the corrosion of mild steel by adsorption. EEAP yielded a higher maximum efficiency of 89.7% in contrast with that of EEVA - 76.9% - at 4.0g/L. As inhibition efficiency increased, concentrations of both plants increased but decreased when temperature increased. Metal-extract interaction obeyed the Langmuir adsorption isotherm.

There is limited knowledge in the use of the combination of Vernonia amygdalina and Carica papaya leaf extracts to inhibit corrosion. These extracts have hardly ever been utilized together, considering prior discoveries.

2.9 Measurements and Units of Corrosion

The rate of corrosion is the speed at which any given metal degrades in a specific environment. Corrosion rate depends on environmental conditions as well as the type and condition of the metal and it is evaluated with respect to weight loss in metal, density of metal, surface area of the metal, and time of exposure. Corrosion rates determine the life span of metal-based structures as well as maintenance requirements for structures. Techniques employed in measuring corrosion rates includes (but not limited to):

- i. Weight loss
- ii. Hydrogen evolution
- iii. Change in electrical resistance
- iv. Visual examination
- v. Optical methods
- vi. Depth of pitting
- vii. Oxygen absorption
- viii. Film resistance measurements

Corrosion rate is usually expressed in milligram per dm^2 per day (mdd), inches penetration per year (ipy), millimeter penetration per year ($mmyr^{-1}$), mils penetration per year (mpy) amongst others.

The most widely used unit is mils penetration per year since it uses tiny integers to indicate corrosion rate in terms of penetration. (Agu, 2021).

Mathematically:

$$\text{C. R. (mpy)} = \frac{534W}{\rho AT} \tag{2.1}$$

where W- weight loss (mg) A-area of specimen ($inches^2$) ρ- density of specimen (g/cm^3) T- exposure time (hours)

Corrosion rate can also be measured and expressed in terms of weight loss and current/electricity as:

$$CR = \frac{W}{AT} = \frac{MJ}{nF} \qquad (2.2)$$

Where, J = current density (A/m^2), n = number of electrons, M = atomic mass (g/mol), F = Faraday's constant (96500 C/mol)

2.10 Efficiency of Inhibitors

Corrosion inhibitors are assessed based on their efficiency. Inhibitor efficiency is the percentage reduction in corrosion rate in the presence of inhibitor as compared to its absence. It is mathematically expressed as:

$$\varepsilon_i = \frac{CR_o - CR_i}{CR_o} \; x \; 100 \qquad (2.3)$$

where, ε_i = inhibitor efficiency.

CR_o = corrosion rate without inhibitor.

CR_i = corrosion rate with inhibitor.

In general, the efficiency/effectiveness of inhibitors depends on a variety of factors like nature, concentration, chemistry of the inhibitor, surface condition of the metal, operating conditions of the aggressive environment as well as temperature and velocity of the system. Other factors affecting the efficiency of inhibitors include flow regime, quantity of water, pH of the system, micro-organisms, dissimilar metals in the same system, nature of the environment amongst others (Agu, 2021).

2.11 Significance of Sulphuric Acid (H_2S0_4)

Sulphuric acid (Hydrogen sulphate) also known as oil of vitriol is a colourless, odourless, toxic chemical, and highly corrosive acid. It is prepared industrially by the reaction of water with sulphuric trioxide which is created by the chemical reaction of oxygen and sulphur dioxide, either through the contact process or the chamber method. It is a chemical utilized primarily in the synthesis of phosphoric acid in modern industries. Metal producers use it in large quantities because it is effective in deoxidizing iron and steel (Cheremisinoff & Rosenfeld 2010).

It often serves as a measure of a country's industrialization due to the enormous transformation processes in which it is utilized. Sulphuric acid is a fundamental raw material utilized in several industries and manufacturing processes. Phosphate fertilizer manufacturing consumes a sizeable amount of the sulphuric acid produced; other uses include copper leaching, inorganic pigment production, petroleum refining, paper production, and industrial organic chemical production, explosives, dyes, drugs, as well as metallurgical processes (James & Speight 2017).

In this study, H_2SO_4 is used to check the corrosion rate of mild steel in the presence and absence of inhibitors because it is extremely corrosive when it meets storage facilities, engineering components, pressure vessels amongst others.

2.12 Mild Steel

Mild steel also known as plain-carbon steel is an alloy comprised of iron, carbon, silicon, manganese, sulphur, phosphorus, and aluminum in trace amounts. The quantity of the alloying element affects the steel's quality, strength, ductility, and hardness.

It is relatively ductile, tough, machinable, and weldable and these properties allow its usage in a variety of engineering applications. In most cases, the use for which mild steel was created did not include corrosion as it possesses a poor resistance to corrosion especially in acidic environments (Alaneme et al., 2016).

Acids are used in almost every manufacturing process, particularly phosphoric, nitric, sulfuric, and hydrochloric acids. They are employed in the production of fertilizers, paper, dyes, leather, explosives, and metals. These acids attack engineering components constituting a key problem for industries the need for the protection of steel against corrosion as pressure, reaction, transport, and storage devices in the service environment meet these acids (Omotosho, 2016). Acidic solutions are frequently employed in industrial procedures including acid cleaning, pickling, descaling, and drilling for oil and gas exploration; as a result, iron and steel vessels or surfaces utilized in these conditions are susceptible to corrosion (FioriBimbi et al., 2015).

As the first thing to consider, corrosion resistance of metals and alloys is a fundamental characteristic connected to how easily these metals react with a specific environment. Controlling the rate of corrosion when exposed to various corrosive conditions is one of the primary issues arising from the expanding use of this metal in manufacturing and construction businesses (Umeozokwere et al., 2016).

2.13 Significance of Corrosion Studies

Corrosion endangers the structural integrity and is a major cause of catastrophic failure in equipment used in the chemical, petrochemical, transportation, and construction industries as well as in bridges, nuclear facilities, airplane parts, and other equipment. Corrosion is a natural, slowly developing phenomena. The atmosphere, the composition of the metal, and the metallurgical, chemical, and electrochemical qualities are the key factors influencing the rate. In industrial equipment and building design, corrosion is frequently underestimated because it takes time to determine its extent (Popov, 2015).

Even though the mechanism and even the in-depth explanation of corrosion are complex, engineers may effectively control corrosion if they pay close attention to understanding the underlying principles on which it most often operates.

Corrosion is important for three key reasons: economy, safety, and environmental preservation. With the help of corrosion scientists, corrosion engineers work to prevent material losses as well as the resulting economic losses that come from the corrosion of pipelines, tanks, metal parts of machinery, ships, bridges, marine constructions, and other structures.

By producing breakdown (with catastrophic results) of items like pressure tanks, boilers, metallic containers for dangerous substances, turbine blades and rotors, bridges, airplane parts, and automotive steering mechanisms, corrosion can jeopardize the safety of functioning equipment. While designing equipment for nuclear power plants and the disposal of radioactive waste, safety is a key factor. In addition to wasting the metal itself, corrosion also wastes the energy, water, and labor that went into creating and fabricating the metal structures in the first place. Rebuilding damaged equipment necessitates further expenditure of all these resources, including metal, energy, water, and human labor (Uhlig & Revie, 2008).

2.14 Prediction Models

In the course of this study, the prediction models used were Artificial Neural Network (ANN) and Multiple Regression method (MR). These models helped us to determine the effect of certain variables on the corrosion rate of mild steel in sulphuric acid solution using the synergistic effect of Carica papaya Leaf extract and Bitter leaf extract as green inhibitors.

2.14.1 Artificial Neural Networks (ANN)

a. ANN is a powerful machine learning technique inspired by the human brain’s neural structure.
b. It can learn complex relationships between input features and target variables.

c. ANN models consist of interconnected layers of artificial neurons, each with an activation function.
d. These networks can handle non-linear relationships, making them suitable for intricate problems.

2.14.2 Multiple Regression (MR)

a. MR is a statistical method used to model the relationship between a dependent variable (target) and multiple independent variables (features).
b. It assumes a linear relationship between the features and the target.
c. MR coefficients repreCertainly: Here are some recent scientific references where Artificial Neural Network (ANN) prediction models have been applied.
d. Practical ANN Prediction Models for the Axial Capacity of Square CFST Columns.
e. In this study, two machine-learning algorithms based on the ANN model were proposed to estimate the ultimate compressive strength of square concretefilled steel tubular (CFST) columns. The models achieved high accuracy using a dataset of 1022 specimens from experimental tests. The ANN models outperformed the Eurocode 4 design code in predicting column capacity1.
f. Significance of ANN Analytical Models for Predicting Material Properties.
g. This paper reviews typical ANN applications for predicting various properties (e.g., corrosion, structural, tribological) of different materials in different environments).
h. Comparative Study of ANN and SVM Models.
i. A comprehensive study explored the concepts and methodologies through which ANN and Support Vector Machine (SVM) models have been used3.
j. ANN for Temperature Prediction.

k. ANN has been found to be a promising tool for predicting temperature due to its ability to handle complex and nonlinear atmospheric variables. It has shown significant improvements in weather element prediction and accuracy4.
l. ANN Prediction Model for Compressive Strength of Geopolymer Concrete.
m. Researchers developed an efficient ANN model to predict the compressive strength of geopolymer concrete based on curing temperature and time. The model achieved an R-squared value of 0.855.
n. These studies demonstrate the versatility and effectiveness of ANN models across various scientific domains.

In the course of the study, both ANN and MR have their merits, and the choice depends on the specific problem and available data. It was discovered that ANN gave better results in terms of the prediction with regards to the dependent variable which was the experimental corrosion rate than the Multiple regression method. This is because ANN can capture nonlinear patterns, handle complex relationships, and learn from historical data while MR on the other hand can handle simplicity and interpretability, assumes linear relationships and a well-established statistical method. In this case also, the independent variables are concentration of the Acid and the Inhibitor and Time of exposure.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Equipment and Materials

These materials and equipment were used for this work:

- *Vernonia amygdalina* and *Carica papaya* leaf extracts.
- Sulphuric acid (H_2SO_4).
- Distilled water.
- Measuring cylinders
- Beakers
- Thread
- Plastic containers
- Funnel
- Emery papers
- White sieve cloth
- Guillotine shearing machine
- Drilling machine
- Metal coupons
- Sticks - for hanging the thread and adequate suspension of coupons.
- Generator, extension, and stabilizer - Power supply

- Electronic analytical weighing balance
- Acetone
- Syringes – for inserting extracts into various study environments.
- Rags - for cleaning
- Detergents - for washing
- PPEs – hand gloves, face mask, and laboratory coat.
- Table – for experimental set-up
- Grinder machine
- Clock/stopwatch

3.2 Phytochemical Study of the Plant Leaf Specimen

Plant leaf phytochemical studies were carried out at the Federal University of Technology Owerri's Crop Science Laboratory. The purpose of the analyses was to identify the phytochemical components of the examined plant leaves using fresh leaf samples.

3.2.1 Determination of Phenol's Content

To determine the content of phenol in the plant-leaf, the mixture of about 200mg of the leaf extract with 10 mL concentrated methanol was shaken at room temperature for 30 min. The mixture was centrifuged for 15 min, after which, the supernatant was decanted and used for the spectrophotometric analysis of phenol.

Thereafter, each 1mL of the leaf extract was added to a commensurate volume of folin-ciocaltcau reagent plus the addition of 2mL of 20 % Na_2CO_3 medium. Using a reagent blank set to zero, the absorbance was measured in a spectrophotometer set at 560 nm. The following formula was used to determine the phenol content:

% Phenol $= \frac{100}{W_s}\ x\ \frac{a_b}{a_t}\ x\ C\ x\ \frac{V_t}{V_u} D$ (3.1)

Where, w_s = sample's weight.

a_b = sample's absorbance. a_t =

tannin's absorbance solution. c_t =

tannin solution's concentration. v_t

= total extract (filtrate) volume. v_a

= Volume of filtrate analyzed.

D = Dilution factor.

3.2.2 Determination of Hydrogen Cyanide (HCN)

The determination of hydrogen cyanide in the examined fresh leaf-samples was achieved using a conical flask containing 100 mL of water (distilled) wherein about 1.0g had been dispersed. Two strips of picrate paper were draped over the mixture using a rubber stopper. For eighteen hours, the setup was incubated at ambient temperature. Sixty milliliters of distilled water were used to elute each picrate paper strip.

Potassium cyanide was used to create a standard cyanide solution that was diluted to 0.5 mg/mL. Together with the samples, 1 milliliter of the standard solution and 100 milliliters of distilled water were incubated for one night. Like the sample, it was processed and eluted in 60 milliliters of water. A spectrophotometer was used to test the eluents' absorbance at 540 nm. The following formula was used to determine the HCN content:

$$\text{HCN Content} = \frac{1{,}000}{10}\ x\ \frac{a_b}{a_t}\ x\ C_t \qquad (3.2)$$

Where,

a_b = sample's absorbance.

a_t = tannin's standard absorbance for HCN solution.

c_t = tannin solution's concentration.

3.2.3 Alkaloids

In 100mL of a 10% acetic acid in ethanol solution, a determined weight of 2.0 g of each processed sample was distributed. After a vigorous 30-minute shaking, the mixture was left to remain at room temperature for four hours. Using Whatman filter paper (No. 42), the mixture was filtered at the conclusion of this time. A quarter of the initial volume of the filtered extract was obtained by evaporating it. The alkaloids were precipitated out of the extract by adding strong ammonia solution dropwise. Up till it was too much, ammonia was added continually. After cooling in a desiccator and being cleaned with 1% NH_4OH solution, the precipitated alkaloid was filtered, dried at 105°C, and weighed. The relationship shown below was used to determine the alkaloid content:

$$\%\ \text{Alkaloids} = \frac{W_f - W_i}{Weight\ of\ sample}\ x\ 100 \qquad (3.3)$$

Where,

W_f = empty filter paper's weight.

W_i = the weight of both filter paper and alkaloid precipitate.

3.2.4 Quantification of Tannin

The processed plant leaves fresh, dried, and ground were weighed out at 5.0 g and distributed throughout 100 mL of distilled water. The mixture was filtered using Whatman's filter paper (No. 42) after being shaken for 30 minutes at room temperature. Until a 100 cc filter was obtained, the residue was rinsed with distilled water.

A 50 mL volumetric flask was filled with an aliquot of the extract (2 mL) and an equivalent proportion of folin-Dennis reagent. A saline sodium carbonate solution of around 2 milliliters was added. After being distilled to a volume of 50 milliliters, the liquid was left to sit at room temperature for 90 minutes.

Tannic acid was used to make a standard tannin solution, which was then diluted to the required concentration. The diluted standard underwent t tannin contain

$$\% \text{ Tannin} = \frac{100}{W_s} \; x \; \frac{a_b}{a_t} \; x \; \frac{C_t}{1{,}000} \; x \; \frac{V_t}{V_u} \; x \; D \qquad (3.4)$$

Where, w_s = sample's weight.

a_b = sample's absorbance.

a_t = tannin's standard absorbance solution.

c_t = tannin solution's concentration.

v_t = total extract (filtrate) volume.

v_u = volume of analyzed filtrate.

D = Dilution factor.

3.3 Production of the Plant-Leaf Extract

The leaves of *Vernonia amygdalina* and *Carica papaya* plants were collected within the Federal University of Technology, Owerri (FUTO) and nearby villages, then they were ground in an electric grinder that was moisture- and dirt-free. The crushed leaves were collected in a basin that was set up at the bottom of the grinder. The sole difference between the methods employed to extract the "juice" from the leaves of *Vernonia amygdalina* and *Carica papaya* plants was the use of palm oil. During the squeezing process, a filter (clean, white cloth) was employed to separate the residue from the juice.

To ensure a pure filtrate, this filtering procedure was repeated. The filtrate was kept at room temperature in a container. This was used as the experimental stock inhibitor solution, from which measured concentrations were added to different solutions.

3.4 Acid Preparations and Calculations

The corrosive environment, 1.5 M H_2SO_4 was prepared using the following relationship:

$$\text{Stock Concentration } (C_I) = \frac{\%\, purity\ of\ acid\ x\ density}{Molar\ mass\ of\ acid} \qquad (3.5)$$

Where,

% purity of H_2S0_4 acid = 94%.

Density of H_2S0_4 =1.84g/cm^3.

Also, molar mass of acid = molar mass of H_2S0_4 + molar mass of distilled water

= 98 + 1.0 = 99.01 g/mol

The volume of the stock needed was evaluated using the formula:

$$C_1V_1 = C_2V_2 \qquad (3.6)$$

Where,

C_1 = stock concentration.

C_2 = required molarity of the acid (1.5 M).

V_1 = volume of stock solution needed to prepare the acid solution.

V_2 = volume of acid required (1000 cm^3).

Since 1.84g/cm^3 is equivalent to 1.84 g/mL, converting the density of H_2S0_4 from mL to liters, we multiply by 1000 to get 1840g/L; C_1 can be calculated thus: So, Stock Concentration (C_1) $= \frac{37}{100}\ of\ \frac{1840 g/L}{99.0\ g/mol}$

$$C_1 \cong \underline{17.47M}$$

Therefore, V_1

$= (C_2V_2)/C_1$

$= \frac{1.5\ x\ 1000}{17.47}$

$V_1 \sim \underline{85.86\ cm^3}$

Therefore, 85.86 cm^3 of the stock solution was required to prepare a 1.5 M concentration of H_2S0_4 solution, made up to 1000 cm^3 in a 1L standard flask.

3.5 Weight Loss Technique

Weight loss or Gravimetric Technique are common methods for evaluating the corrosion behavior of materials. The setup for a weight loss experiment typically involves exposing a metal specimen to a corrosive environment for a specified duration and measuring the mass loss of the specimen.

The Gravimetric Technique is based on the experimental determination of weight loss and the area of the samples of steel coupons after the attack because of exposure to the corrosive environment (H_2S0_4 medium). This was done following (ASTM G 1-03) standard procedure.

The already-treated metal coupons, which were 4 cm × 4 cm in size, were weighed before being submerged in test media containing control solution and green inhibitors in a range of concentrations. The samples were taken out of the test media after each time, weighed again, and then put back inside the desiccator.

The mild steel coupons were submerged for 24, 48, 72, 96, and 120 hours in a solution containing 1.5 M of H_2SO_4 together with different concentrations of VA and CP (5 mL, 10 mL, 15 mL, and 20 mL), and this was done both with and without the corrosion inhibitor.

These inhibitor doses were added to a container containing the different test pieces. A total number of 17 study environments were set up. For each concentration in this case, a control was created. Five (5) steel coupons were immersed in a set of containers containing 1.5 M H_2SO_4 solution wherein the inhibitors had been added at 5 mL, 10 mL, 15 mL, and 20 mL respectively. The inhibitor concentrations of the synergetic admixture (SA) were prepared using a novel fractional substitution method. Concentrations of either CP or VA had the constant concentration (2mL) and were maintained at 5 mL (2 mL + 3 mL), 10 mL (2 mL + 8 mL), 15 mL (2 mL + 13 mL), and 20 mL (2 mL + 18 mL). The technique develops a practical approach of customizing the inhibitor to result in greater inhibitor effectiveness.

Another study environment containing a blank solution of 1.5 M H_2SO_4, without the addition of any inhibitor, was set up to serve as the control. After every 24 hours, a steel coupon was taken out of the inhibitor solution and control solution for 5 consecutive days. In essence, the specimens were completely submerged in each of the 17 test solutions for a total exposure time of 120 hours, with readings obtained every 24 hours for 5 days. The weight of the samples before and after immersions were obtained using the electronic (Ohaus) weighing, and the results were accurately documented. To accurately determine the weight of the coupons, they were washed with distilled water, dried, and then weighed.

After the exposure duration, the specimens were removed from the corrosive environment and cleaned to remove any corrosion products. The specimen was then dried and weighed to determine its final mass. To ascertain the weight loss, final mass was subtracted from the initial mass. This was essential in obtaining the weight loss data as well as the corrosion rate and inhibitor efficiency as earlier reported by previous studies; Omotosho 2016; Ferreira, da Silva, Mantovani, & Cote 2009; Davis, 2007). Tables 3.1 and 3.2 show the various metal-inhibitor-acid combinations and experimental duration.

Table 3.1: Metal-inhibitor-acid combinations

Inhibitor Concentration (mL) (VA and CP)	**Solution Metal**	**Duration/Interval**
mL (control)	1.5 M H_2S0_4 Mild steel	All readings were taken every 24 hours for five (5) days.
5mL	1.5 M H_2S0_4 Mild steel	
10mL	1.5 M H_2S0_4 Mild steel	
15mL	1.5 M H_2S0_4 Mild steel	
20mL	1.5 M H_2S0_4 Mild steel	

Table 3.2: Metal-synergetic inhibitor- acid combinations [CP maintained at 2 mL while the remaining concentration was augmented by VA]

Inhibitor Concentration (mL)	Media	Metal	Duration
3VA + 2CP	1.5M H_2S0_4	Mild steel	All readings were taken every 24 hours for five (5) days.
8VA + 2CP	1.5M H_2S0_4	Mild steel	
13VA + 2CP	1.5M H_2S0_4	Mild steel	
18VA + 2CP	1.5M H_2S0_4	Mild steel	

Table 3.3: Metal-synergistic inhibitor-acid combinations

[VA maintained at 2 mL while the remaining concentration was augmented by CP]

Inhibitor Concentration (mL)	Media Metal	Duration
2VA + 3CP	1.5M H_2S0_4 Mild steel	All readings were taken for 24 hours for five (5) days.
2VA + 8CP	1.5M H_2S0_4 Mild steel	
2VA + 13CP	1.5M H_2S0_4 Mild steel	
2VA + 18CP	1.5M H_2S0_4 Mild steel	

The corrosion rate of each coupon was calculated using equation 3.7 as shown:

$$\text{Corrosion Rate (CR)} = \frac{534\,w}{DAt} \qquad (3.7)$$

where,

CR = Corrosion Rate (mm/yr)

w = weight loss (g)

D = density of steel = 7.85g/cm^3

t = exposure time (hourr)

A = Surface area of coupon (cm^2)

Surface Area of coupon was calculated using equation 3.8 as shown:

$$A = 2(LB + LT + BT) - 2\frac{\pi d^2}{4} + \pi dT \quad (3.8)$$

where; L = length of coupon (cm)

B = breadth of coupon (cm)

T = Thickness of coupon (cm)

d = diameter of the hole drilled on the coupon.

3.6 Fabrication of Mild Steel Coupons

Mild steel coupons were fabricated using the foot shear cutter. To accurately assess the weight loss, the mild steel metal sheets were mechanically cut into square coupons (as schematically shown in Figure 3.1) with the following dimensions: 4.0 cm by 4.0 cm by 0.1 cm (suitable enough to fit into the test apparatus) and a round hole of diameter, 0.2 cm to enable the suspension of the coupons into the media using threads.

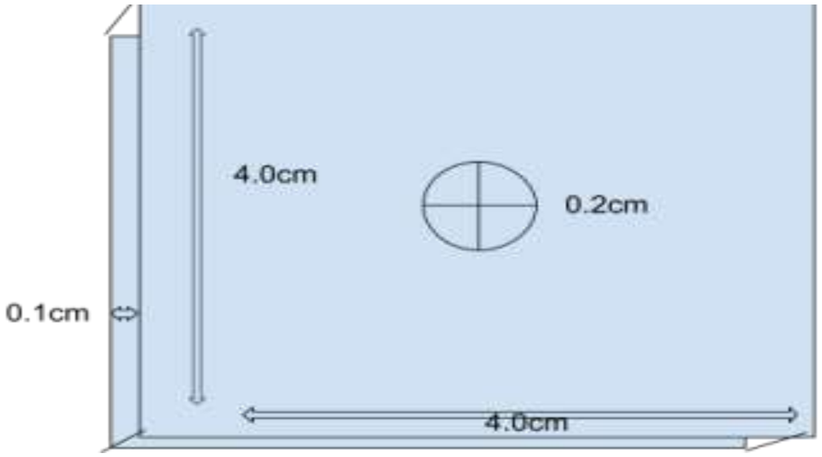


Figure 3.1: Schematic illustration of the fabricated mild steel coupon used for the study.

After being scrubbed with emery paper, washed in ethanol, and distilled water, and then degreased with acetone, the steel coupons were cleaned. Before the experiment began, the steel coupons had additional treatment with emery paper, were cleaned with acetone, and dried before getting their initial weights.

3.7 Data-Driven Prognostic Analysis of Corrosion Rate Based on Experimental Measurement

In this work, an artificial neural network also known as machine learning and the multiple regression method will be used to predict the corrosion rate. The following methodology will be utilized and implemented as follows.

3.7.1 Artificial Neural Network

Artificial neural networks perform like the human brain in data management, processing, and analysis. It has a functionality that resembles a biological neuron, which is known as the neuron or an interconnected processor (Ndukwe & Anyakwo, 2017). This protocol model has found applications in both Sciences and Engineering. In Sciences, implementing ANN in composites can significantly improve two major aspects: accuracy in modeling nonlinear relations and estimating the influence of many input parameters on material’s performance. Moreover, many studies have shown that ANNs are highly accurate in modeling the mechanical behavior and tribological characteristics of composite materials as a function of various process parameters. In the field of Medicine, prediction of Heart Disease using deep Convolutional Neural Networks, Researchers have employed DL architectures such as convolutional neural networks (CNNs), recurrent NNs, and deep belief networks in areas like recognizing human speech, computer vision, audio recognition, natural language processing, drug design, bioinformatics, and medical image processing. State-of-the-art in Artificial Neural Network applications survey provides a taxonomy of ANNs and highlights current trends in ANN applications across various research areas because it's a valuable resource for understanding the focus of researchers in this field. ANN also has practical aspects of the design and use in Materials Engineering as it has proved to be a practical tool for modeling and prediction.

In essence, the artificial network neurons are connected by weighted links which convey signals across the neurons. The input link is accounted for by a new activation level which at the same time sends it in the form of an output signal. The neuron is expected to compute the sum of the weighted inputs and match the outcome with a threshold number. The features and sequence of operation are explained and illustrated below;

1. **Input Layer:** The **input layer** receives the initial data or features. Each node (or neuron) in this layer corresponds to a specific input feature.
2. **Hidden Layers**: The **hidden layers** lie between the input and output layers. Each node in a hidden layer performs calculations based on the input data and passes the result to subsequent layers. The number of hidden layers and the number of nodes in each layer can vary. Deep neural networks often have multiple hidden layers, allowing them to learn complex patterns.
3. **Weights** (w): **Weights** represent the strength of connections between nodes. Each connection from one node to another has an associated weight. During training, the neural network adjusts these weights to minimize the error between predicted outputs and actual outputs.
4. **Bias** (b): **Bias** terms are additional parameters associated with each node. They allow the network to shift the activation function (like a threshold) and control the output. Bias helps the neural network fit the data better by introducing flexibility.

5. **Activation Function** determines the output of a node based on its weighted sum of inputs and bias. Common activation functions include **ReLU (Rectified Linear Unit)**, **sigmoid**, and **tanh** and they introduce non-linearity, allowing the network to model complex relationships.
6. The **output layer** produces the final predictions or results. The number of nodes in this layer depends on the problem type:
    - For binary classification, there's usually one node with a sigmoid activation function.
    - For multi-class classification, each class corresponds to a node with softmax activation.
    - For regression tasks, there's a single node with a linear activation.
7. **Neurons (Nodes)**: Each node (neuron) in the neural network corresponds to a mathematical function that processes input data. Nodes in hidden layers perform calculations and transform the data, gradually learning to represent complex patterns.
8. **Forward Propagation**: input data flows through the network layer by layer. Each node computes its output based on weights, bias, and activation function. The final output is obtained from the output layer.
9. **Back-propagation** is the process of adjusting weights and biases during training. It involves computing gradients and updating parameters to minimize the error (loss) between predicted and actual outputs.
10. **The loss function** quantifies the difference between predicted and actual outputs. Common loss functions include **mean squared error (MSE)** for regression and **cross-entropy** for classification.

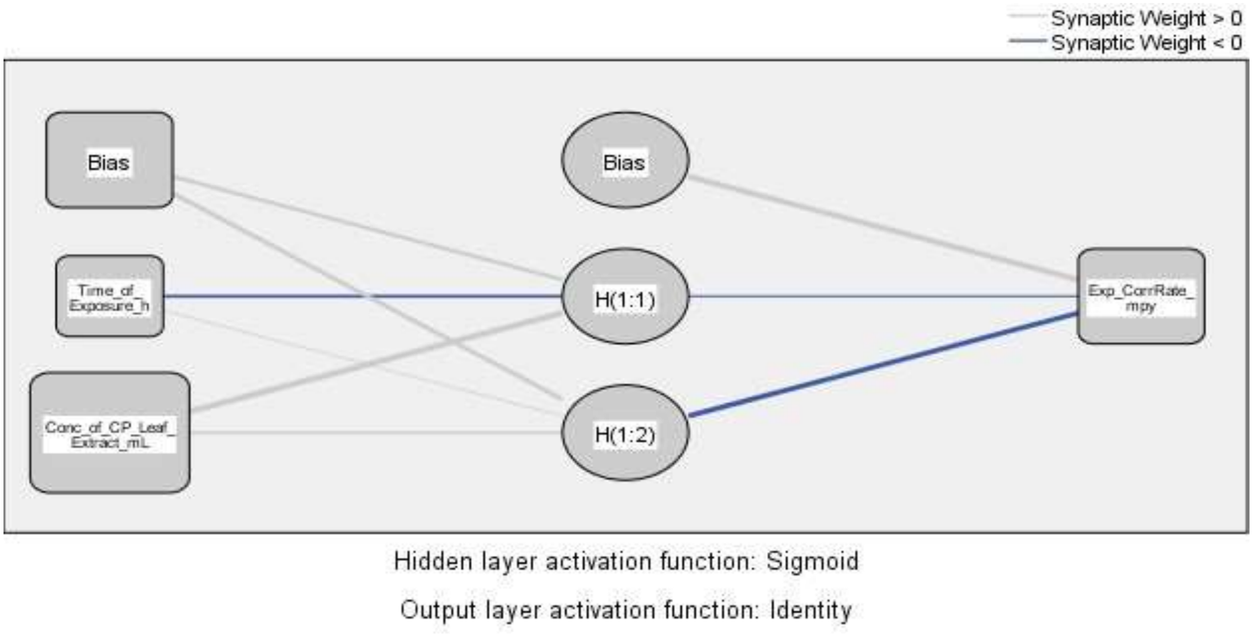


Figure 3.2: ANN networks for the current study

Consequently, the other link to the neuron qj is known as the bias, which is a value that is arbitrarily chosen to oversee the network's input as denoted in equation (3.9).

Furthermore, the output of the neuron is likely to be -1 if the threshold is greater than the net input. However, the neuron becomes unity if the net input is the same or more than the threshold. The ANN's net input can be computed by equation (3.9) (Anyakwo & Ndukwe, 2017)

$$Net_j = \sum (s_i * p_{ij}) + q_j \tag{3.9}$$

Where,

Net_j = net input. Which is the inhibitors s_i = unit i's output which is the corrosion rate p_{ij} = the connection's weight emanating from unit i in the previous layer to unit j. q_j = unit bias. The activity of the unit is modified by the bias, which functions as a threshold. Bias can also be called s squashing function owing to its capability to map a large domain of input into a range that is between 0 and unity (Han et al., 2012).

The sigmoid's function $f(Net_j)$ modifies the input concentration which invariably may be within the range of positive and negative infinity to a veritable number within the range of 1 and 0. The sigmoid activation function is more often utilized in the back-propagation networks (Anyakwo and Ndukwe, 2017).

$$f(Net_j) = 1/(1 + e^{-Netj}) \qquad (3.10)$$

Where,

Net_j = net input.

The artificial neural network's predictive protocol employed in the current study has been earlier reported (Ndukwe, 2017).

3.7.2 Multiple Regression

The need for the use of multiple regression was to forecast the corrosion rate as obtained from the experiment with the consideration of how it could be influenced by other independent variables like; concentration of acid, time of immersion of the steel coupon in the study environment, and the concentration of the plant-leaf extract. The same method as previously reported (Ndukwe, 2017) was used in the current study.

The mathematical representation of the above expression is given below:

Corr Rate$_{\textbf{Predicted by MR}}$ = $h_o + h_1$ (time of exposure) + h_2 (concentration of extract) 3.10 Where,

Corr Rate$_{\text{Predicted by MR}}$ = the predicted value of the corrosion rate as obtained from the experiment. h_o = the intercept along Corr Rate axis.

h_1 = the difference in Corr Rate for each 1 raise in exposure time. h_2 = the difference in Corr Rate for each 1 raise in the concentration of the plant-leaf extract.

3.7.3 Implementation of the Data-Driven Prognostic Model

The IBM® SPSS® software was used to implement the artificial neural network and multiple regression models (Eq. 3.3 to Eq. 3.5). The IBM® SPSS® software platform includes big data integration, text analysis, open-source extensibility, powerful statistical analysis, a large library of machine learning algorithms, and seamless application deployment (SPSS®, n.d.). Users of different skill levels may utilize SPSS thanks to its simplicity, adaptability, and scalability. Additionally, it may assist you in identifying new possibilities, enhancing efficiency, and lowering risk for projects of all sizes and degrees of complexity. Artificial neural networks and multiple regression are fully integrated in the SPSS software. The software has been used successfully by other researchers as mentioned earlier in engineering and scientific fields. he same processing as the sample. Using a spectrophotometer, the absorbance of the standard and sample solutions was measured at 760 nm following the incubation. The following formula was used to determine the

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Effect of addition of plant leaf extract of *Vernonia amygdalina* on the corrosion of mild steel immersed in 1.5M H_2SO_4.

The results of the influence of addition of plant leaf extract of *Vernonia amygdalina* (VA) on the corrosion of mild steel immersed in 1.5M H_2SO_4 are presented in Table 4.1 and graphically presented in Figures 4.1 and 4.2 for corrosion rate and inhibition efficiency respectively. The mild steel coupons in the uninhibited solution of 1.5M H_2S0_4 recorded higher corrosion rates reaching the maximum of 0.35 mm/yr at 48 hours, whereas specimens immersed in inhibited solutions all had lesser corrosion rates. The least corrosion rate (highest performance) of approximately 0.11 mm/yr was recorded for the solution with inhibitor concentration of 20mL VA at 24 hours while maximum corrosion rate achieved was 0.26 mm/yr after 24 hours from 5 mL VA. High corrosion rates were observed when 5 and 10 mL of *Vernonia amygdalina* extracts were added to 1.5M H_2S0_4 medium. The highest corrosion rate of 0.26 mm/yr was observed at 48 hours of addition of 5 mL of the plant-leaf extract to the 1.5 M H_2SO_4 solution wherein the mild steel coupon had been immersed. However, the corrosion rate decreased as the addition of the inhibitor increased to 15 mL and 20 mL respectively. Consequently, the inhibition efficiency was observed to increase with time in the first 48 hours but started to decline after 72 hours as depicted in Figure 4.2.

The maximum corrosion inhibition efficiency of 64.8 % was attained at 24 hours after the addition of 20 mL of *Vernonia amygdalina* leaf extract in 1.5 M H_2SO_4 medium containing the mild steel coupon. Afterwards, a continuous decrease in inhibition efficiency was observed until about 18.65 % was recorded after 120 hours.

In essence, about 47.36 % boost in inhibition efficiency was attained by increasing the concentration of the *Vernonia amygdalina* leaf extract from 5 mL to 20 mL.

Whereas, for the addition of 5 mL of the leaf extract, the decline in inhibition effectiveness reached 78.42 % from 24 hr to 120 hr. For the addition of 20 mL concentration of the extract, the inhibition efficiency was observed to decrease by 55.30 %.

Table 4.1: Effect of addition of plant leaf extract of *Vernonia amygdalina* on corrosion of mild steel immersed in 1.5 M H_2S0_4

	Control	5 mL		10 mL		15 mL		20 mL	
Exp. Time (hours)	Cor. Rate (mm/y)	Cor. Rate (mm/y)	I.E. (%)	Cor. Rate (mm/y)	I.E. (%)	Cor. Rate (mm/y)	I.E. (%)	Cor. Rate (mm/y)	I.E. (%)
24	0.3115	0.2394	23.15	0.1624	47.87	0.1338	57.06	0.1097	64.80
48	0.3465	0.2561	26.09	0.1822	47.42	0.1505	56.55	0.1274	63.22
72	0.2494	0.2199	11.81	0.1411	43.40	0.1379	44.72	0.1231	50.63
96	0.2170	0.1863	14.13	0.1813	16.43	0.1581	27.16	0.1421	34.52
120	0.1763	0.1713	2.80	0.1707	3.15	0.1566	11.17	0.1434	18.65

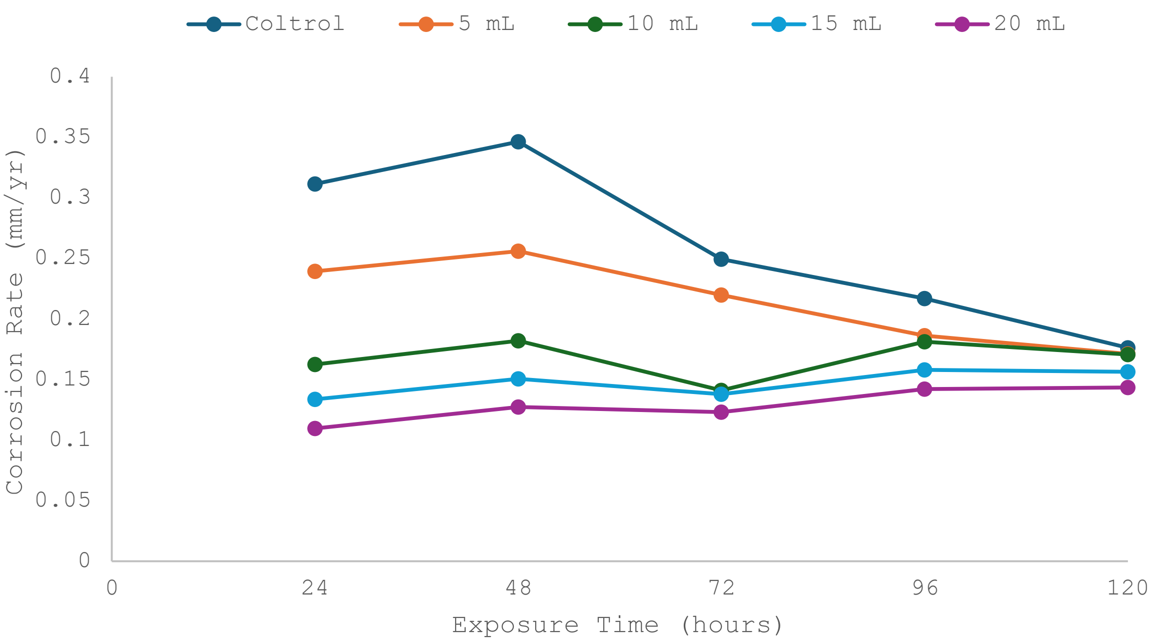


Figure 4.1: Effect of addition of plant leaf extract of Vernonia amygdalina on the corrosion rate of mild steel immersed in 1.5M H_2SO_4

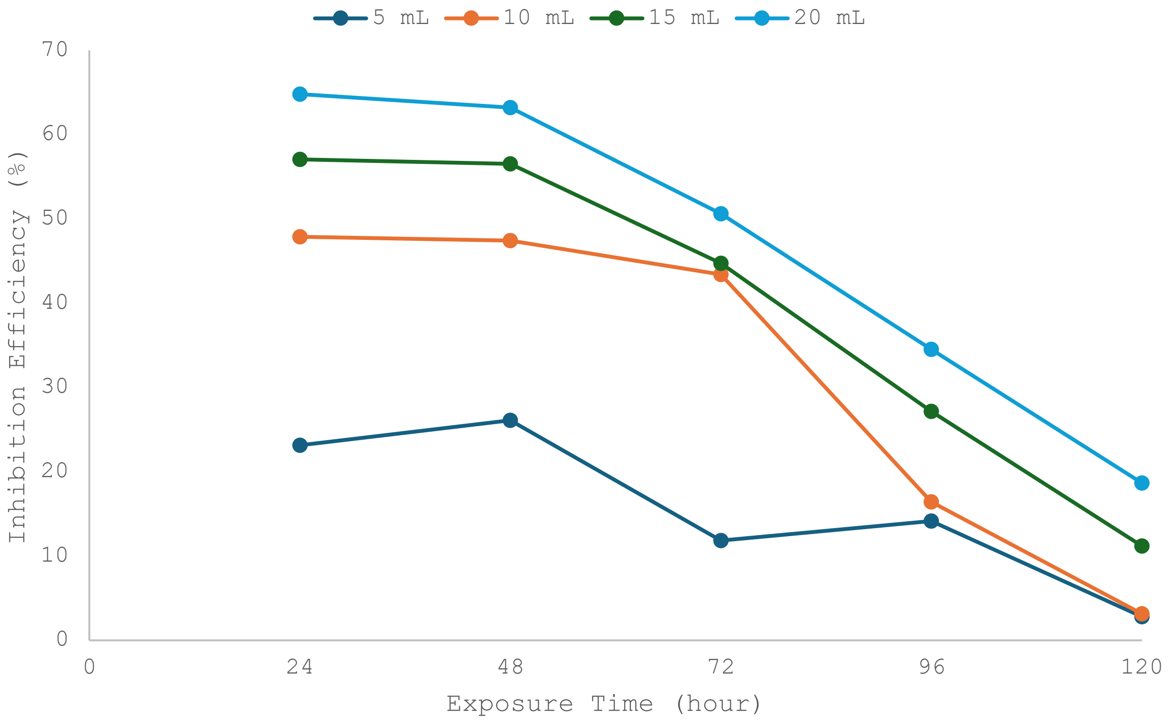


Figure 4.2: Effect of Time on the Inhibition efficiency of plant leaf extract of *Vernonia amygdalina* on the degradation of mild steel immersed in 1.5 M H_2S0_4.

This observation revealed that although the extract of *Vernonia amygdalina* leaf inhibited the corrosion of steel, it was not tenacious enough at all concentrations to adequately deter the corrosion of mild steel in 1.5 M H_2SO_4 after a longer period. The rate of steel corrosion in another reported study with a greater acidic concentration (2 M H_2SO_4) was observed to decrease as the concentration of *Vernonia amygdalina* leaf extract increased, indicating that the extract prevents mild steel corrosion in H_2SO_4 (Oriji, 2021).

4.1.1 Prediction of corrosion behavior of the leaf-extracts of *Vernonia amygdalina* plant in 1.5 M H_2SO_4

The modeling of the corrosion inhibition behavior of the leaf-extracts of *Vernonia amygdalina* and papaya plants in 1.5 M H_2SO_4 was achieved using multiple regression (MR) and artificial neural network (ANN). In the present study, the dependent variable being the experimental corrosion rate was predicted considering the influence of other independent variables like concentration of acid, leaf-extract concentration, and the time of exposure.

The results of the prediction of the corrosion rates of mild steel in 1.5 M H_2SO_4 obtained by the uninhibited and inhibited (leaf-extract of *Vernonia amygdalina*) media using ANN and MR are presented in Tables 4.2 – 4.4 and shown in Figures 4.3 – 4.5.

The mild steel corrosion inhibition in H_2SO_4 (1.5 M) by *Vernonia amygdalina* leaf extract was modelled by multiple regression (Tables 4.2 and 4.3) to give the following predictive equation (Equation 4.1).

$$\mathbf{CorrRate}_{\text{VA in } H_2SO_4 \text{ by MR}} = 0.277 - 0.007 \text{ (conc. of leaf-extract)} \qquad 4.1$$

Table 4.2: Prediction of corrosion inhibition of mild steel in 1.5 M H_2SO_4 medium by the leaf-extracts of *Vernonia amygdalina* using MR and ANN

Case	**Time of Exposure (h)**	**Conc. of H_2SO_4 (M)**	**Conc. Of VA Leaf Extract (mL)**	**Exp_ CorrRate** (mm/yr)	**Predicted Exp_ CorrRate by ANN**	**Pred. Error**	**Predicted Exp_ CorrRate by MR**	**Pred. Error**
1	24	1.5	0	0.3115	0.2915	-0.02	0.2678	-0.0437
2	48	1.5	0	0.3465	0.2835	-0.063	0.2587	-0.0878
3	72	1.5	0	0.2494	0.2574	0.008	0.2496	0.0002
4	96	1.5	0	0.217	0.2193	0.0023	0.2405	0.0235
5	120	1.5	0	0.1763	0.1896	0.0133	0.2314	0.0551
6	24	1.5	5	0.2394	0.2553	0.0159	0.2349	-0.0045
7	48	1.5	5	0.2561	0.2348	-0.0213	0.2258	-0.0303
8	72	1.5	5	0.2199	0.203	-0.0169	0.2167	-0.0032
9	96	1.5	5	0.1863	0.1815	-0.0048	0.2076	0.0213
10	120	1.5	5	0.1713	0.1723	0.001	0.1985	0.0272
11	24	1.5	10	0.1624	0.1856	0.0232	0.202	0.0396
12	48	1.5	10	0.1822	0.1705	-0.0117	0.1929	0.0107
13	72	1.5	10	0.1411	0.1683	0.0272	0.1838	0.0427
14	96	1.5	10	0.1813	0.1681	-0.0132	0.1747	-0.0066
15	120	1.5	10	0.1707	0.1678	-0.0029	0.1656	-0.0051
16	24	1.5	15	0.1338	0.1343	0.0005	0.169	0.0352
17	48	1.5	15	0.1505	0.1314	-0.0191	0.1599	0.0094
18	72	1.5	15	0.1379	0.1441	0.0062	0.1508	0.0129
19	96	1.5	15	0.1581	0.1582	0.0001	0.1417	-0.0164
20	120	1.5	15	0.1566	0.1648	0.0082	0.1326	-0.024
21	24	1.5	20	0.1097	0.1179	0.0082	0.1361	0.0264
22	48	1.5	20	0.1274	0.1177	-0.0097	0.127	-0.0004
23	72	1.5	20	0.1231	0.1242	0.0011	0.1179	-0.0052
24	96	1.5	20	0.1421	0.1398	-0.0023	0.1088	-0.0333
25	120	1.5	20	0.1434	0.1561	0.0127	0.0997	-0.0437

Table 4.3: Prediction of corrosion inhibition of mild steel using the leaf-extracts of Vernonia amygdalina plant by multiple regression

Medium	**Model coefficients**		
	Constant	**Time of exposure (h)**	**Conc. of leafextract (mL)**
H_2SO_4	0.277	0.000	-0.007

Furthermore, the artificial neural network's prediction of the experimental rate of corrosion (dependent variable) [Table 4.2 and Figure 4.3] indicated the importance of the independent variables [Table 4.4]. Results showed that the concentration of the leaf-extract had a greater effect on the prediction of the corrosion rate by 68.1 % followed by the time of exposure (31.9 %).

Table 4.4: Independent Variable Importance and Parameter Estimates of the prediction of corrosion inhibition of mild steel in 1.5 M H_2SO_4 medium by the leafextracts of Vernonia amygdalina using ANN

Independent Variable Importance

	Importance
Time_of_Exposure	0.319
Conc._of_VA_Leaf_Extract	0.681

Parameter Estimates

Predictor		Predicted		
		Hidden Layer 1		Output Layer
		H(1:1)	H(1:2)	Exp._CorrRate
Input Layer	(Bias)	-3.050	1.500	
	Time_of_Exposure	-1.584	1.875	
	Conc._of_VA_Leaf_Extract	-2.224	-2.104	
Hidden Layer 1	(Bias)			-1.362
	H(1:1)			3.389
	H(1:2)			1.341

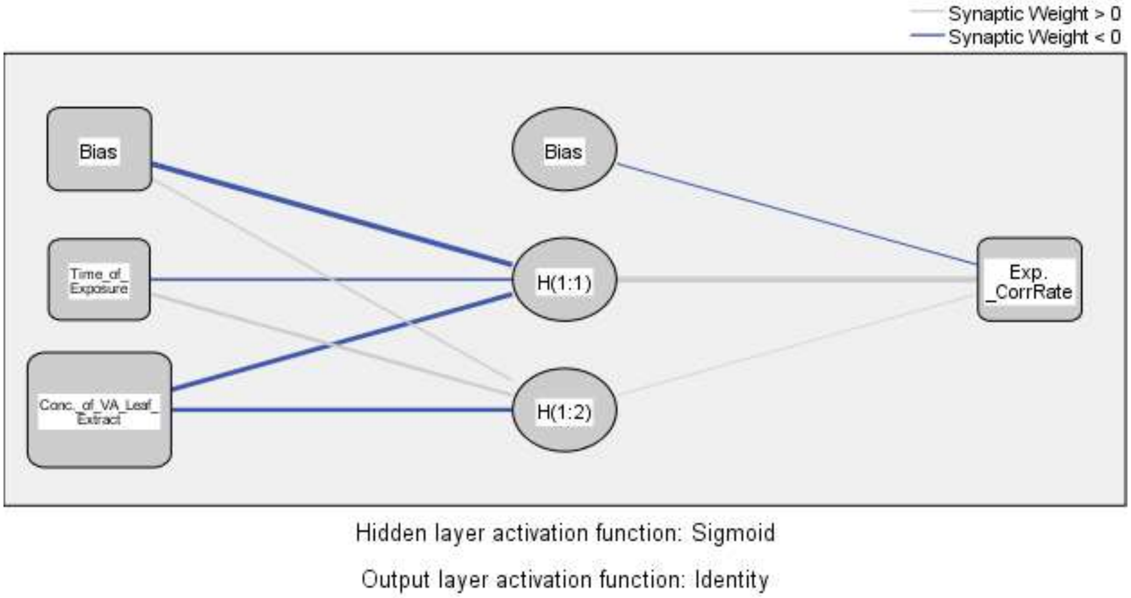


Figure 4.3: ANN diagram for predicting the corrosion inhibition of mild steel in 1.5 M H_2SO_4 by the leaf-extract of Vernonia amygdalina plant

The inaccuracy in predictions by MR and ANN is presented in Table 4.2 and shown in Figure 4.4. From Figure 4.4, the trend of the curves for the predicted values by ANN was observed to be closer to that of the experimental corrosion rate values.

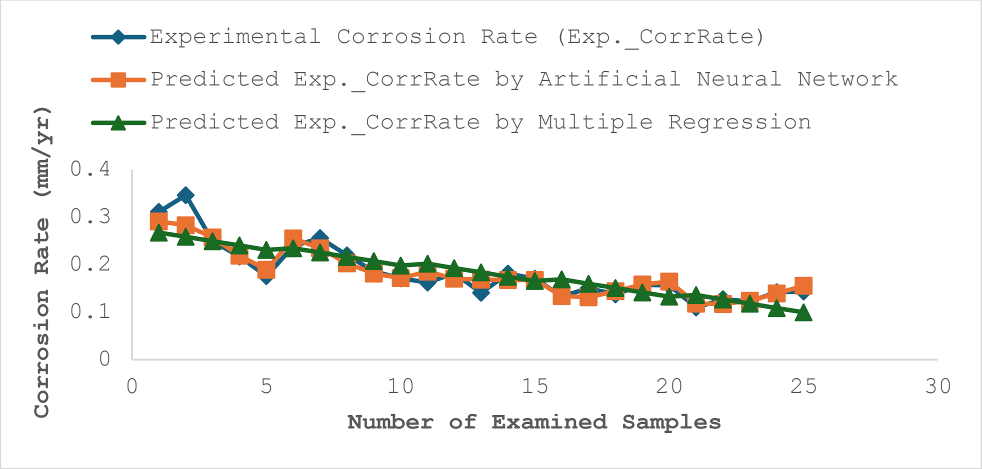


Figure 4.4: Error in prediction of corrosion inhibition of mild steel in 1.5 M H_2SO_4 by the leaf-extracts of Vernonia amygdalina plant using MR and ANN

In other words, predictions by ANN were found to have lesser errors than those from the MR as indicated in Figure 4.4. This outcome is in agreement with the previous report on the prediction of the corrosion inhibition of mild steel in H_2SO_4 by Sida acuta (Ndukwe and Anyakwo, 2017). The reason for the satisfactory performance of ANN could be because of its flexibility in handling non-linear relations.

4.2 Effect of addition of plant leaf extract of Carica papaya on the corrosion of mild steel immersed in 1.5M H_2SO_4

The prevention of corrosion of mild steel in 1.5 M H_2SO_4 by the addition of the leaf extract of Carica papaya is presented in Table 4.5 and shown in Figures 4.5 and 4.6 for corrosion rate and inhibition efficiency respectively. The rate at which the mild steel degraded in the 1.5 M acidic solution was found to decrease with increase in the addition of the Carica papaya leaf extract from 5 mL to 20 mL. The highest corrosion rate of 0.178 mm/yr was obtained after 96 hours of the addition of 5 mL papaya leaf-extract. As the addition of the leaf extract increased to **20 mL**, the highest inhibition efficiency of about 86.89 % was observed after 48 hours. As time progressed, the inhibition efficiency gradually declined to 73 % after 120 hours. In general, noticeable improvements in corrosion inhibition of mild steel, immersed in 1.5 M H_2SO_4 were recorded following the addition of papaya leaf extracts in comparison with the results earlier reported for the addition of Vernonia amygdalina leaf extracts. The decrease in the inhibition efficiency with time could be caused by the attack of the acid on the inhibiting constituent of the plant extract adsorbed on the surface of the steel.

Table 4.5: Effect of addition of plant leaf extract of Carica papaya on corrosion of mild steel immersed in 1.5M H_2SO_4

	Control	5 mL		10 mL		15 mL		20 mL	
Exp. Time (hours)	**Cor. Rate (mm/y)**	**Cor. Rate (mm/y)**	**I.E. (%)**	**Cor. Rate (mm/y)**	**I.E. (%)**	**Cor. Rate (mm/y)**	**I.E. (%)**	**Cor. Rate (mm/y)**	**I.E. (%)**
24	0.3115	0.1497	51.95	0.1059	66.02	0.0867	72.18	0.0429	86.22
48	0.3465	0.1707	50.72	0.1200	65.37	0.0970	72.00	0.0454	86.89
72	0.2494	0.1452	41.79	0.0953	61.77	0.0643	74.21	0.0409	83.58
96	0.2170	0.1778	18.05	0.1064	50.98	0.0469	78.40	0.0408	81.20
120	0.1763	0.1648	6.52	0.1284	27.16	0.0837	52.50	0.0476	73.00

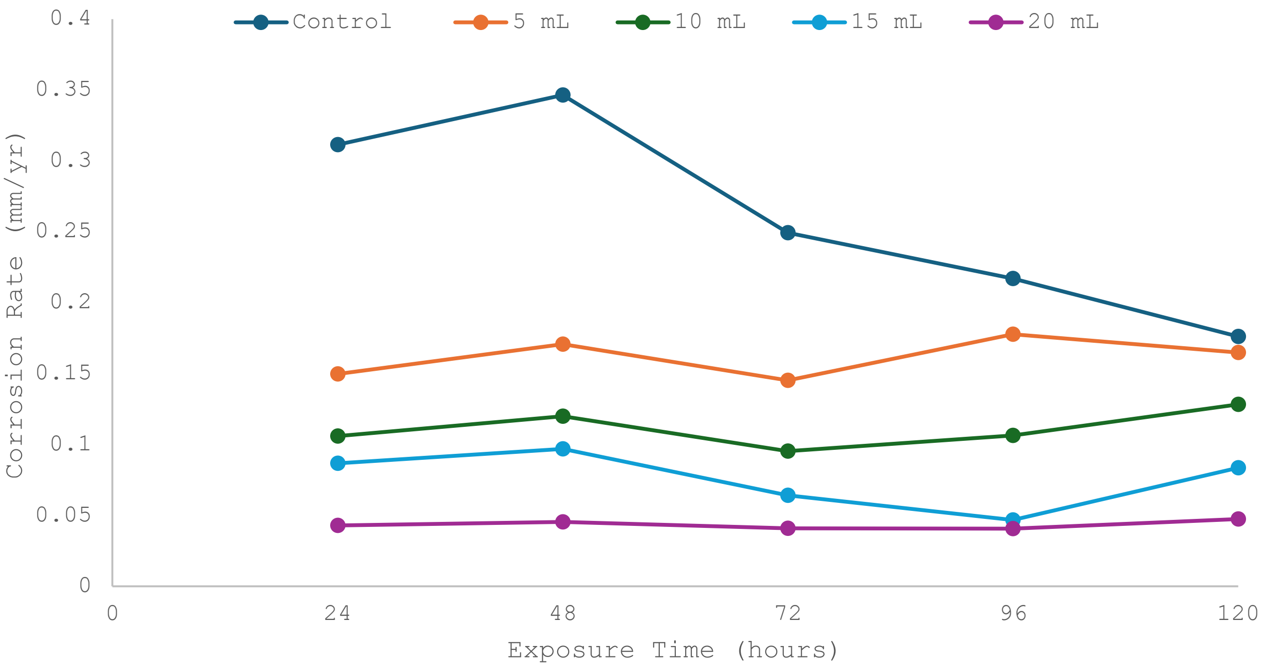


Figure 4.5: Effect of addition of plant leaf extract of Carica Papaya on the corrosion rate of mild steel immersed in 1.5M H_2SO_4

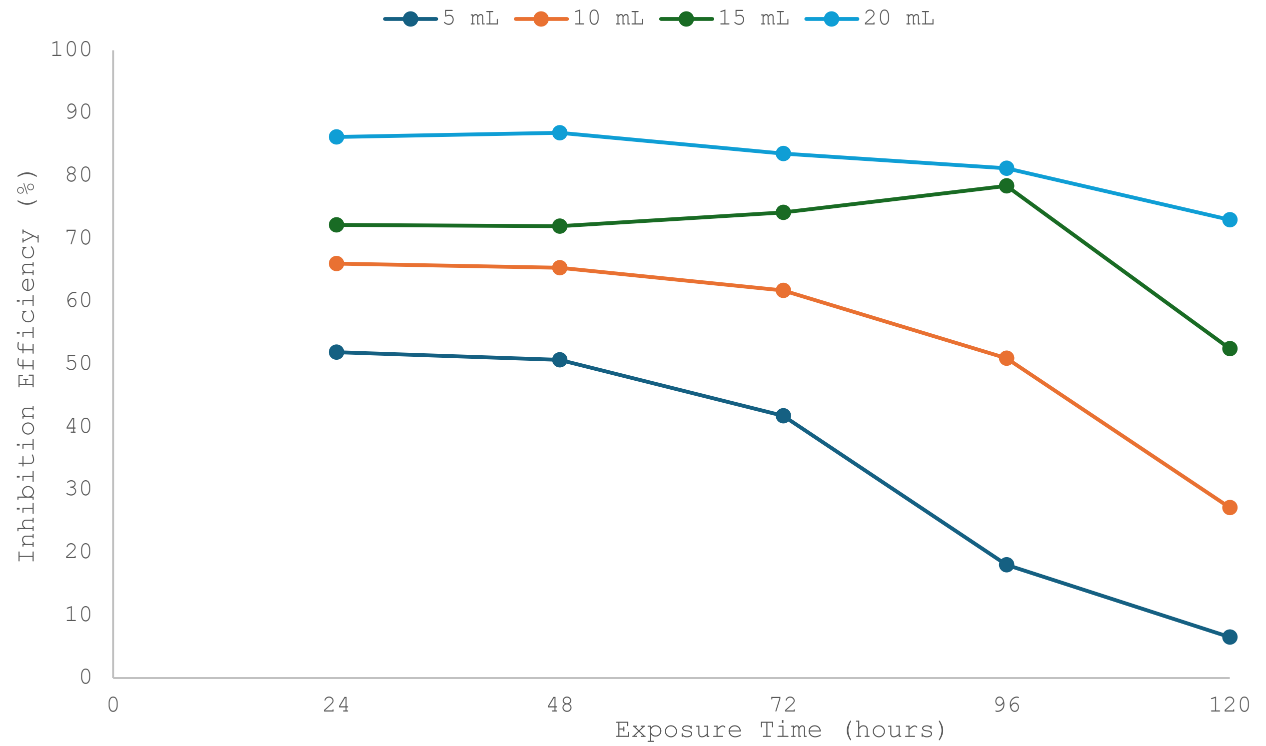


Figure 4.6: Effect of time on the inhibition efficiency of plant leaf extract of Carica papaya on mild steel immersed in 1.5M H_2S0_4

Essentially, raising the concentration of the papaya leaf extract from 5 mL to 20 mL resulted in a 24.80% increase in inhibitory effectiveness. Whereas after the addition of 5mL of the leaf extract, the drop in inhibitory efficacy reached 77.7 % from 24 hr to 120 hr. The inhibitory effectiveness was found to drop by 8.3% upon adding 20 mL of the extract at 120 hr.

4.2.1 Prediction of corrosion behaviour of the leaf-extracts of Carica papaya plant in 1.5 M H_2SO_4

Tables 4.6 to 4.8 and Figures 4.7 to 4.8 give the findings of the prediction of the mild steel corrosion rates in 1.5 M H_2SO_4 solution under uninhibited and inhibited (leaf-extract of Carica papaya) using ANN and MR.

The following prediction equation (Equation 4.2) was obtained by modeling the mild steel corrosion inhibition in H_2SO_4 (1.5 M) by Carica papaya leaf-extract (Tables 4.6 and 4.7).

$$\mathbf{CorrRate}_{\mathrm{CP\ in}\ H_2SO_4\ \mathrm{by\ MR}} = 0.257 - 0.010\ (\text{Conc. of leaf-extract}) \qquad 4.2$$

Table 4.6: Prediction of corrosion inhibition of mild steel in 1.5 H_2SO_4 medium by the leaf-extracts of Carica papaya using MR and ANN

Case	Time of Exposure (h)	Conc. of H_2SO_4 (M)	Conc. Of CP Leaf Extract (mL)	Exp_ CorrRate (mm/yr)	Predicted Exp_ CorrRate by ANN	Pred. Error	Predicted Exp_ CorrRate by MR	Pred. Error
1	24	1.5	0	0.3115	0.3217	0.0102	0.2496	-0.0619
2	48	1.5	0	0.3465	0.2874	-0.0591	0.2419	-0.1046
3	72	1.5	0	0.2494	0.2527	0.0033	0.2343	-0.0151
4	96	1.5	0	0.217	0.2246	0.0076	0.2266	0.0096
5	120	1.5	0	0.1763	0.206	0.0297	0.219	0.0427
6	24	1.5	5	0.1497	0.1984	0.0487	0.1977	0.048
7	48	1.5	5	0.1707	0.1744	0.0037	0.19	0.0193
8	72	1.5	5	0.1452	0.16	0.0148	0.1824	0.0372
9	96	1.5	5	0.1778	0.1534	-0.0244	0.1747	-0.0031
10	120	1.5	5	0.1648	0.152	-0.0128	0.1671	0.0023
11	24	1.5	10	0.1059	0.1114	0.0055	0.1457	0.0398
12	48	1.5	10	0.12	0.1062	-0.0138	0.1381	0.0181
13	72	1.5	10	0.0953	0.1056	0.0103	0.1304	0.0351
14	96	1.5	10	0.1064	0.1077	0.0013	0.1228	0.0164
15	120	1.5	10	0.1284	0.1114	-0.017	0.1151	-0.0133
16	24	1.5	15	0.0867	0.0684	-0.0183	0.0938	0.0071
17	48	1.5	15	0.097	0.0694	-0.0276	0.0862	-0.0108
18	72	1.5	15	0.0643	0.0718	0.0075	0.0785	0.0142
19	96	1.5	15	0.0469	0.075	0.0281	0.0709	0.024
20	120	1.5	15	0.0837	0.0788	-0.0049	0.0632	-0.0205
21	24	1.5	20	0.0429	0.0471	0.0042	0.0419	-0.001
22	48	1.5	20	0.0454	0.0487	0.0033	0.0343	-0.0111
23	72	1.5	20	0.0409	0.0507	0.0098	0.0266	-0.0143
24	96	1.5	20	0.0408	0.0531	0.0123	0.019	-0.0218
25	120	1.5	20	0.0476	0.0558	0.0082	0.0113	-0.0363

Table 4.7: Prediction of Corrosion Inhibition of Mild Steel using the Leaf-extracts of Carica papaya Plant by Multiple Regression

Medium	Model coefficients		
	Constant	Time of exposure (h)	Conc. of leaf-extract (mL)
H_2SO_4	0.257	0.000	-0.010

Additionally, the significance of the independent factors [Table 4.8] was demonstrated by the artificial neural network's prediction of the experimental rate of corrosion (dependent variable) [Table 4.6 and Figure 4.8]. The concentration of the leaf extract had a bigger impact on the prediction of the corrosion rate by 84.7 %, followed by the exposure period (15.3 %), according to the results.

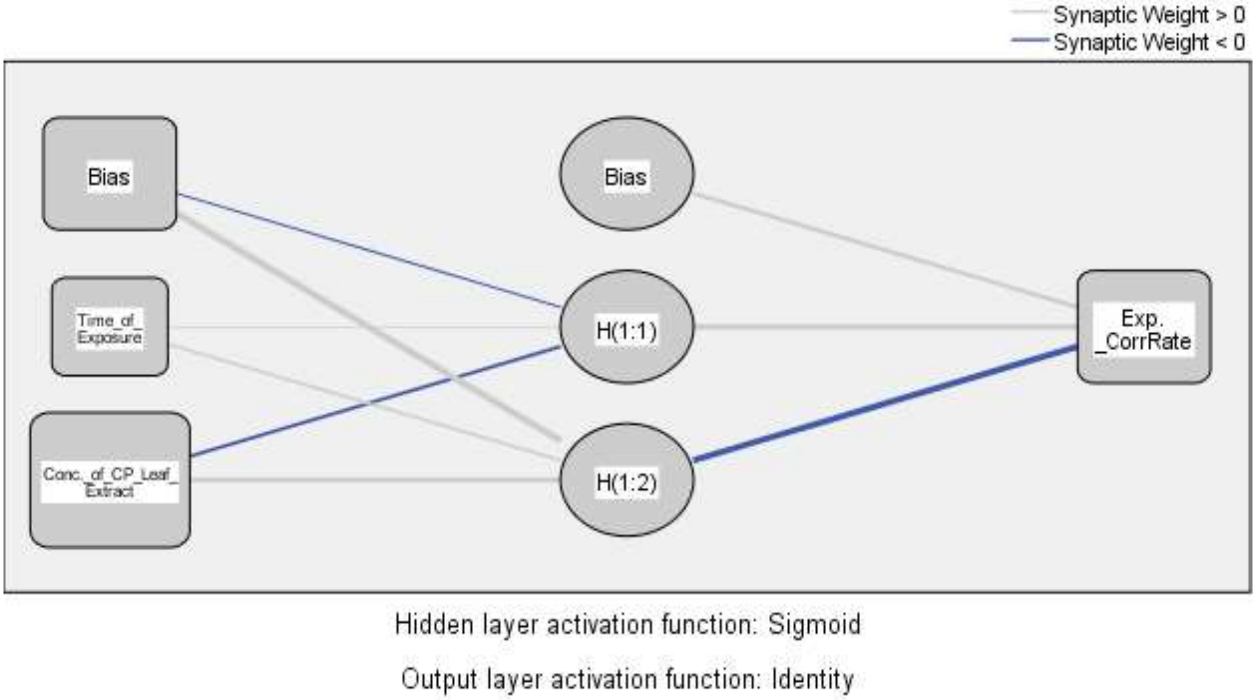


Figure 4.7: ANN diagram for predicting the corrosion inhibition of mild steel in 1.5 M H_2SO_4 by the leaf-extract of Carica papaya plant

Table 4.8: Independent variable importance and parameter estimates of the prediction of corrosion inhibition of mild steel in 1.5 H_2SO_4 medium by the leafextracts of Carica papaya using ANN

Independent Variable Importance	
	Importance
Time_of_Exposure_h	0.153
Conc_of_CP_Leaf_Extract_mL	0.847

Parameter Estimates				
Predictor		Predicted		
		Hidden Layer 1		Output Layer
		H (1:1)	H (1:2)	Exp._Corr Rate
Input Layer	(Bias)	-.461	3.301	
	Time_of_Exposure	.144	.843	
	Conc._of_CP_Leaf_Extract	-1.022	2.180	
Hidden Layer 1	(Bias)			1.484
	H(1:1)			2.193
	H(1:2)			-2.773

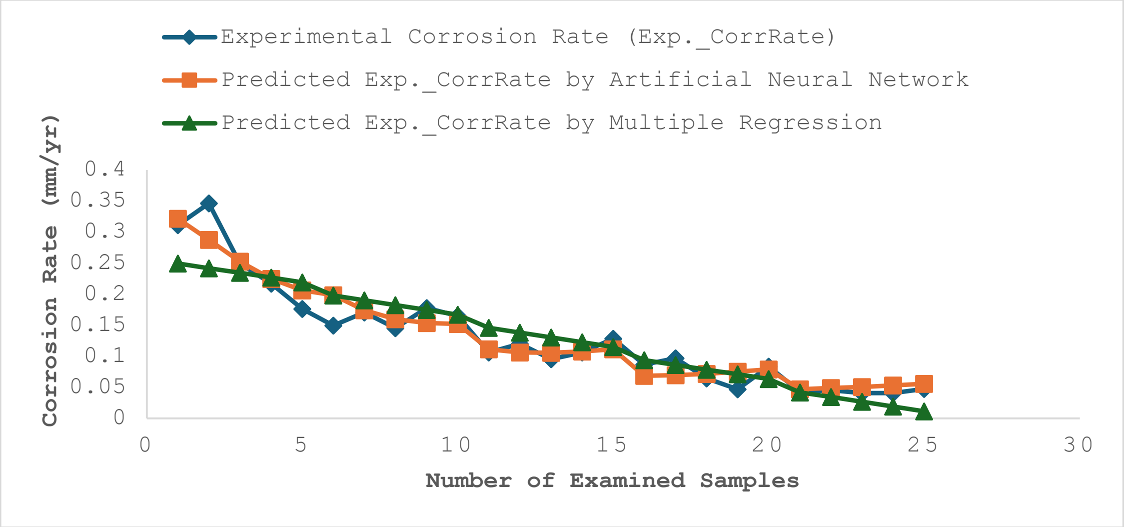


Figure 4.8: Error in prediction of corrosion inhibition of mild steel in 1.5 M H_2SO_4 by the leaf-extracts of Carica papaya plant using MR and ANN

Figure 4.8 and Table 4.6 both present the MR and ANN's inaccurate predictions. From Figure 4.8, the trend of the curves for the predicted values using ANN approaches the experimental corrosion rate values more closely. In other words, it was discovered that ANN forecasts had lower errors than MR predictions. This result is consistent with the earlier findings on Clerodendrum splendens' prediction of the mild steel corrosion inhibition in H_2SO_4 (Ndukwe and Anyakwo, 2017). The adaptability of ANN in managing non-linear relations may be the source of its good performance.

4.3 Effect of addition of the combination of Vernonia amygdalina (VA) and Carica papaya leaf-extracts on the corrosion of mild steel immersed in 1.5M H_2S0_4 [CP maintained at 2 mL while the remaining concentration was augmented by VA]

The results of the deterrence of degradation of mild steel in 1.5 M H_2S0_4 by the synergistic effects of Vernonia amygdalina and Carica papaya are represented in Tables 4.9 and shown in Figures 4.9 and 4.10 respectively for corrosion rate and inhibition efficiency. The addition of the synergy of extracts in the first experimental run had the introduction of papaya maintained at 2 mL while the remaining concentration was augmented by the Vernonia amygdalina leaf extract to make up for 5, 10, 15, and 20 mL. The corrosion rate of mild steel in the study environment was observed to decrease with increase in the addition of the combination of extracts.

The maximum inhibition efficiency was obtained when the combination of 18 mL of VA and 2 mL of CP was added (Table 4.9 and Figure 4.10). The introduction of the papaya leaf extract was observed to improve the corrosion inhibition of steel better than the addition of only the Vernonia amygdalina leaf extract (by comparing the values in Table 4.1 and Table 4.9).

Table 4.9: Effect of addition of plant leaf extract of Vernonia amygdalina and Carica papaya on the corrosion of mild steel immersed in 1.5M H_2S0_4 [CP maintained at 2 mL while the remaining concentration was augmented by VA]

	Control	**3 mL VA + 2 mL CP**		**8 mL VA + 2 mL CP**		**13 mL VA + 2 mL CP**		**18 mL VA + 2 mL CP**	
Exp. Time (hours)	**Cor. Rate (mm/y)**	**Cor. Rate (mm/y)**	**I.E. (%)**	**Cor. Rate (mm/y)**	**I.E. (%)**	**Cor. Rate (mm/y)**	**I.E. (%)**	**Cor. Rate (mm/y)**	**I.E. (%)**
24	0.3115	0.1982	36.37	0.1561	49.90	0.1252	59.81	0.1098	64.76
48	0.3465	0.2050	40.84	0.1760	49.20	0.1211	65.05	0.0886	74.43
72	0.2494	0.1685	32.44	0.1247	50.00	0.1138	54.36	0.0961	61.46
96	0.2170	0.1851	14.70	0.1485	31.56	0.1222	43.67	0.1127	48.07
120	0.1763	0.1739	1.34	0.1651	6.31	0.1212	31.23	0.1150	34.75

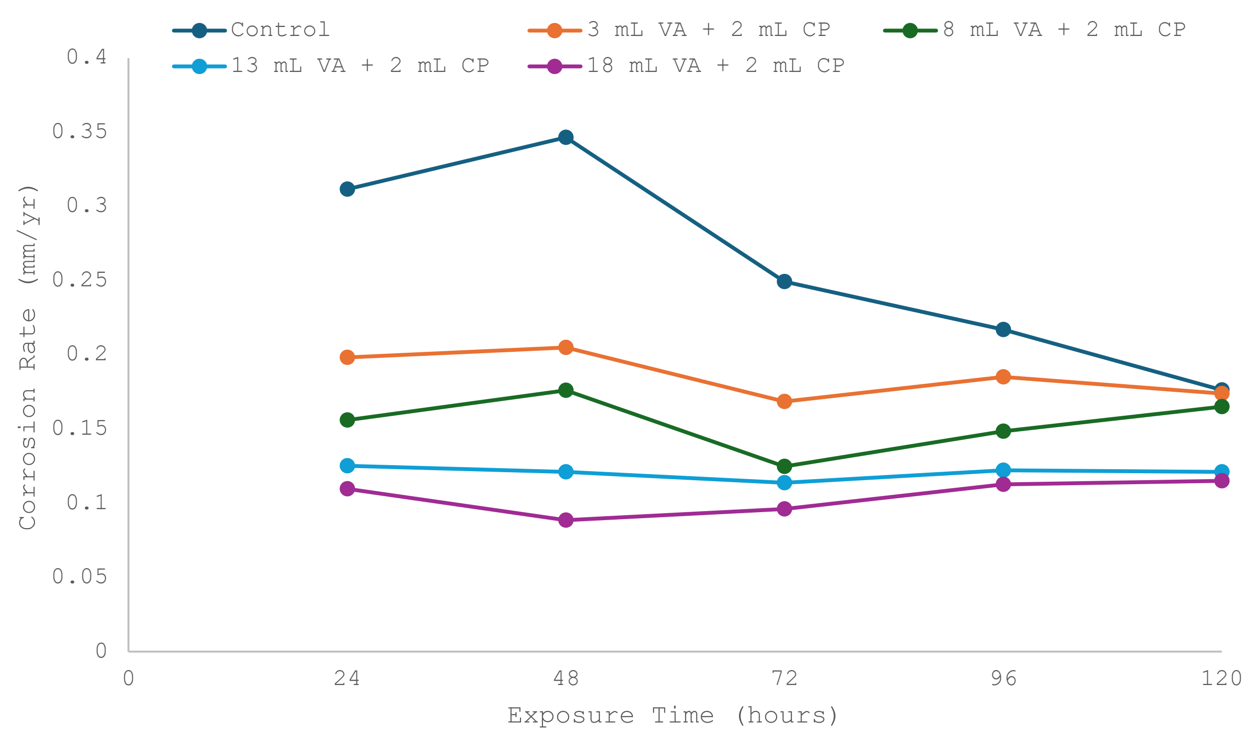


Figure 4.9: Effect of addition of plant leaf extract of Vernonia amygdalina and Carica Papaya on the corrosion rate of mild steel immersed in 1.5 M H_2SO_4

Elevating the concentration of the combination of Vernonia amygdalina and Carica papaya leaf extracts from 3mL VA plus 2mL CP to 18 mL VA plus 2mL CP resulted in a 28.07% increase in inhibitory efficacy. Conversely, the inhibitory effectiveness dropped by 92.89% from 24 hours to 120 hours with the addition of 3 mL of VA and 2 mL of CP of the leaf extracts. It was discovered that adding 18 mL VA and 2 mL CP of the extracts reduced the inhibitory efficacy by 30.19 % at 120 hr.

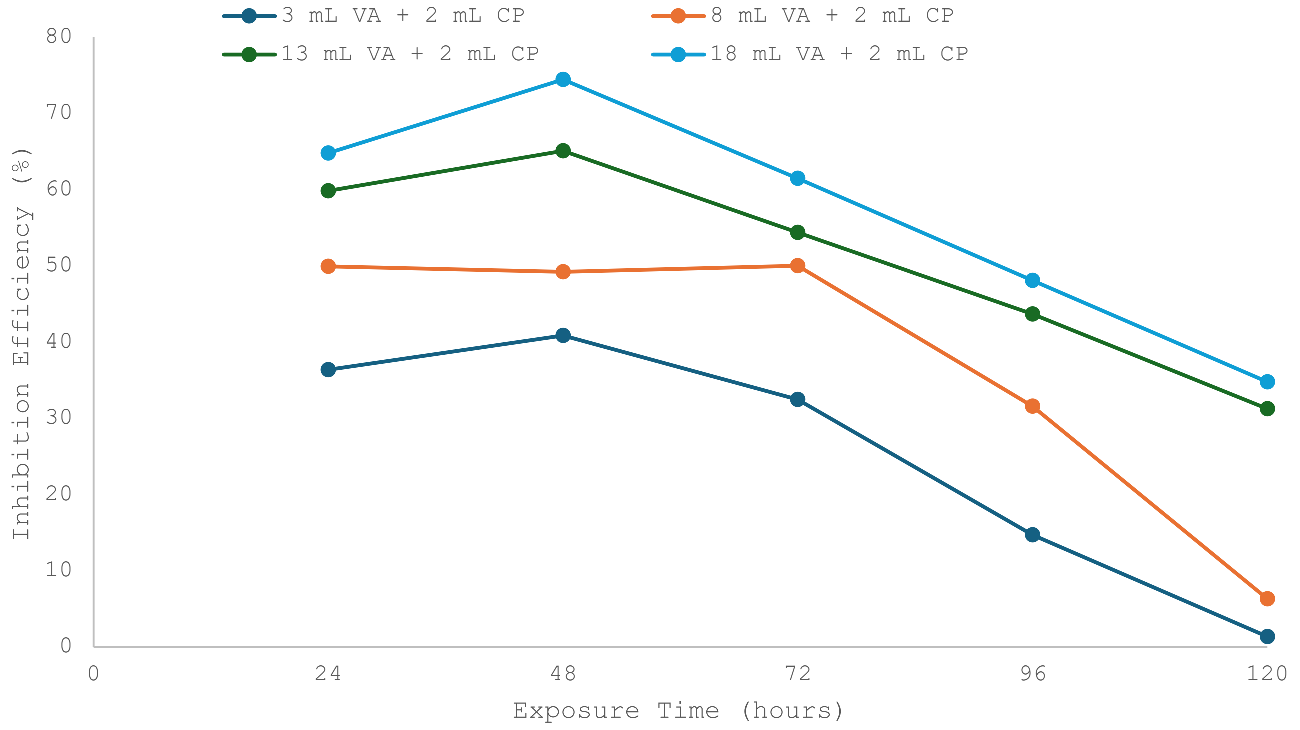


Figure 4.10: Effect of Time on the Inhibition efficiency of plant leaf extract of Vernonia amygdalina and Carica papaya on mild steel immersed in 1.5 M H_2S0_4

4.3.1 Prediction of corrosion behaviour of the leaf-extracts of Vernonia amygdalina (VA) and Carica papaya (CP) plants in 1.5 M H_2SO_4 [CP maintained at 2 mL while the remaining concentration was augmented by VA]

Tables 4.10 to 4.12 and Figures 4.11 to 4.12 demonstrate the findings from the use of ANN and MR to estimate the corrosion rates of mild steel in 1.5 M H_2SO_4 under uninhibited and inhibited conditions (leaf extracts of Carica papaya and Vernonia amygdalina plants).

Table 4.10: Prediction of corrosion inhibition of mild steel in 1.5 H_2SO_4 medium by the leaf-extracts of Vernonia amygdalina (VA) and Carica papaya (CP) [CP maintained at 2 mL while the remaining concentration was augmented by VA] using MR and ANN

Case	**Time of Exposure (h)**	**Conc. of H_2SO_4 (M)**	**Conc. Of CP and VA Leaf-Extracts (mL)**	**Exp_ CorrRate** (mm/yr)	**Predicted Exp_ CorrRate by ANN**	**Pred. Error**	**Predicted Exp_ CorrRate by MR**	**Pred. Error**
1	24	1.5	0	0.3115	0.3299	0.0184	0.25848	-0.05302
2	48	1.5	0	0.3465	0.2973	-0.0492	0.24947	-0.09703
3	72	1.5	0	0.2494	0.2573	0.0079	0.24047	-0.00893
4	96	1.5	0	0.217	0.224	0.007	0.23146	0.01446
5	120	1.5	0	0.1763	0.2043	0.028	0.22246	0.04616
6	24	1.5	5	0.1982	0.2333	0.0351	0.2208	0.0226
7	48	1.5	5	0.205	0.1996	-0.0054	0.21179	0.00679
8	72	1.5	5	0.1685	0.1796	0.0111	0.20278	0.03428
9	96	1.5	5	0.1851	0.1718	-0.0133	0.19378	0.00868
10	120	1.5	5	0.1739	0.1711	-0.0028	0.18477	0.01087
11	24	1.5	10	0.1561	0.1518	-0.0043	0.18311	0.02701
12	48	1.5	10	0.176	0.1417	-0.0343	0.17411	-0.00189
13	72	1.5	10	0.1247	0.1402	0.0155	0.1651	0.0404
14	96	1.5	10	0.1485	0.1432	-0.0053	0.15609	0.00759
15	120	1.5	10	0.1651	0.1482	-0.0169	0.14709	-0.01801
16	24	1.5	15	0.1252	0.1156	-0.0096	0.14543	0.02023
17	48	1.5	15	0.1211	0.1158	-0.0053	0.13642	0.01532
18	72	1.5	15	0.1138	0.1187	0.0049	0.12742	0.01362
19	96	1.5	15	0.1222	0.1231	0.0009	0.11841	-0.00379
20	120	1.5	15	0.1212	0.1284	0.0072	0.1094	-0.0118
21	24	1.5	20	0.1098	0.1013	-0.0085	0.10774	-0.00206
22	48	1.5	20	0.0886	0.103	0.0144	0.09874	0.01014
23	72	1.5	20	0.0961	0.1056	0.0095	0.08973	-0.00637
24	96	1.5	20	0.1127	0.1089	-0.0038	0.08073	-0.03197
25	120	1.5	20	0.115	0.1129	-0.0021	0.07172	-0.04328

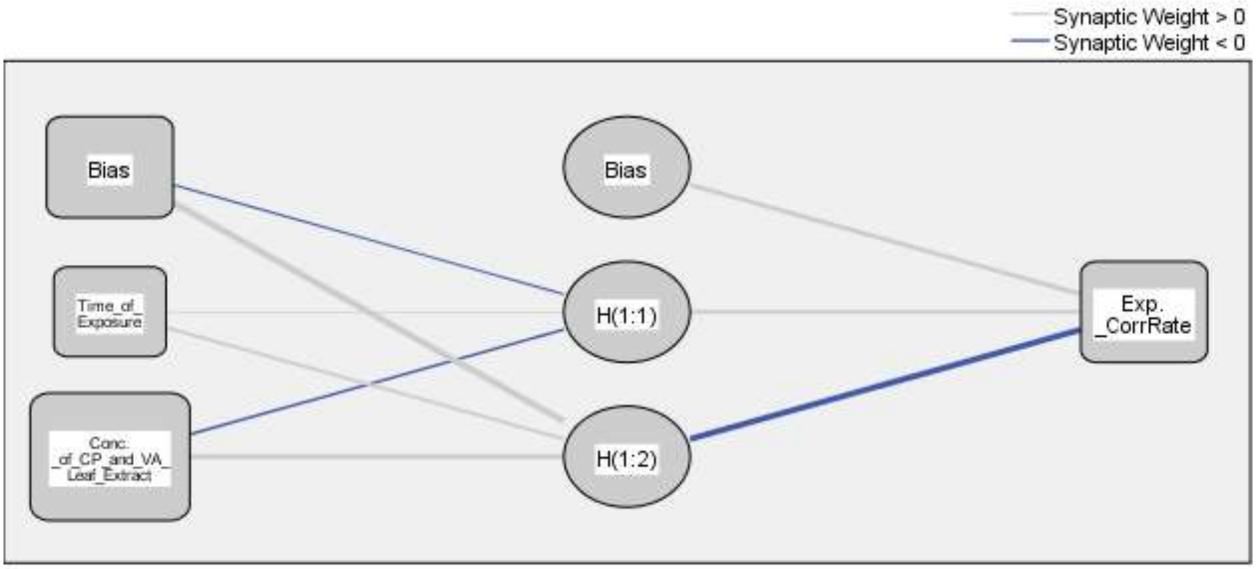
The following prediction equation (Equation (4.3)) was generated by modelling the mild steel corrosion inhibition by the combination of the leaf extracts of Carica papaya and Vernonia amygdalina plants in H_2SO_4 (1.5 M) using multiple regression (Tables 4.10 and 4.11):

$$\mathbf{CorrRate}_{\mathrm{CPandVA\ in}\ H_2SO_4\ \mathrm{by\ MR}} = 0.267 - 0.008\ (\text{Conc. of leaf-extract}) \qquad 4.3$$

Table 4.11: Prediction of Corrosion Inhibition of Mild Steel using the combination of Leaf-extracts of Carica Papaya and Vernonia amygdalina Plants by Multiple Regression [CP maintained at 2 mL while the remaining concentration was augmented by VA]

Model coefficients			
Medium	**Constant**	**Time of exposure (h)**	**Conc. of leaf-extract (mL)**
H_2SO_4	0.267	0.000	-0.008

Additionally, Table 4.10 and Figure 4.11's analysis of the artificial neural network's prediction of the experimental rate of corrosion (dependent variable) revealed the significance of the independent factors [Table 4.12]. The concentration of the leaf extract had a bigger impact on the prediction of the corrosion rate by 77.7 %, according to the results, which were followed by the exposure duration (22.3%).



Hidden layer activation function: Sigmoid

Output layer activation function: Identity

Figure 4.11: ANN diagram for predicting the corrosion inhibition of mild steel in 1.5 M H_2SO_4 by the leaf-extracts of Carica papaya and Vernonia amygdalina Plants

Table 4.12: Independent Variable Importance and Parameter Estimates of the prediction of corrosion inhibition of mild steel in 1.5 H_2SO_4 medium by the leaf-extracts of Carica Papaya and Vernonia amygdalina Plants [CP maintained at 2 mL while the remaining concentration was augmented by VA] using ANN

Independent Variable Importance	
Time_of_Exposure_h	0.223
Conc_of_CPandVA_Leaf_Extra	0.777

Parameter Estimates

Predictor		Predicted		
		Hidden Layer 1		Output Layer
		H (1:1)	H (1:2)	Exp._CorrRate
Input Layer	(Bias)	-.404	3.479	
	Time_of_Exposure	.325	1.229	
	Conc._of_CP_and_VA_ Leaf_Extract	-1.007	2.350	
Hidden Layer 1	(Bias)			2.006
	H (1:1)			1.701
	H (1:2)			-3.185

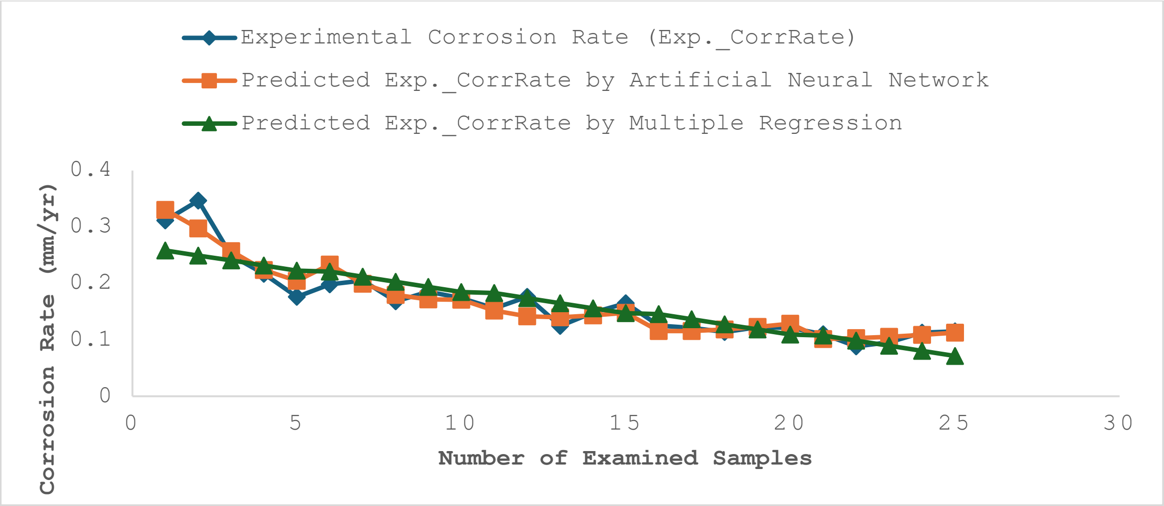


Figure 4.12: Error in prediction of corrosion inhibition of mild steel in 1.5 M H_2SO_4 by the leaf-extracts of Carica papaya and Vernonia amygdalina Plants using MR and ANN

The inaccuracy of the MR and ANN forecasts is reported in Table 4.10 and depicted in Figure 4.12. The trend of the curves for the predicted values using ANN as seen in Figure 4.12 tends to be closer to that of the experimental corrosion rate values. In other words, predictions made by ANN were shown to have lower errors than those made by MR. This result is consistent with the earlier findings on Voacanga Africana's prediction on the mild steel corrosion inhibition in H_2SO_4 (Ndukwe and Anyakwo, 2017). The flexibility of ANN in managing non-linear interrelationships may be the source of its good performance.

4.4 Effect of addition of the combination of Vernonia amygdalina and Carica papaya leaf-extracts on the corrosion of mild steel immersed in 1.5 M H_2SO_4 [VA maintained at 2 mL while the remaining concentration was augmented by CP]

The addition of the synergy of extracts in the second experimental run had the introduction of Vernonia amygdalina maintained at 2 mL while the remaining concentration was augmented by the carica papaya leaf extract to make up for 5, 10, 15, and 20 mL as presented in Table 4.13 and Figures 4.13 and 4.14. The lowest corrosion rate amongst synergy admixtures is evident in 18mL CP + 2 mL VA with a rate of 0.043 mm/yr after 72 hours.

Table 4.13: Effect of addition of the combination of Vernonia amygdalina and Carica papaya leaf-extracts on the corrosion of mild steel immersed in 1.5M H_2S0_4 [VA maintained at 2 mL while the remaining concentration was augmented by CP]

	Control	**2 mL VA + 3 mL CP**		**2 mL VA + 8 mL CP**		**2 mL VA + 13 mL CP**		**2 mL VA + 18 mL CP**	
Exp. Time (hours)	**Cor. Rate (mm/y)**	**Cor. Rate (mm/y)**	**I.E. (%)**	**Cor. Rate (mm/y)**	**I.E. (%)**	**Cor. Rate (mm/y)**	**I.E. (%)**	**Cor. Rate (mm/y)**	**I.E. (%)**
24	0.3115	0.1836	41.08	0.1428	54.15	0.1675	46.23	0.0493	84.16
48	0.3465	0.1924	44.46	0.1376	60.30	0.0833	75.95	0.0597	82.77
72	0.2494	0.1321	47.01	0.1090	56.28	0.0678	72.80	0.0432	82.68
96	0.2170	0.1841	15.18	0.1148	47.11	0.0718	66.92	0.0634	70.76
120	0.1763	0.1588	9.88	0.1324	24.89	0.0775	56.01	0.0686	61.11

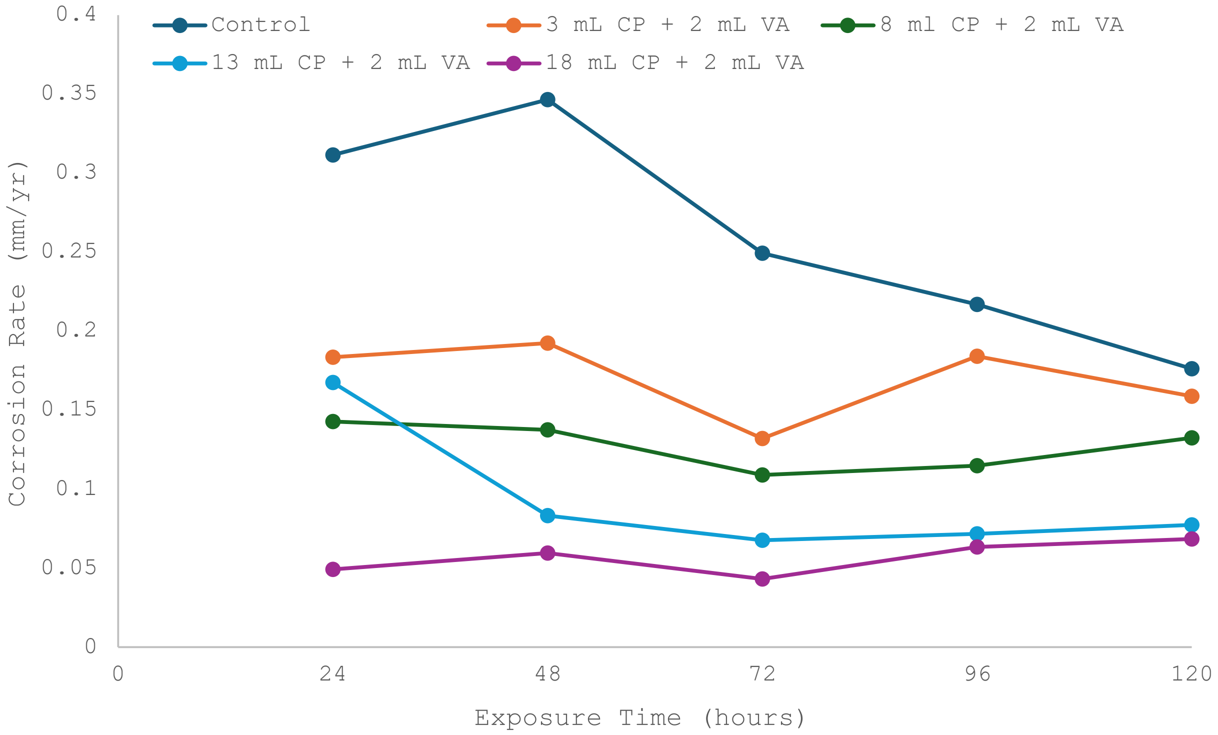


Figure 4.13: Effect of addition of plant leaf extract of Carica Papaya and Vernonia amygdalina on the corrosion rate of mild steel immersed in 1.5 M H_2SO_4

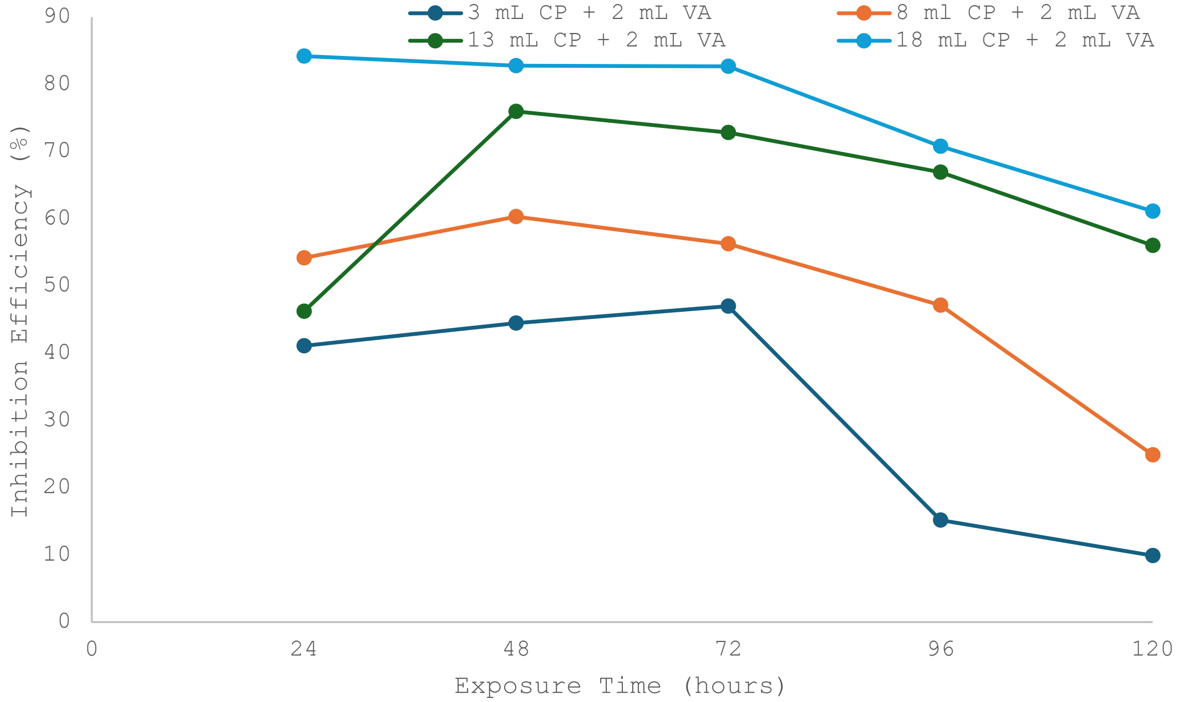


Figure 4.14: Effect of Time on the Inhibiton efficiency of plant leaf extract of Carica Papaya and Vernonia amygdalina on mild steel immersed in 1.5M H_2S0_4

The rate at which the steel corroded in 1.5 M H_2SO_4 was observed to decrease with an increase in the concentration of the combination of Vernonia amygdalina and Carica papaya leaf-extracts. The highest corrosion rate of 0.19 mm/yr was achieved following the addition of the combination of 2 mL Vernonia amygdalina and 3 mL Carica papaya after 48 hours. The outcome of the addition of more Carica papaya (18 mL) was found to improve the inhibition efficiency to a maximum value of 84.16 % after 24 hours. This showed that CP has a greater inhibition effect on mild steel than VA and the synergistic mixtures evident at higher concentrations.

Elevating the concentration of the combination of Vernonia amygdalina and papaya leaf extracts from 2 mL VA plus 3 mL CP to 2 mL VA plus 18 mL CP resulted in a 34.40% increase in inhibitory effectiveness. In contrast, adding 2 mL of VA and 3 mL of CP of the leaf extracts caused the inhibitory efficiency to decrease by 61.81% from 24 hours to 120 hours. On the other hand, the inhibitory effectiveness was found to be decreased by 30.19% at 24 - 120 hours by adding 2 mL VA with 18 mL CP of the extracts.

4.4.1 Prediction of corrosion behaviour of the leaf-extracts of Carica papaya (CP) and Vernonia amygdalina (VA) plants in 1.5 M H_2SO_4 [VA maintained at 2 mL while the remaining concentration was augmented by CP]

Table 4.14 and Figures 4.15 to 4.16 represent the findings for prediction of the mild steel corrosion rates in 1.5 M H_2SO_4 solution under uninhibited and inhibited (leafextracts of Carica papaya (CP) and Vernonia amygdalina (VA) plants) using ANN and MR.

Table 4.14: Prediction of corrosion inhibition of mild steel in 1.5 H_2SO_4 medium by the leaf-extracts of Vernonia amygdalina (VA) and Carica papaya (CP) [VA maintained at 2 mL while the remaining concentration was augmented by CP] using MR and ANN

Case	**Time of Exposure (h)**	**Conc. of H_2SO_4 (M)**	**Conc. Of VA and CP Leaf-Extracts (mL)**	**Exp_ CorrRate** (mm/yr)	**Predicted Exp_ CorrRate by ANN**	**Pred. Error**	**Predicted Exp_ CorrRate by MR**	**Pred. Error**
1	24	1.5	0	0.3115	0.3299	0.0184	0.25848	-0.05302
2	48	1.5	0	0.3465	0.2973	-0.0492	0.24947	-0.09703
3	72	1.5	0	0.2494	0.2573	0.0079	0.24047	-0.00893
4	96	1.5	0	0.217	0.224	0.007	0.23146	0.01446
5	120	1.5	0	0.1763	0.2043	0.028	0.22246	0.04616
6	24	1.5	5	0.1982	0.2333	0.0351	0.2208	0.0226
7	48	1.5	5	0.205	0.1996	-0.0054	0.21179	0.00679
8	72	1.5	5	0.1685	0.1796	0.0111	0.20278	0.03428
9	96	1.5	5	0.1851	0.1718	-0.0133	0.19378	0.00868
10	120	1.5	5	0.1739	0.1711	-0.0028	0.18477	0.01087
11	24	1.5	10	0.1561	0.1518	-0.0043	0.18311	0.02701
12	48	1.5	10	0.176	0.1417	-0.0343	0.17411	-0.00189
13	72	1.5	10	0.1247	0.1402	0.0155	0.1651	0.0404
14	96	1.5	10	0.1485	0.1432	-0.0053	0.15609	0.00759
15	120	1.5	10	0.1651	0.1482	-0.0169	0.14709	-0.01801
16	24	1.5	15	0.1252	0.1156	-0.0096	0.14543	0.02023
17	48	1.5	15	0.1211	0.1158	-0.0053	0.13642	0.01532
18	72	1.5	15	0.1138	0.1187	0.0049	0.12742	0.01362
19	96	1.5	15	0.1222	0.1231	0.0009	0.11841	-0.00379
20	120	1.5	15	0.1212	0.1284	0.0072	0.1094	-0.0118
21	24	1.5	20	0.1098	0.1013	-0.0085	0.10774	-0.00206
22	48	1.5	20	0.0886	0.103	0.0144	0.09874	0.01014
23	72	1.5	20	0.0961	0.1056	0.0095	0.08973	-0.00637
24	96	1.5	20	0.1127	0.1089	-0.0038	0.08073	-0.03197
25	120	1.5	20	0.115	0.1129	-0.0021	0.07172	-0.04328

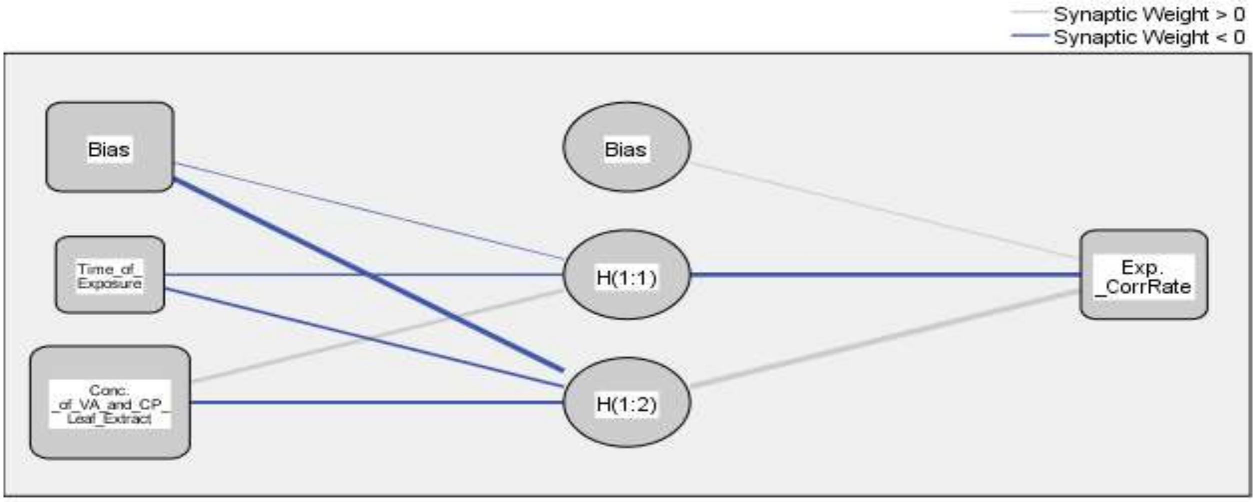
The following prediction equation (Equation (4.4)) was obtained by modelling the mild steel corrosion inhibition in H_2SO_4 (1.5 M) by Carica papaya (CP) and Vernonia amygdalina (VA) plants (Tables 4.14 and 4.15).

$$\textbf{CorrRate}_{\text{VAandCP in } H_2SO_4 \text{ by MR}} = 0.277 - 0.001 \text{ (time of exposure)} - 0.010 \text{ (conc. of leaf-extract)} \qquad 4.4$$

Table 4.15: Prediction of Corrosion Inhibition of Mild Steel using the combination of Leaf-extracts of Vernonia amygdalina and Carica Papaya Plants by Multiple Regression [CP maintained at 2 mL while the remaining concentration was augmented by VA]

	Model coefficients		
Medium	**Constant**	**Time of exposure (h)**	**Conc. of leaf-extract (mL)**
H_2SO_4	0.277	-0.001	-0.010

The artificial neural network's prediction of the experimental rate of corrosion (dependent variable) [Table 4.16 and Figure 4.16] further demonstrated the significance of the independent factors [Table 4.4]. The concentration of the leaf extract, which had a bigger impact on the corrosion rate prediction by 81.4%, was followed by the exposure period, which had a 18.6% greater impact on the results.



Hidden layer activation function: Sigmoid

Output layer activation function: Identity

Figure 4.15: ANN diagram for predicting the corrosion inhibition of mild steel in 1.5 M H_2SO_4 by the leaf-extracts of Vernonia amygdalina and Carica papaya Plants

Table 4.16: Independent Variable Importance and Parameter Estimates of the prediction of corrosion inhibition of mild steel in 1.5 H_2SO_4 medium by the leafextracts of Vernonia amygdalina and Carica Papaya Plants [CP maintained at 2 mL while the remaining concentration was augmented by VA] using ANN

Independent Variable Importance

	Importance
Time_of_Exposure_h	0.186
Conc_of_VAandCP_Leaf_Extracts	0.814

Parameter Estimates

Predictor		Predicted		
		Hidden Layer 1		Output Layer
		H (1:1)	H (1:2)	Exp._CorrRate
Input Layer	(Bias)	-.140	-2.958	
	Time_of_Exposure	-.311	-.769	
	Conc._of_VA_and_CP_Leaf_Extract	1.340	-1.337	
Hidden Layer 1	(Bias)			.277
	H (1:1)			-1.697
	H (1:2)			5.014

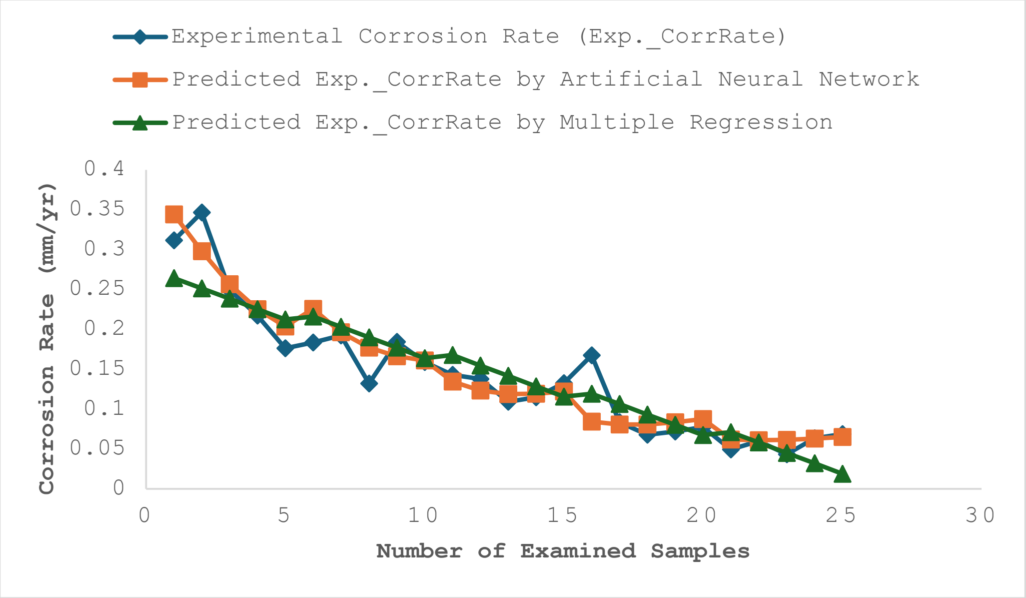


Figure 4.16: Error in prediction of corrosion inhibition of mild steel in 1.5 M H_2SO_4 by the leaf-extracts of Vernonia amygdalina and Carica papaya Plants using MR and ANN

Figure 16 and Table 4.13 both give data illustrating the inaccuracy of MR and ANN predictions. The trend of the curves for the predicted values using ANN appeared to be closer to that of the experimental corrosion rate values, as shown in Figure 16. In other words, it was discovered that predictions made by ANN had lower errors than those made by MR. This result is consistent with the earlier study on the prediction of the corrosion inhibition of mild steel in H_2SO_4 by Landolphia Dulcis (Ndukwe and Anyakwo, 2017). It is possible that ANN's adaptability in managing non-linear interactions is what accounts for its good performance

4.5 Phytochemical Analyses of the Examined Plant Leaves

The fresh papaya leaves were found to have a higher percentage of alkaloids (3.9 %) than the Vernonia amygdalina leaves (2.8 %). The observed content of alkaloid in the bitter leaf was slightly higher than the 2.16 % that was earlier reported (Ugueri et al., 2015). Other phytochemicals obtained in the plant leaves were observed to be slightly greater in papaya leaves than in Vernonia amygdalina leaves as follows: Tannin – 0.893 % in papaya, and 0.830 % in Vernonia amygdalina leaves; Phenol – 0.250 % in papaya, and 0.164 % in Vernonia amygdalina leaves; and Phytate – 0.330 % in papaya, and 0.222 % in Vernonia amygdalina leaves. However, the reverse was the case for the presence of cyanide with the Vernonia amygdalina leaves having 138.0 mg/kg more than the 79.5 mg/kg content in papaya leaves. The summary of the phytochemical analyses of the examined plant leaves can be found in Table 4.17.

Table 4.17: The Phytochemical Analyses of Carica papaya and Vernonia amygdalina leaves

Sample	Tannin (%)	Phenol (%)	Alkaloid (%)	Phytate (%)	Hydrogen Cyanide (mg/kg)
Fresh Papaya Leaves	0.893	0.250	3.90	0.330	79.50
Fresh Vernonia amygdalina leaves	0.830	0.164	2.80	0.222	138.00

While earlier studies acknowledged the presence of the aforementioned phytochemicals in papaya and Vernonia amygdalina leaves (Ayoola & Adeyeye, 2010; Ekan et al., 2009; Ugueri et al., 2015), the phytochemicals obtained in the Vernonia amygdalina leaves by previous results were found to be higher than the present study for Phytate (3.95 %), Tannin (9.62 %), and Phenol (3.24 %) (Ugueri et al., 2015). This disparity may have been occasioned using air-dried samples for the phytochemical study as reported (Ugueri et al., 2015). According to (Qureshi, 2015), there is a general explanation for this development: while green plant leaves have active metabolic and synthesizing machinery and chloroplasts, which may lead to the formation of new compounds, intermediates, or secondary metabolites, the dried composition of plant leaves undergoes no further enzymatic or metabolic alteration, and all compounds can be recovered in a natural, unaltered form.

CHAPTER FIVE

CONCLUSION, RECOMMENDATION, AND CONTRIBUTION TO KNOWLEDGE

5.1 CONCLUSION

From the current investigation on the corrosion inhibition of mild steel submerged in a 1.5 M H_2SO_4 solution utilizing plant leaf extracts of Vernonia amygdalina (VA), Carica papaya (CP), and a combination of both, the following conclusions can be drawn:

1. The examined leaf extracts prevented the corrosion of mild steel in 1.5 M H_2SO_4. The inhibition efficiency was observed to increase with increase in the concentration of the leaf-extract.
2. For *Vernonia amygdalina* leaf extract, maximum inhibition efficiency attained was 64.8% with the addition of 20 mL concentration at 24 hours.
3. The *carica papaya* (CP) leaf-extract outperformed the bitter leaf (VA) extract with a maximum inhibition efficiency of 86.89% with 20 mL concentration and at 48 hours of exposure time.
4. When VA and CP leaf extracts were combined, they demonstrated superior corrosion inhibition when compared to VA alone.
5. The mixture of 18 mL of VA and 2 mL of CP showed the inhibition efficiency of 74.43% at 48 hours of exposure time.
6. The mixture of 18 mL of CP and 2 mL of VA attained an inhibition efficiency of 84.16% at 24 hours.
7. ANN forecasts had lesser errors than MR predictions, indicating that ANN is better at predicting the corrosion inhibition behaviour of mild steel in 1.5 M sulphuric acid solution than MR.
8. The fresh papaya leaves were found to have a higher percentage of alkaloids (3.9 %) than the Vernonia amygdalina leaves (2.8 %). Other phytochemicals

obtained in the plant leaves were observed to be slightly greater in Carica papaya leaves than in Vernonia amygdalina leaves as follows: Tannin – 0.893 % in papaya, and 0.830 % in Vernonia amygdalina leaves; Phenol – 0.250 % in Carica papaya, and 0.164 % in Vernonia amygdalina leaves; and Phytate – 0.330 % in papaya, and 0.222 % in Vernonia amygdalina leaves. However, the reverse was the case for the presence of cyanide with the Vernonia amygdalina leaves having 138.0 mg/kg more than the 79.5 mg/kg content in papaya leaves.

In conclusion, the research indicates that Vernonia amygdalina and Carica papaya leaf extracts are potentially able to prevent mild steel from corroding in a 1.5M H_2SO_4 environment. Additionally, mixing these plant extracts can result in a stronger suppression of corrosion. However, because inhibition efficiency tends to decline with time, it is important to consider these inhibitors' long-term efficacy. Because ANN accurately captures complicated corrosion behavior, using it for prediction modeling is advised.

5.2 RECOMMENDATION

The following are some recommendations based on the results of the study on the corrosion prevention of mild steel in a 1.5M H_2SO_4 solution using plant leaf extracts of Vernonia amygdalina (VA), Carica papaya (CP), and their mixture:

1. For both Vernonia amygdalina and Carica papaya leaf extracts, as well as their mixtures, further research should be done to fine-tune the ideal inhibitor doses. This will increase the effectiveness of corrosion inhibition while lowering the expense of using an inhibitor.
2. To identify the causes of the plant-based inhibitors' decreased efficacy, it is recommended to conduct research on the mechanisms of degradation of the

inhibitors over time. This information can direct the creation of inhibitors with greater stability.

5.3 CONTRIBUTIONS TO KNOWLEDGE

1. A new understanding of the synergistic effect of VA and CP inhibiting the corrosion of mild steel in 1.5 M H_2SO_4 has been established.
2. For the first time, a predictive model has been used to forecast the corrosion inhibition behavior of mild steel in 1.5 M H_2SO_4 by the leaf-extracts of VA and CP using Artificial Neural Network (ANN) and Multiple Regression (MR).

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APPENDIX

APPENDIX A.1: Computation of the area of steel coupon

Dimension of metal coupon = 5 cm x 5cm x 0.1 cm

Hole diameter = 0.2cm

$$A = 2(LB + LT + BT) - 2\frac{\pi d^2}{4} + \pi d T$$

where; L = length of coupon (cm)

B = breadth of coupon (cm)

T = Thickness of coupon (cm)

d = diameter of the hole drilled on the coupon.

APPENDIX A1: Ohaus Analytical Weighing balance

APPENDIX A2: Mild steel immersed in environment containing inhibitors

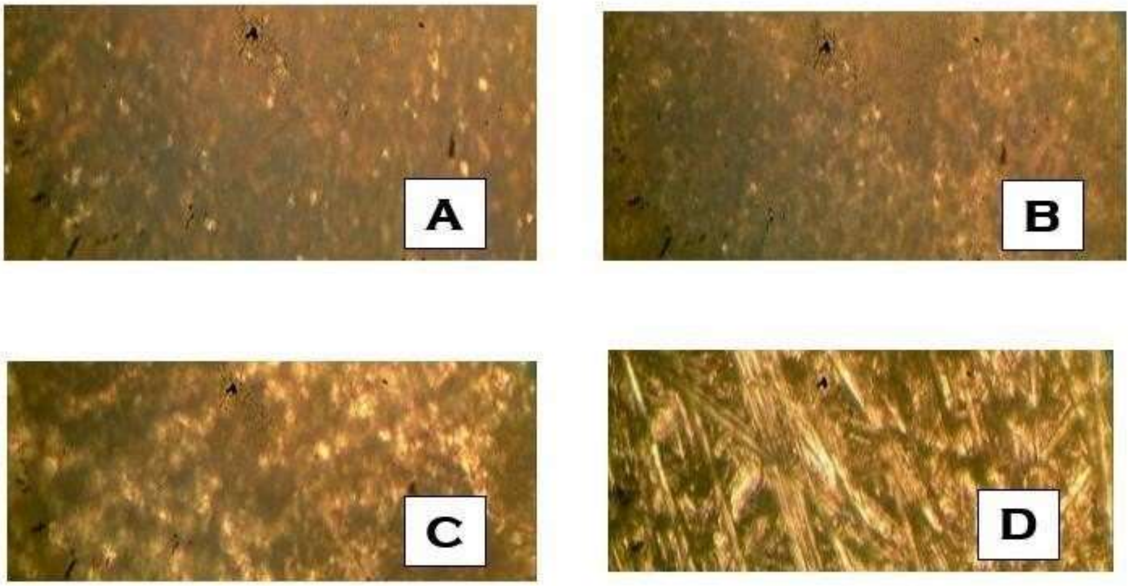
APPENDIX B: INHIBITOR CONCENTRATION

APPENDIX B1: Trend of inhibitor concentration performance in corrosion rate terms

S/N	DESCRIPTION	TREND	BEST PERFORMING	LEAST PERFORMING
1	VA	Control > 5mL > 10mL > 15mL > 20mL	20mL	5mL
2	CP	Control > 5mL > 10mL > 15mL > 20mL	20mL	5mL
3	VA + CP (FIXED CONC)	Control > 3mLVA + 2mLCP > 8mLVA + 2mL CP > 13mL VA + 2mLCP > 18mL VA + 2mL CP	13mL VA + 2mL CP	3mLVA + 2mL CP
4	VA (FIXED CONC) + CP	Control > 2mL VA+3mL CP > 2mLVA+8mLCP > 2mL VA + 13mL CP > 2mL VA + 18mL CP	2mL VA + 8mL CP	2mL VA + 3mL CP

APPENDIX B2: Trend of inhibitor concentration performance in terms of inhibitor efficiency

S/ N	DESCRIPTION	TREND	BEST PERFORMING	LEAST PERFORMING
1	**VA**	20 mL > 15mL > 10 mL > 5mL	15mL	5 mL
2	**CP**	20mL>15mL>10mL>5mL	20 Ml	5 mL
3	**VA+CP (FIXED)**	18 mL VA+ 2 mL CP > 13 mL VA + 2mL CP > 8mL VA + 2mL CP > 3mL VA + 2mL CP	18 mL VA + 2mL CP	3mL VA + 2mL CP
4	**CP+VA (FIXED)**	18 mL VA+ 2 mL CP > 13 mL VA + 2mL CP > 8mL VA + 2mL CP > 3mL VA + 2mL CP	18mL CP + 2mL VA	3 mL CP + 2mL VA



APPENDIX B1: Micrographs (X 200) of mild steel coupons: (A) before immersion, (B) after immersion for 24 hours, (C) after immersion for 72hours, and (D) after immersion for 120 hours.

About 2160g of fresh leaves were used to successfully complete the research.