UNIVERSITY OF NAIROBI

PREPARATION AND EVALUATION OF RUST REMOVAL SOLUTION FOR ANTICORROSIVE PROPERTIES

BY

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I56/7894/2017

A Thesis Submitted in Partial Fulfillment of the Requirements for the Award of the Degree of Master of Science in Industrial Chemistry of the University of Nairobi

August, 2022

DECLARATION

I declare that this thesis is my original work and has not been submitted elsewhere for research. Where other people's work or my own work has been used, this has been properly acknowledged and referenced in accordance with the University of Nairobi requirements.

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ABSTRACT

The deterioration of metal surface especially iron due to oxidation or other chemical reactions results in the formation of rust. Rust consists of hydrated iron (III) oxide ($Fe_2.O_3. nH_2O$), which is generated when iron, is in contact with both moisture and oxygen. The formation of rust causes enormous loss to the economy of the country and compromises the integrity of the structures. Therefore, there is a need to develop solutions which can remove rust from metallic surfaces. The objective of this study was to prepare some rust removal formulations using selected reagents and to evaluate their rust removal properties. The formulations were prepared using compositions of different low molecular weight organic acids (LMWOs) at room temperature. Formulation one contained citric acid, sulphamic acid, and iron sulphate whereas, formulation two was composed of acetic acid, sulphamic acid, and iron sulphate. Formulation three contained hydroxyacetic acid, sulphamic acid, and iron sulphate. Formulation four was composed of oxalic acid, sulphamic acid, and iron sulphate, whereas formulation five was composed of extracted citric acid, sulphamic acid, and iron sulphate. The study established that the % rust removal for formulation one was in the range of 35-63%, 71-85%, and 77-92%, after 30 minutes, 60 minutes, and 90 minutes respectively. The percentage of the rust removed by formulation two ranged from 38-60%, 60-87% and 73-79%, after 30 minutes, 60 minutes and 90 minutes, respectively. The percentage rust removal by formulation three was 62-77%, 78-81% and 55-88% while for formulation four the range was 14-29%, 32-63% and 11-21% and for formulation five the range was 0.3-66%, 0-1.6 % and 0.7-1.9 % after 30, 60, and 90 minutes respectively. The study showed that at room temperature after 30 minutes the percentage rust removal was in the following order: Formulation 3 with a mean of 81%, followed by formulation 1 at 47.6%, then formulation 2 at 42.4%. This was followed by formulation 5 and 4 at 22.7% and 22.5% respectively. FTIR analysis was conducted on the composition of all formulations before and after the reaction with the rusted metal surface to establish the functional groups involved in the process of rusting. The FTIR study showed that the peaks produced by formulations had some peaks disappear, others shifting from original positions. Based on the study, the prepared formulations indicated the ability to remove rust from the rusted nails of this project. The amount of removed rust depended on the nature of the formulation. Formulation one gave the optimum rust removal property at room temperature.

ACKNOWLEDGEMENT

Foremost, I would love to express my sincere gratitude to the almighty God for the strength and courage He gave me to pursue this course. Secondly, I also want to appreciate my supervisors Prof. Amir Yusuf and Dr. John Onyatta, for their continued support of my MSc research, for their motivation, patience, and immense knowledge they bestowed upon me throughout the process.

My sincere thanks also go to my entire family, my Mum, my late dad, siblings, and every friend who encouraged me to continue pressing on through their resources or their word of advice. Further, I cannot fail to recognize the great role played by the University of Nairobi analytical laboratory technologists through the efforts of Mr. Mwangi, Dr. Rop, and Ms. Alice for coming through every time I sought their assistance.

Last but not least, I would also want to thank my classmates of 2017 class for always having a word of encouragement and working as a team throughout the course.

TABLES OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND ACRONYMS

EDTA	Ethylenediamine tetraacetic acid
FTIR	Fourier transform infrared spectrometer
MAS	Magnesium aluminium silicate
PDMS	Polydimethylsiloxane
ppm	Parts per million
Rev/min	Revolutions per minute
Sa	Anodic surface
Sc	Cathodic surface
V	Volt
v/v	Volume per volume
W1	Intial sample weight
W2	Stained weight
W3	Weight after rust removal

CHAPTER ONE

INTRODUCTION

1.1 Background Information

The coating that occurs on iron surfaces is usually referred to as rust. The presence of rust (hydrated iron (III) oxide ($Fe_2O_3.H_2O$)) on the steel or iron surface can cause damage to the surface and when this happens, more of the metal surface will be exposed to oxygen, moisture and oxidation continues to occur. Rust is a corrosion product (reddish-brown) of iron consisting of several components (Evans and Taylor, 1972). Iron has certainly been the most applied and must have been among the first where serious corrosion problems were encountered though it was not the first metal utilized by man (Morgan, 1988). Rust exists in different combinations, as a chemical compound mainly of iron and oxygen to form reddish-orange color. Rust formation speed can be increased if an alloy (iron) is exposed in corrosive environments (Yari *et al*., 2017). Figure 1.1 shows a corroded industrial pipe.

Figure 1.1: Rusted material (Evans and Taylor, 1972)

Rust has devastating impacts on alloys (iron-based), which eventually can thin them until they are unsuitable for their original intended use. Excessive rusting leads to the bursting of pipelines and collapsing of structures. Rust also compromises the iron components' aesthetic appeal (Beacon, 2002). With the exception of Gold, other elements have oxidizing potential that is less positive that of oxygen gas. The half reduction potential for iron is as shown by the following half equations.

$Fe^{2+}(aq) + 2e^{-} \rightarrow Fe\ (s)$ $E^{0}=-0.44V$(1.1)

$Fe^{3+}(aq) + 3e- \longrightarrow Fe\ (s)$ $E^{0}=0.036V$ (1.2)

$O_2\ (g) + 2H_2O\ (l) + 4e^{-} \rightarrow 4OH^{-}(aq)$ $E^{0}=+0.40V$ (1.3)

Rust generates an oxide due to oxidation due to a difference in electrical potential in the electrolyte between the two materials. This difference creates an anode-cathode system, with the anode readily giving up electrons, whereas cathode electrode accepts electrons (antiqueengines.com, 2018). The oxygen atoms, either from an electrolyte or from the atmosphere, are transferred through the electrolyte during the rusting process. The atoms (oxygen) then react with the iron to form iron oxide, indicating that rusting can be reduced if the electrolyte is removed from the reaction, as shown by reactions 1.4 and 1.5.

$2Fe\ (s) + O_2\ (g) + H_2O\ (l) + 4e^{-} \rightarrow 2Fe^{2+}\ (aq) + 4e^{-} + 4OH^{-}$ (1.4)

$2Fe\ (OH)_2(aq) \xrightarrow{(\mathbf{O2,\ H2O})} Fe_2O_3.nH_2O\ (s)$ (1.5)

Corrosion is a natural process thus there is a tendency of iron and steel to combine at the lowest energy level with oxygen and water vapor, which leads to formation of hydrated iron oxide which produces an insoluble reddish brown solution of $Fe(OH)_3$.

1.1.1 Rust remover

Rust remover is a liquid solution consisting of a blend of synergetic anti-oxidants and passivators. The remover is used to remove rust from any metallic iron and steel surfaces. Additionally, it contributes to the rust proofing of metals before any painting or coating application. On many occasions, there is always a need to remove rust from various objects like nails, bolts, engine parts, etc (Beacon, 2002).

Rust is a corrosion product of iron composed of different constituents (Evans and Taylor, 1972). The redox reaction prevails when iron interacts with oxygen in the presence of water and air moisture to form a red oxide product. Rust is a term used to describe iron corrosion and its alloys like steel, whereas corrosion is an operation of the slow destruction of metals when exposed to the environment. It is a term that covers the deterioration of metal by oxidation or other chemical reactions (Astrene, 2011).

The presence of rust (iron oxide) on the steel or iron surface can flake off and when this happens, more of the metal surface will be exposed to oxygen and oxidation continues to occur. On most metals rust can eat through the material leading to its destruction. When the metal is eaten away by rust, it is unable to withstand or support much weight. Items like bolts that are expected to hold chairs, desks, structures, bridges and buildings together weakens after rusting hence causing structural failure. The formation of rust leads to loss mainly in the damages to properties and economic losses.

1.2 Statement of the problem

Rust prevails in various environments of machines and facilities (iron and steel surfaces) when in contact with air and moisture, it results to the economic losses and deterioration of performance of machines and facilities. Hence there’s a need to develop a solution for removing rust from metallic surfaces. Most materials in use today are made of iron, which is prone to rust, which has made it necessary to develop ways of removing rust from these materials. Most if not all of these rust removers are imported. There is, therefore, a need to formulate rust removers locally to assist in saving our foreign exchange reserves.

1.3 Objectives

1.3.1 General objective

The general objective of this study was to prepare and evaluate the efficiency of various rust removal formulations.

1.3.2 Specific objectives

The specific objectives of the study were to:

(i). Evaluate rust removing efficiency of the various rust remover formulations.

(ii). To assess the functional group changes in the complexes formed from iron and sulphamic acid, acetic acid, citric acid, and hydroxyacetic acid.

(iii). To determine the optimum rust remover formulation in removing rust.

1.4 Justification and significance of the study

Kenya’s corrosion cost is indeed significant (Pierre, 2006). The successive reviews on corrosion concluded that it constitutes an enomous cost to the gross national product (GNP) of a country. The yearly corrosion cost (2019 GNP) of the United States per Uhlig’s report was found to be $276 billion, equivalent to 2.1 percent. (Virmani, 2002; Zeferani, 2015).

The cost of managing corrosion using rust removal formulations is therefore correspondingly high which necessitates its importation at great cost. According to the Nace.org report 2015, Kenya exchanges about $45.31 billion in anti-rust and corrosion products, with 29.3% used in the agricultural sector, 17.4% in the manufacturing industry, and 67.8% used in the service industry. Coming up with a viable rust remover in Kenya will therefore save the country from importation costs. By producing the formulations locally, Kenya will be saving importation costs worth USD 0.6 million annually (Exportgenius, 2021).

CHAPTER TWO

LITERATURE REVIEW

2.1 Chemistry of iron

Iron is a metallic compound in group VIII, which is the first of the triadic nickel, iron, or cobalt. The electronic configuration of iron is [Ar] $3d^6$ $4s^2$ whereby valencies of 2 and 3 are common. About 4.5% of the lithosphere is a composition of iron, making it the second most common metal in nature. The chief ores of iron are hematite (Fe_2O_3), magnetite (Fe_3O_4), siderite ($FeCO_3$), limonite ($Fe_2O_3.3H_2O$), and iron pyrites (FeS_2) (Lagroix *et al.,* 2016). Notably, iron is known to have true allotropes in its purest form. First is the delta iron, characterized as a body-centered cubic (stable at 1390 ^oC), and the gamma iron has a face-centered cubic structure (paramagnetic). Finally, alpha iron exists at 773 ^oC and is body-centered and ferromagnetic (can be easily magnetized). Natural iron is also known to have a mixture of stable isotopes (iron-56, iron 54, iron-57, and iron-58). Further, pure iron is also known to exist, is very reactive, and ignites spontaneously (Britannica.com, 2022).

2.1.1 Forms of Iron

Iron exists in different forms. The main types of iron include cast/pig iron, high carbon steel, mild steel, steel, and medium carbon steel.

2.1.2 Cast/pig Iron

This is a form of an impure iron that contains about 93% iron, 3.5% carbon, 1% manganese, 1% silicon, 0.1% sulfur, and 2% phosphorous. Small pieces of cast iron can be hammered when hot or cold, as it melts sharply, unlike when in large quantities. Pig iron is mainly applied in the manufacture of steel and wrought iron is used produce products such as stoves, fancy cast ironwork, railing, guttering, radiators, cylinder blocks, and lamp posts. Pig iron is used in the manufacture of steel using two main processes: Open-hearth process and Bessemer process, which are utilized to vary carbon content to about 0.1 to 1.5% and phosphorous and sulfur to 0.05% or less (Nptel, 2021).

2.2 Isolation of Iron

Iron is applied daily in making steel, cast iron, or wrought iron, and their properties are enhanced using other elements, such as carbon, manganese, phosphorous, or even sulfur. The first stage of iron extraction is smelting whereby, iron is extracted from its ore and reduced to iron oxides with carbon, an impure product referred to as a pig/cast iron (Bell, 2017). Notably through the process of rusting of materials, iron is able to degrade back to its initial form, leading to the formation of the iron ores.

The smelting process of iron is carried out in a blast furnace, a steel-clad, firebrick structure with dimensions of 100 feet high and 20 feet internal diameter. In the blast furnace, the oxide ores are broken into pieces about the size of a fist, but for the case of siderite ($FeCO_3$), it is first roasted outside the furnace to convert it to iron (III) oxide. The converted iron oxides are then mixed with carbon and limestone in the furnace (Mousa, 2019). However, as the iron passes through the furnace, there is the formation of iron carbide (Fe_3C) and iron phosphide (Fe_3P). The impure iron is melted to a temperature of 1200 ^{o}C, which is collected at the bottom. Figure 2.1 is a blast furnace operation with the major reactions prevailing at each phase.

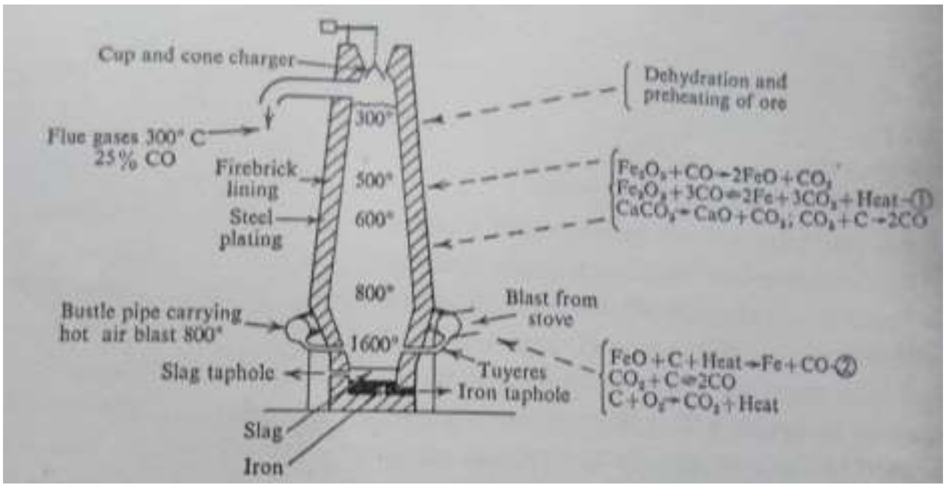


Figure 2.1: Blast furnace operation (Mousa, 2019)

The application of the calcium carbonate (limestone) is the formation of calcium oxide, for the removal of acid oxides after combination with silica, through the formation of calcium silicate ($CaSiO_3$), which is collected at the bottom of the blast as slug. Notably, the blast furnace is maintained at some point, due to crumbling and the cracking of the brick lining.

Also, as a part of serving operations of the blast, there is constant temperature and time recording to ensure optimal operation of the blast. Finally, quality control is done within the blast, whereby the charged samples are checked on their chemical composition and mechanical properties (strength and hardness) (Studentlesson.com, 2022).

2.2.1 The Siemens-Martin open hearth process

In this process, there is the utilization of the basic lining, reverberatory in nature, to be able to remove phosphorous from the pig iron. The operation of the furnace is such that there is a deflection of the flame down on the charge, whereby pre-heated gas is produced with excess pre-heated air that is fed into the furnace and ignited. Notably, the outgoing flue gases are utilized in heating the incoming air in the furnace. The pig iron, quicklime, and steel scrap mixtures are then fed into the furnace. At about 1600 ºC, most of the impurities in the molten metal are heated up (Mousa, 2019). Figure 2.2 shows the siemens- martin heart process.

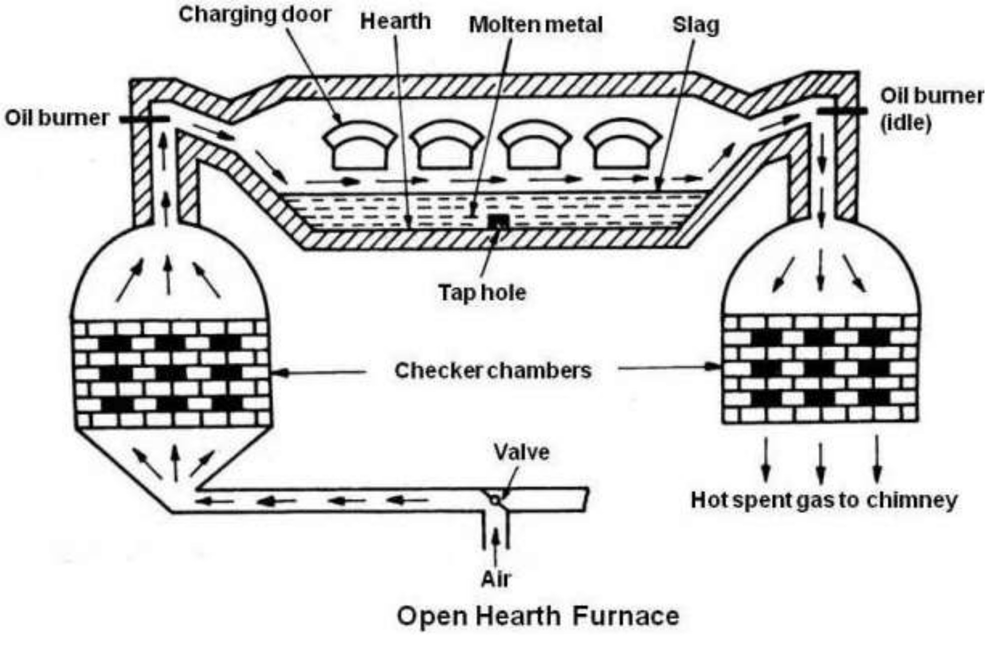


Figure 2.2: Open Hearth Furnace (Toppr.com, 2022)

The core impurities heated up during the process include silicon, manganese, and carbon, as shown by equations 1.6, 1.7, and 1.8.

$$Si\ (s) + O_2\ (g) \rightarrow SiO_2\ (s) \qquad (1.6)$$

$Mn\ (s) + 1/2O_2\ (g) \rightarrow MnO\ (s)$ (1.7)

$C\ (s) + 1/2O_2\ (g) \rightarrow CO\ (g)$ (1.8)

Silica combines with oxides of calcium, Iron (II), and manganese to form molten silica slag ($MsiO_3$) where (M=Ca, Fe or Mn), while carbon monoxide escapes in the flue gases. Further, there is an addition of oxidizers to remove the remaining amount of carbon, silicon, sulfur, and phosphorous. The acid components of silicon dioxide, phosphorous pentoxide, and sulfur trioxide combine with basic compounds of calcium oxide. The silicon dioxide, sulfur trioxide, and phosphorous pentoxide formed, pass into the slag (Mousa, 2019).

2.2.2 The Bessemer process

The process is widely applied in Britain for about 5% of its steel output. The Bessemer converter is a pear-shaped vessel that is made of steel plates lined with dolomite. Calcium oxide is first charged as a slag, and then preceded by a molten pig iron, which is run horizontally and compressed with air-blast at the bottom. Figure 2.3 shows the Bessemer process.

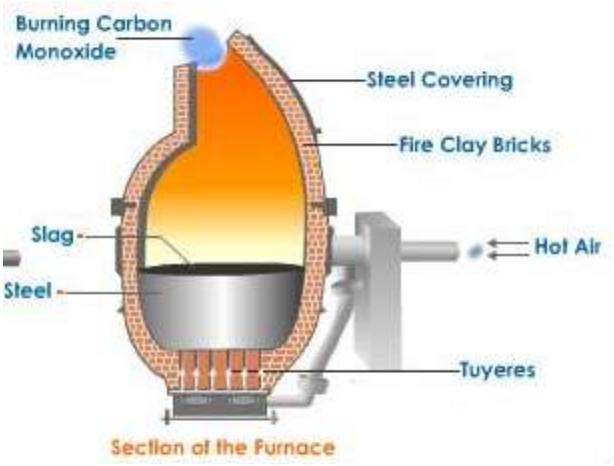


Figure 2.3: Bessemer Process (Rabu, 2010)

There is heat liberation due to the burning of the impurities, leading to maintaining of the required temperature keeping the metal liquid, whereby burning carbon monoxide (CO) comes out of the converter mouth (Mousa, 2019). There is an addition of deoxidizer to raise the content of carbon to achieve the required value after pouring out the steel into a ladle. The produced slag is then sold as a fertilizer. The Bessemer process is relatively cheap but requires high amounts of fuel, and has slower operations in comparison with the open-hearth process. Further, the process is desirable in making high-quality hard steel.

2.3 Classification of steel

Steel is classified on the amount of carbon content and includes high and medium carbon and mild steel. The carbon amount determines the application of steel.

2.3.1 Mild steel

This kind of steel has a carbon content of 0.1-0.2%, which is fairly soft, malleable, and ductile. It can be hammered and pressed while hot. It is mainly applied in making boilerplates, bars, tubes, nuts, bolts, rivets, and grinders.

2.3.2 Medium carbon steel

This is steel that has a carbon content of about 0.2-0.7%. It is malleable and ductile but harder than mild steel. It can be hardened, tempered, and forged. It is mainly applied in making axles, casting, rails, and girders (rules.dnvgl.com, 2009).

2.3.3 High carbon steel

This is a type of steel that contains 0.6 to 1% of carbon with manganese ranging from 0.3 to 0.9%, and are thus applied for the manufacture of high strength wires, cutting tools of all types, hard steel parts, and engines of different kinds (rules.dnvgl.com, 2009).

2.3.3.1 Treatment of medium and high carbon steels

Hardening and tempering techniques are applied to reinforce high and medium carbon steels lead metals to gain on desired properties such as ductility, malleability, stiffness, among others. Annealing is a process whereby steel is heated to bright red at a temperature of 950 °C and then slowly cooled to achieve metal softness, making it easy to be machined. Tempering, on the other hand, focuses on reheating of hard steel at a temperature of about 200-310 °C and then quenched with water. The resulting metal is thus less hard but tough, stronger, and more malleable. Finally, the hardening process prevails whereby after the metal is heated, it is quickly cooled by quenching it in oil or water, thus becoming hard and brittle as opposed to being tough (Huyett, 2004).

2.3.3.2 Alloys of steel

Notably, all steels are composed of manganese and silicon. Other components contained by steels include nickel, chromium, vanadium, tungsten, and other transition metals. An alloy of steel containing 12% manganese is hard and tough and is mainly used in making safes, grinding machines, and railway line construction.

Stainless steel is a kind of an alloy that contains 13-18% chromium and about 0-6% nickel. It is mainly applied in making garden tools, car parts, chemical plants, and watch-cases. High-speed tool steel is an alloy that contains vanadium, chromium, and 15% tungsten, an alloy that is hard and has the highest melting point of all metals. Invar is also an alloy that contains 36% nickel and exhibits a very low coefficient of thermal expansion mainly applied in making clock pendulums and measuring instruments (Huyett, 2004).

Other carbon alloys include; Alnico, which contains Fe, Ni, Cu, Al, and Co, and is utilized in making permanent magnets for magnetos and loudspeakers. Silicon steels with 1% silicon are applied in making springs. Silicon steels make electromagnets due to their low magnetic retentivity and high permeability.

Wrought Iron: This is a kind of iron with less than 0.1% carbon, made by smelting pig iron with Fe_2O_3that oxidizes the impurities. Wrought iron is rather soft but tough, malleable, and ductile, showing greater fatigue resistance, thus resisting corrosion better than steel. The wrought steel is thus mainly applied in making railway couplings, crane hooks, and chains (Nptel, 2021).

Pure iron is made through the reduction of pure iron (II) oxide; heating of iron (II) oxalate with the hydrogen of through thermal decomposition of pentacarbonyl iron (0) ($Fe(CO)_5$). There is formation of a pale viscous liquid, whereby carbon dioxide is passed over a finely divided solution at 120 ^oC, leading it to lose its magnetic power. Pure iron is mainly applied in making electric motors and transformers. The main physical properties of pure or almost pure iron include; Iron being silvery, with a melting point of 1535 ^oC and a density of 7.9 g/cm^3 (Nptel, 2021).

Allotropy and ferromagnetism entail chemical iron properties. Further, it has high electronegativity properties in the standard electrode potential, unlike other preceding elements in the periodic table. Iron is stable in dry air. However, it rusts in moist air conditions.

2.4 Corrosion versus rusting of metals

The corrosion of metal is termed as the process of the gradual breakdown of metals within their environments, whereas rusting is a form of corrosion, specifically the oxidation of iron or its alloys (Lister, 2001).

The absolute amount of power is required to convert elements from their natural ores and minerals to the metal. Naturally, the metals revert back to their natural states when exposed to the environment. It is therefore only natural that when these metals are exposed to their environments they would revert back to the original state in which they were found (Rharphelle, 2017). The first-hand iron corrosion product, for instance, is $Fe(OH)_2$ (or more probable $FeO{\bullet}nH_2O$), but the cause of action of water and oxygen can yield other products having dissimilar colors: For instance, hydrated ferric oxide ($Fe_2O_3{\bullet}nH_2O$), formerly indicated as $Fe(OH)_3$, is reddish-brown rust core component (Paul and Fuller,2014; Saji, 2009).

The amount of energy required for converting ore of iron to metallic iron is turned back when the corrosion of iron prevails to form the original compound. Corrosion energy released generally depends on the amount of power stored by the metal, which varies from one element to another. It is comparatively great for elements such as aluminium, iron and magnesium, and comparatively small for metals such as silver, copper, gold and copper (Reza and Hooshmand, 2014).

2.4.1 Rusting and corrosion of metals in water

Metals decomposition can take place in salt solutions, basic media, and sea water. In almost all of these systems, corrosion occurs significantly only if there is the presence of dissolved oxygen (Kateřina and Alexander, 2006). The solutions of water speedily dissolve oxygen from the air, which is the point source of the required oxygen to enable the process of corrosion (James, 2013). The common type of corrosion is the oxidation of iron when exposed to a moist condition as outlined by Equation 2.1.

$$Fe\ (s) + ½\ O_2(g) + H_2O\ (l) \rightarrow Fe\ (OH)_2(aq) \qquad (2.1)$$

In Equation 2.1, iron combines with oxygen and water to form an insoluble reddish-brown corrosion product that falls off the solution (Kain, 2014). During the rusting process in the ambience air, drying occurs, where ferrous hydroxide is oxidized yielding a red-brown ferric oxide (rust) or $Fe_2O_3.nH_2O$, as given by equation 2.2 (Marie *et al.*, 2020).

$$Fe\ (OH)\ (aq) \xrightarrow{[\mathbf{O2},\ \mathbf{2H2O}]} Fe_2\ O_3.\ nH_2O \qquad (2.2)$$

2.4.2 Rusting and corrosion electrochemistry

The electrochemical reaction is termed as a chemical reaction which leads to electrons transfer; between a substance and the solid electrode (Denny *et al*., 2016). The procedure also involves oxidation-reduction of the species. Since metallic corrosion is nearly an electrochemical process, it is essential to conceptualize the characteristic of electrochemical reactions (Pierre, 2006). The process determines the rate of the rusting of the materials such as iron or of its alloys.

2.4.3 Anodic process

In the reaction of hydrochloric acid and zinc, hydrogen ions are converted to hydrogen gas while zinc metal is oxidized to zinc ions. The evolution of hydrogen reaction arises from varieties of acids and metals, comprised of strong acids such as sulfuric, perchloric, hydrofluoric and formic acids (Deleanu *et al.*, 2009). The major anodic reaction for iron is indicated Equations 2.3.

$$Fe(s) \rightarrow Fe^{2+} + 2e \qquad (2.3)$$

The overall anodic reaction occurring during corrosion of metal M can be written as shown by equation 2.4.

$$M(s) \rightarrow M^{n+} + n\ e \qquad (2.4)$$

The deterioration of metal “M” to an ion with n+ valence charge and n electrons discharge depends on metal characteristics (Frankel and Sridhar, 2008).

Depletion of the hydrogen ions at the cathodic surface interferes with either alkaline hydroxyl (OH^-) ions or the acidic hydrogen (H^+) equilibrium, thus making the solution less acidic or basic at the corroding surface. In neutral water, the anodic deterioration of some iron evolves sensible amount of energy to dissociate water directly, as shown by equation 2.5.

$$2H_2O (l) + 2e^- \rightarrow H_2 (g) + 2OH^-(aq) \qquad (2.5)$$

The concentration variation of hydrogen ions or increase in hydroxyl ions can be indicated by pH meter, through color variation, depicting anodic and cathodic reactions (Pierre, 2006).

2.5 Types of rust

The oxidation process is perceived as a general chemical reaction that leads to electrons loss (one or more) in an ion, molecule, or atom. Rust is termed as an oxidation process when iron or iron materials react in presence of moisture and oxygen (Cwst.co.uk, 2020). Notably, there are three main kinds of rust which include:

2.5.1 Red rust

This is a form of rust, which is a composition of three components which include; iron/steel, water, and oxygen. The red rust is present when there is prolonged exposure of iron/steel to water and oxygen on the atomic level, with the chemical formula of FeO. Once the process of rusting begins, then, the metal starts to deteriorate (Albanycountyfasteners.com, 2021). Figure 2.4 shows red rust (Albanycountyfasteners.com, 2021).

Figure 2.4: Red Rust (Albanycountyfasteners.com, 2021)

2.5.2 Black rust

Black rust is a form of rust stemming from Iron (III) oxides, with the chemical formula of (Fe_3O_4), formed due to the presence of limited oxygen and low moisture. Iron (III) oxide is a combination of iron (I) and Iron (II) oxides. The black rust is visually detected as a thin black film appearing like a black stain, which is a result of the oxidation of iron in an inadequate oxygen environment (armorvici.com, 2021). Further, the black rust has something covering them, preventing oxygen from reaching the surface. Figure 2.5 shows black rust (Armorvici.com, 2021).

Figure 2.5: Black Rust (armorvici.com, 2021)

2.5.3 Yellow rust

Yellow rust is kind of rusting dominating in places of high moisture content. The affected areas are largely exposed to water over a prolonged time, thus existing as iron-oxide hydroxide (FeO (OH) H_2O). The yellow rust is known to be very soluble. The yellow rust is detectable in metal pieces of equipment as the rust runs and drips. Figure 2.6 shows yellow rust (Bellmont.com, 2021).

Figure 2.6: Yellow Rust (Bellmont.com, 2021)

2.5.4 Brown rust

The brown rust stems from iron (III) oxides when they are oxidized with high oxygen presence and in low moisture (Fe_2O_3) (cwst.co.uk, 2020). It forms as a result of excess oxygen and water presence to give drier rust. Brown rust is also termed to be localized rust as it presents itself through the non-uniform distribution of spots only in certain areas, unlike the whole metal surface. Figure 2.7 shows brown rust (Bellmont.com, 2018).

Figure 2.7: Brown Rust (Bellmont.com, 2018).

2.5.5 White rust

White rust is a form of rust that prevails on the surface of iron plating. White rust appears as a powderly coating of the white iron oxide, with a chemical formula of ($Fe(OH)_2$) (Albanycountyfasteners.com, 2021). The oxidation of the iron plates starts immediately after being exposed to the atmosphere. Figure 2.8 shows the white rust.

Figure 2.8: White Rust (Albanycountyfastners.com, 2021).

2.5.6 Blue rust

Blue rust is a form of rust that thrives in the marine environment due to the presence of complex hydrated metal chloride salts, which exist in the atmosphere leading to the formation of the blue color (Circuitnet.com, 2021). Figure 2.9 shows the blue rust. The chemical formula for blue rust is Fe_3O_4 is as result of an electrochemical conversion coating of iron metal.

Figure 2.9: Blue Rust (purefreeform.com, 2021).

2.6 Stages of rusting

There are three main stages during the rusting process and are composed of stages 1, 2, and 3.

2.6.1 Stage 1(surface rust stage)

This is the first stage of rusting, whereby there is the realization of black, white, or reddish spots on the surface of the metals. In this stage, the spots appear in small patches as the color of the material becomes less uniform. This stage exists due to the failure of the protective film used to protect the material, such as chromium oxide, applied in iron protection (reliance-foundry.com, 2021).

2.6.2 Stage 2 (etched stage)

In this stage, there is the degradation of the ferrous material since there is the formation of the scales on ferrite materials (Fe_2O_3). The rust scales combine with the molecules which make up the first layer of the metal. Moreover, there is an uneven formation of the scales in this stage. This leads to etching or pitting of the material, weakening it. Further, there is the formation of several oxides, such as a red oxide (Fe_2O_3) that peels in the presence of water due to a lack of reinforced adherence.

2.6.3 Stage 3 (penetration stage)

At this stage, there is the formation of the surface molecules of red iron oxide in either Powderly or granular state. The red oxide powder becomes loose and falls off, whereas the remaining darker iron oxides, over time, spread over the surface.

2.7 Prevention of rust

The main methods used to descale rust or corroded materials include organic, inorganic, or metallic coatings.

2.7.1 Organic coating

The application of organic or metallic barrier coatings between a material and a possibly aggressive environment is the most widely applied technique of protecting materials from corrosion. Classes of coatings includes: inorganic, organic and metallic coatings. (Wessling and Posdorfer, 1999). In 1997, organic coating worth $5.56 billion was sold, as unveiled by the U.S. Department of Commerce Census Bureau in the U.S. (Denny, 2006).

Makhlouf, (2011), notes that more protection of the metal can be achieved by application of a proper coating material today than by merely covering a surface to reduce contact of an environment with the substrate. Of prime significance is in the improvement of high-performance organic coatings in the petroleum industry, which generated most of the fundamental components from which resins (synthetic) were worked out through petroleum cracking, creating multiple useful compounds that are unsaturated and are fundamental in the construction of large resin polymers such as vinyl and acrylics. The solvents important for the resins solutions were also derived from natural petroleum gas (Veleva, 2012). The construction blocks for polyurethanes and new coatings of epoxies are other derivatives generated by the refining of products of petroleum (Pierre, 2006).

An example of organic coating is acrylics polymers such as poly(meth) acrylates, which are polymers utilized in the automobile industry based on their ability to resist corrosion and hydrolysis in both basic and acid media. The structure of the monomer of the polymethacrylate repeating unit is as given in Figure 2.10.

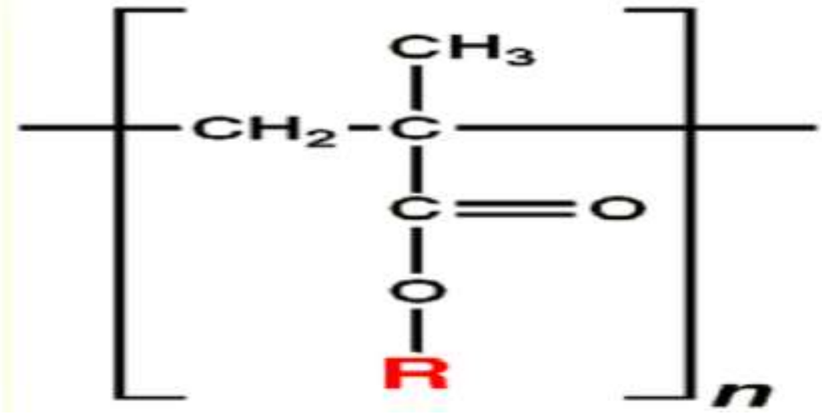


Figure 2.10: Structure of polymethacrylate repeating unit (Holmes *et al*., 2008).

Other organic coatings applied in rust resistance are composed of organic inhibitors derived from natural products such as organic compounds with pigments, flavonoids, and ascorbic acid, as they contain active compounds (nitrogen, oxygen, and sulphur) (AL-Lamei *et al*., 2020).

2.7.2 Inorganic coatings

Inorganic coatings can be generated through an act of a chemical reaction to clays ($Al_2O_3.$ $2SiO_2.2H_2O$), ceramics (SiO_2. Al_2O_3), silicates (SiO_3^{2-}), carbon (C), and glass (SiO_4), just to mention a few. If there is concern over corrosion or contamination of the product, then glass-lined metals are applied. (Fuller and Paul, 2014). Some treatments to generate inorganic coatings can change the metal surface layer into a film which is a protective metallic oxide or compound that has finer resistance of corrosion than the natural oxide film. In some cases, these treatment processes are also used as initial steps before painting (Virmani, 2002).

An example of inorganic polymers applied in the market includes silicones. Silicones are polymerized to form polysiloxanes (organosilicone polymers) with the general structure $[Si(R_2)\text{-}O]_n$ whereby R-CH_3 is thus referred to as poly (dimethyl siloxanes). Inorganic polymers repeat unit example is as shown in Figure 2.11.

Figure 2.11: polydimethylsiloxane (PDMS) (polymerdatabase.com, 2021).

Polysilanes are inorganic coatings made up entirely of silicon with two substituent groups attached to each silicon. Depending on the side groups, the coating finds wide applications ranging from high crystalline, rigid to very flexible coatings. Figures 2.12 and 2.13 shows the polysilane monomer and polymer respectively.

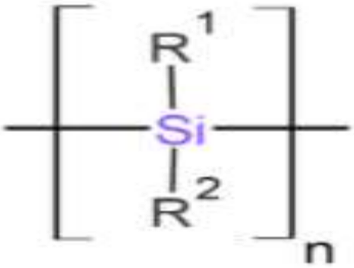


Figure 2.12: Silane monomer (polymerdatabase.com, 2021).

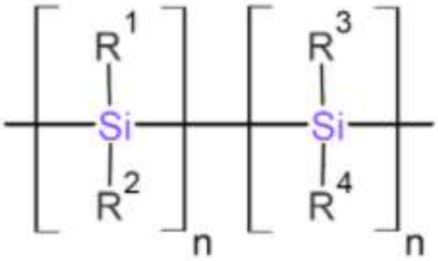


Figure 2.13: polysilane polymer (polymerdatabase.com, 2021).

3.7.3 Metallic coatings

For many rugged services, the choice of a metal coating is preferred (Saeed *et al*., 2017). Where severe impact, abrasion, or high temperatures are a part of the materials selection consideration, the use of metallic coatings should be considered (Biwer *et al*., 2015). All the same, for service in the inherency of an electrolyte, it is essential to evaluate if there are any galvanic incompatibilities between the metallic coating and the substrate that is applied (Pierre, 2006). If there is a gap in the protective coating and contact ingrained between the two distinguishable metals by the presence of some aqueous electrolyte, corrosion is either accelerated. The ingrained process depends on the immediate conditions (Posdorfer and Wessling, 1999). Example of metallic protective operations includes; electroplating, hot-dip galvanizing, thermal spray metalizing e.t.c.

3.7.3.1: Electroplating

Electroplating is a process by which materials migrate through a solution from a positive electrode to a negative electrode onto the iron materials to prevent rusting. To ensure that iron is electroplated with the desired materials, such as zinc, there is the preparation of its surface by ensuring contaminants are removed that might interfere with the surface bonding. This is a three-step process; iron cleaning surface (use of solvents or physical process), treatment, and rinsing operation (Libretexts.org, 2020). The treatment operation ensures that iron surface modification is achieved, then rinsing to achieve the desired alloy.

3.7.3.2: Hot dipping process

The hot dipping process is whereby iron or steel is coated with a zinc layer. The iron/steel metal is immersed in hot molten zinc at a temperature of around 450 ^{o}C. By immersing the metal, the bonding process takes place, in that a coating is formed that protects iron/steel from rusting. Notably, the hot dipping operations take four stages; the cleaning cycle, using the chemicals. Secondly, there is fluxing, whereby the steel surface is enabled to get wet, galvanizing (dipping steel or ion into molten zinc), and optional post-treatment (Galvanizing.org.uk, 2022).

3.7.3.3: Thermal spraying

The thermal spraying operation is a process whereby cermet, metallic, ceramic, or even some polymeric materials in powder form are fed to a spray gun that is heated nearly to their melting point. The droplets of the desired materials are projected against the surface of the iron material. The impact of the droplets on the surface of iron makes them flow by lamellar pattern adhering to the iron surface, overlapping and interlocking as they solidify (Zavareh *et al*., 2017).

The different compositions are mixed as projected by ArcelorMittal (2013), as shown in Table 2.1.

Table 2.1: Type of coatings, composition and their applications

Coating type	Code	Composition	Example applications
Electro-galvanized	ZE	100% zinc	Internal construction, lighting, electronics, hot and cold applications, furniture and tiles.
Hot dipping galvanized	Z	100% zinc	Roofing, cladding, domestic application and industrial cabinets.
Galfan	ZA	95% zinc, 5% Aluminium	Guttering, profiles, roofing, tumble dryers and air conditioning.
Aluzinc	AZ	43.3% zinc, 55% Aluminium, 1.6% silicon	Facades, roofing, tiles, profiles, tumbles, dryers, toasters, cladding for pipes, housing of heating equipment.
Magnelis		93.5% zinc, 3.5% Aluminium, 3% Magnesium	Marine applications, solar panel frames and supports, safety barriers, structural materials, concrete molds and cable trays.

2.8 Rust removal formulations

Rust removal formulations are made using various products composed of mineral acids, complexing agents, oxidizing agents, and organic acids (Pfeifer, 2016; Newman and Rahfield, 1989).

2.8.1 Use of mineral acids to descale

In removing the metal rust, mineral acids, are applied especially the strong scale dissolvers, which are composed of hydrochloric acid (HCl), sulphuric acid, phosphoric acid, or a combination of hydrochloric acid and ammonium hydrogen fluoride (HCl/NH_4HF_2) (Nouryon, 2020). Equation 2.7 indicates the removal of rust using hydrochloric acid. Similarly, other strong mineral acids react the same way.

$$6\ HCl\ (aq) + Fe_2O_3\ (s) \rightarrow 2\ FeCl_3\ (aq) + 3\ H_2O\ (l) \qquad (2.7)$$

2.8.2 Complexing agents for rust removal

The complexing agents combine with metallic ions to generate complexes that are utilized in rust removals. Others are chelating agents and sequestering agents. Chelating agents are known to complex metals ions into ring structures which are difficult to ionize, thus dissolving them easily in water (Docbrown.info, 2021). The working mechanism of the chelating agent is that it chemically converts the existing rust into an inert coating, able to seal out moisture preventing further rusting (Saidin *et al*., 2010). For instance, ethylenediaminetetraacetic acid (EDTA) is a well-known complexing agent, which has the chemical formula $C_{10}H_{16}N_2O_8$ (Amer, 2004). Equations 2.8 and 2.9 indicate how EDTA complexes Iron (II) and Iron (III) respectively.

$$[\mathrm{Fe}\ (\mathrm{H_2O})_6]^{2+}\ (\mathrm{aq}) + \mathrm{EDTA}^{4-}\ (\mathrm{aq}) \rightarrow [\mathrm{Fe}\ (\mathrm{EDTA}]^{2-}\ (\mathrm{aq}) + 6\mathrm{H_2O}\ (\mathrm{l}) \qquad (2.8)$$

$$[\mathrm{Fe}\ (\mathrm{H_2O})_6]^{3+}\ (\mathrm{aq}) + \mathrm{EDTA}^{4-}\ (\mathrm{aq}) \rightarrow [\mathrm{Fe}\ (\mathrm{EDTA}]^{-}\ (\mathrm{aq}) + 6\mathrm{H_2O}\ (\mathrm{l}) \qquad (2.9)$$

2.8.3 Oxidizing agents for rust removal

Oxidizing agents such as chromic acid or potassium permanganate VII ($KMnO_4$) are utilized in rust descaling due to their oxidizing ability of compounds present in metallic compounds, leading to their dissolution. Potassium manganate (VII) is utilized to remove iron (II) ions, which form scales on metals through an oxidation process as indicated by equation 2.10 (Nakayama *et al*., 2004).

$$3\ \mathrm{Fe}^{2+} + \mathrm{MnO_4}^{-} + 7\ \mathrm{H_2O} \rightarrow 3\ \mathrm{Fe(OH)_3} + \mathrm{MnO_2} + 5\ \mathrm{H}^{+} \qquad (2.10)$$

2.8.4 Use of organic acids for rust removal

Removal of rust is an enormous undertaking in various operations. Examples of household operations include sinks, tubs, and tiles, among others. These formulations have been used for removing lime rust and scale (Pfeifer, 2016). They may contain organic acids like sulfamic acid, hydroxyacetic acid, citric acid, oxalic acid, tartaric acid or combinations of these (Newman and Rahfield, 1989), as they are able to descale. Some of the approaches proposed for removing rust include alkali cleaning method (chelate cleaning method), acid cleaning, electrolytic cleaning method, etc (Nakayama *et al*., 2004). The use of organic acids in preparing rust removal solutions is discussed below.

2.8.4.1 Oxalic acid

Oxalic acid is also called as ethanedioic acid, is a toxic organic acid which is a dicarboxylic acid. The acid has a chemical formula of $C_2H_2O_4$, with 90.03 grams per mol molar mass and with a chemical structure as shown in figure 2.14. It is the simplest dicarboxylic acid.

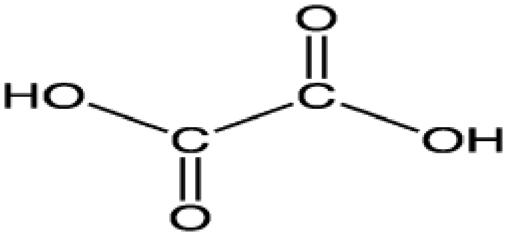


Figure 2.14: Structure of oxalic acid (Eiichi *et al*., 1969).

The properties of oxalic acid are given in Table 2.2.

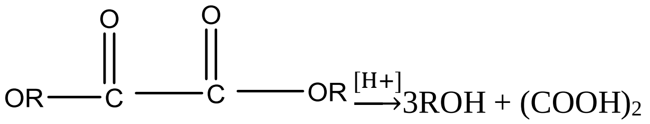
Table 2.2: Properties of oxalic acid (Uditha *et al*., 2012)

Molecular formula	$C_2H_2O_4$
Molecular mass	90.03 g/mol
Boiling point	365.1 ^{o}C
Melting point	189-191 ^{o}C
Density	1.9 g/mL

Oxalate derivatives and oxalic acid are in various natural point sources which comprise of wood, vegetables, plants, and coal. It is also self-produced in the body by metabolism of ascorbic acid (glyoxylic acid) (Eiichi *et al.*, 1969).

Oxalic acid is prepared by oxidation of carbohydrates (glucose or sucrose) using nitric acid. It prepared through reacting carbon monoxide (CO) with methanol and oxygen to generate diesters of oxalic acid, which then produces oxalic acid when subjected to hydrolysis, as shown by equation 2.11 and 2.12.

$$4ROH + 4\,CO + O_2 \rightarrow 2(CO_2R)_2 + 2H_2O\ (l) \qquad (2.11)$$



$$OR-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OR \xrightarrow{[H+]} 3ROH + (COOH)_2 \qquad (2.12)$$

Oxalic acid is an odorless white crystalline solid, melting at 189-191 °C and with a density of 1.9 g/ml. It usually pre-exists in the hydrate form $(COOH)_2 \bullet 2H_2O$. It is acidic in water, soluble in water and forms a colorless solution, (Uditha *et al.*, 2012). Oxalic acid is harmful and toxic. The acid has been used in rust removal by (Newman and Rahfield, 1993). Iron, when dissolved in water, reacts with oxalic acid to form iron oxalate complexes shown by equation 2.13.

$$Fe^{2+} (aq) + H_2 C_2O_4 (aq) + 2H_2 O (I) \rightarrow FeC_2O_4(s) + 2 H_3O^{+}(aq) \qquad (2.13)$$

2.8.4.2 Sulphamic acid

Sulfamic acid also called as sulfamidic acid, amidosulfonic acid, amidosulfuric acid, andaminosulfonic acid is a compound with formula H_3NSO_3. The acid is water-soluble and colorless. The acid melts at 205 °C, and boils at a temperature of 215-225 °C before dissociating at a higher temperature to form nitrogen, water, and sulfur dioxide (Yoshikubo and Suzuki, 2000). Structure of the acid is shown in Figure 2.15.

Figure 2.15: Structure of sulphamic acid (Metzger, 2005).

The properties of sulphamic acid are given in Table 2.3

Table 2.3: Properties of sulphamic acid (Yoshikubo and Suzuki, 2000)

Molecular formula	H_3NSO_3
Molecular mass	97.1 g/mol
Boiling point	215-225 ^oC
Melting point	205 ^oC
Density	2.1 g/cm^3

Sulphamic acid (H_3NSO_3) is regarded as an intermediate substance between sulphamide ($H_4N_2SO_2$) and sulfuric acid. Sulfamic acid industrially is prepared through urea treatment with sulfuric acid (or oleum) and sulfur trioxide mixture. The synthesis is undertaken in two steps as in Equations 2.14 and 2.15

$$CO(NH_2)_2\ (aq) + SO_3\ (g) \rightarrow H_2N\text{- }CONH\text{-}SO_3H\ (aq) \qquad (2.14)$$

$$H_2N\text{-}CONHSO_3H\ (aq) + H_2SO_4\ (aq) \rightarrow CO_2\ (g) + 2\ H_2N\text{-}SO_3H\ (s) \qquad (2.15)$$

In this manner, close to 96,000 tonnes were produced in 1995 (Metzger, 2000). Sulfamic acid aqueous solutions hydrolyzes to ammonium bisulfate due to their instability as indicated by equation 2.16. Its characteristics match that of urea, $(H_2N)_2CO$. Sulfamic is a fairly strong acid, with a Ka value of 0.101 (Pka=0.995). Since, sulfamic solid is not an absorbent, it is utilized as a standard in acidimetry (acid content quantitative assays analysis). It reacts with base to form salts as in equation 2.16.

$$H_3NSO_3(s) + NaOH\ (aq) \rightarrow H_2N\text{-}SO_3Na\ (s) + H_2O\ (l) \qquad (2.16)$$

The research by (Newman and Rahfield, 1993) showed that the acid is effective in rust removal.

2.8.4.3 Hydroxyacetic acid (glycolic acid)

Glycolic acid also termed as hydroxyacetic acid or hydroacetic acid whose structure is given in Figure 2.16.

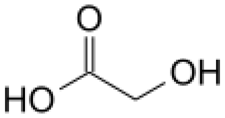


Figure 2.16: Structure of hydroxyacetic acid (Hinago *et al.*, 2005).

The properties of hydroxyacetic acid are as given in Table 2.4

Table 2.4: Properties of hydroxyacetic acid (Miltenberger, 2005)

Molecular formula	$C_2H_4O_3$
Molecular Mass	76.05 g/mol
Boiling Point	Decomposes
Melting point	75 ^oC
Density	1.49 g/cm^3

The acid is crystalline colorless, odorless and hygroscopic solid which is extremely soluble in water. It utilized in the manufacture of various facial-care products. Hydroxyacetic acid can be made using different routes. The usual approach applied is by reacting synthesis gas and formaldehyde (formaldehyde carbonylation) (Hinago *et al.*, 2005). The synthesis reaction is as given by equation 2.17.

$$CH_3OH\ (aq) + CO\ (g) + H_2O\ (l) \rightarrow C_2H_4O_3(s) \qquad (2.17)$$

The other synthesis route is through the reaction of chloroacetic acid with sodium hydroxide preceded by a re-acidification process (Miltenberger, 2005). The other technique includes the hydrolysis of cyanohydrin. The reaction is as shown in equation 2.18.

$$ClCH_2COOH\ (s) + NaOH\ (aq) \rightarrow NaCl(s) + HOCH_2COOH\ (aq) \qquad (2.18)$$

Hydroxyacetic acid is more acidic than acetic acid, due to the withdrawing effect due to the terminal hydroxyl group. The interlocking of the carboxylate group to the metal ions forms a coordination complex. This shows that the OH^- group is concerned in the creation of complexes which is only possible with the loss of its proton (Tiboni *et al.*, 2019).

Glycolic acid is used for tanning and also dyeing agent in the textile industry. In the pharmaceutical sector it is used as a skin care agent. In the processing of food products, it is used as a flavoring (Miltenberger, 2005). Glycolic acid is used as additives for ink emulsion polymers. It is also applied to enhance the coefficient of friction in surface treatment products on tile flooring. It is the major active component (Pine-Sol) in the household cleaning liquid. According to Newman and Rahfield, (1993), the acid was showed to be effective in the removal of rust. Glycolic acid and iron ions react to form a complex (iron-glycolate), as shown by equation 2.19.

$$HOCH_2CO_2^- \text{ (aq)} + Fe^{2+}\text{(aq)} \rightarrow HOCH_2COOFe^+ \text{ (aq)} \qquad (2.19)$$

2.8.4.4 Citric acid

Citric is an organic acid found in fruits. In biochemistry, it is an intermediate product in the citric acid cycle, which prevails due the biological processes of every oxidative organism (Apleblat, 2014). The structure is as shown in Figure 2.17.

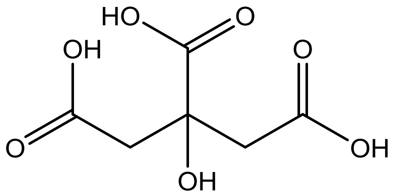


Figure 2.17: Structure of citric acid (Alexander and Apleblat, 2014).

The properties of citric acid are given in Table 2.5.

Table 2.5: Properties of citric acid (Apleblat, 2014)

Molecular formula	$C_6H_8O_7$
Molecular Mass	192.12 g/mol
Boiling Point	175 ^{0}C
Melting Point	153 ^{0}C
Density	1.66 g/cm^3

Not less than a million tons of citric acid annually is applied as an acidifier, flavoring and as a chelating agent (Apleblat, 2014). In fruits such as lemons and limes may contain around 8% of the dry weight (approximately 47 g/l in the juices) (Penniston *et al.*, 2008).The citric acid concentration in lemons and oranges is 0.30 mol/l and 0.005 mol/l approximately. Citric acid can be prepared by activating the juice using hydrated lime ($Ca(OH)_2$) to precipitate out formed calcium citrate, which was then reverted to citric acid by adding dilute sulfuric acid (Verhoff, 2016).Wehmer in 1893 observed penicillium mold, which utilized sugar to produce citric acid. By then, citric acid microbial generation did not become industrially crucial.

In 2007, yearly citric production stood at around 1.6 metric tons (now, this is only 1600 Kg) (Berovic and Legisa, 2007), where more than 50% of this amount was produced by China. .More than 50% of it was used in beverages, food uses (about 20%), detergent uses (about 20%) and other related applications (10%) which includes pharmaceuticals, cosmetics and in the chemical industry. Other uses are in flavoring, beverages and in foods (candies and soft drinks) (ASTM, 2017).

Citric acid is a superior chelating agent, binding metals by making them soluble. In industrial applications, citric is applied to passivate stainless steels and dissolve steel rust (Verhoff, 2016). Citric is also applied in the treatment of water, chelating of metals in hard water, in shampoo to colour the hair. The acid was applied in rust removal by Newman and Rahfield (1993). Citric acid reacts with iron to form an iron citrate complex with the release of hydrogen gas, as shown by equation 2.20.

$$Fe\ (s) + C_6H_8O_7\ (aq) \rightarrow FeC_6H_6O_7\ (aq) + H_2\ (g) \qquad (2.20)$$

2.8.4.5 Acetic acid

Ethanoic acid, (acetic acid) is an organic acid, with chemical formula $C_2H_4O_2$. When undiluted, is called glacial acetic acid. Acetic acid volume concentration in vinegar is no less than 4 percent, which makes acetic acid the major ingredient of vinegar. Ethanoic has a sour and a distinctive pungent taste and smell (OSHA, 2013). It is categorized as a less powerful acid in that, it partially dissociates in solution. Acetic acid in high concentration is corrosive and attacks the skin (Penniston *et al.*, 2008). The structure of acetic acid is as shown in Figure 2.18.

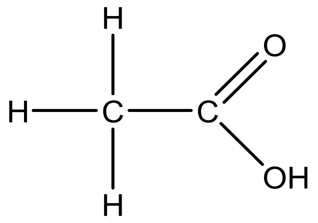


Figure 2.18: Structure of acetic acid (OSHA, 2013).

The properties of acetic acid are presented in Table 2.6

Table 2.6: Properties of acetic acid (Cheung *et al.*, 2007)

Molecular formula	$C_2H_4O_2$
Molecular mass	60.052 g/mol
Boiling point	118 ^oC
Melting point	16.6 ^oC
Density	1.05 g/mL

It is an essential chemical reagent applied in the synthesis of cellulose acetate for polyvinyl acetate applied in films (photographic), glue (wood), fabrics and fibers that are synthetic in households' uses. When acetic acid is diluted, it is applied as descaling agent. In food manufacturing, the acid is not only applied as a condiment but also as an acid regulator. The acetyl group is important to all forms of life in biochemistry applications. When conjugated to coenzyme A, it is fundamental to the metabolism of fats and carbohydrates (Cheung *et al.*, 2007). The synthesis equation for the production is as shown by equations 2.21 and 2.22.

$$C_6H_{12}O_6\ (aq) \rightarrow 3CH_3COOH\ (l) \qquad (2.21)$$

$$2CO_2(g)+4H_2(g) \rightarrow CH_3COOH\ (l)+2H_2O(l) \qquad (2.22)$$

In aqueous solutions, ethanoic being a weak monoprotic acid has a pKa value of 4.76 (Cheung *et al.*, 2011). In solid acetic acid, the molecules form chains; individual molecules being interconnected by bonds. In the vapour at 120 °C, dimers can be detected. Dimers also occur in the liquid phase in dilute solutions in non-hydrogen-bonding solvents (Briggs *et al.*, 1991) which are disrupted by hydrogen-bonding solvents. The dissociation enthalpy of the dimer is estimated to occur at 65.0–66.0 kJ/mol, while dissociation entropy is 154–157 J mol^{-1} K^{-1} (Togeas, 2005).

Liquid ethanoic acid is a polar (deliquescent) protic medium, analogous to water and ethanol with a temperate static relative permittivity dielectric constant value of 6.2. It dissolves not only in compounds that are polar but also in non-polar compounds. The miscibility and solvent characteristics of ethanoic acid make it an essential industrial chemical, used as a solvent in dimethyl terephthalate production (Cheung *et al.,* 2011).

The global requirement for acetic acid is close to 6.5 million metric tons annually of which about 1.5 million metric tons per year done through recycling; the rest is produced from methanol using phosphoric acid as a catalyst. To a higher degree, the production of acetic acid is by methanol carbonylation. In this technique, methanol and carbon monoxide reacts to form ethanoic acid according to Equation 2.23

$$H_3C\text{-}OH\ (aq) + CO\ (l) \rightarrow H_3C\text{-}COOH\ (l) \qquad (2.23)$$

Most acetic acid, generation was done by acetaldehyde oxidation. Acetaldehyde can be produced by acetylene hydration. This was the common technology in the 1900s as well as in advanced modern production processes (Jones, 2000). Also, bacteria are also utilized in its production and the general chemical reaction is given in equation 2.24.

$$C_2H_5OH\ (aq) + O_2\ (g) \rightarrow CH_3COOH(s) + H_2O\ (l) \qquad (2.24)$$

A dilute solution of alcohol covered with Acetobacter and kept in an aerated place will ferment to vinegar within a few months. Industrially, vinegar-production goes faster by improving bacterial oxygen supply (Chotani *et al.,* 2007). Acetic acid as chemical reagent is used to yield other chemical compounds (Malveda and Funada, 2011). The acid has been utilized by Newman and Rahfield, (1993), in rust formulation, for removal of scales.

2.9 Additives used in enhancing the efficiency of organic acid for rust removers

The additives utilized in enhancing anti-rust formulations are composed of magnesium aluminium silicate that enable the easier flow of the formulation with xanthium gum ($C_{35}H_{49}O_{29}$) acting as a stabilizer. Ammonium chloride is used as an acidifier in the formulations; to enhance the formation of a protective layer on cleaned materials, and grapthol green ($C_{32}HCl_{15}CuN_8$) acting as a heat stabilizer and a coloring agent.

2.9.1 Use of magnesium aluminium silicate

Magnesium aluminium silicate (MAS) is a natural mineral (polymer) which is derived from polished and purified clay. The compound has a molecular weight of 482.99 g/mol with a molecular formula of $Al_2Mg_2O_{15}Si_5$. The other major names which are used to refer to the mineral include: Aluminium Magnesium salt, Veegum T, Magnesium Aluminosilicate among others.

The compound being a mixture of smectite (composition of saponites and montmorillonites) is applied as either a dispersing agent or a suspending agent. It makes it (antirust products) to flow easily (Satit and Thaned, 2009). The polymer is also instrumental in enabling anti rust products to have better viscosity which enables easier flow.

2.9.2 Xanthium gum

This is a hetropolysaccharide which is generated as a result of fermentation of the xathomonascampestris bacteria. The structure of this compound is a composition of 1, 4-joined D- glucose with the side chains composed of one glucoronic and two mannose molecules. This compound is able to hydrate in water and extremely stable to pH from 2 to 11. At the low concentrations; the compound shows very high viscosity properties with pseudo plastic characteristics. These two characteristics make the compound to be used as a stabilizer and as a suspending agent in anti-rust products (Philips and Williams, 2009).

2.9.3 Ammonium chloride

Ammonium chloride is a white solid and soluble in water to about 37% with a chemical formula of NH_4Cl. The compound has a melting point of 338 ^{o}C, molar density of 1.53 g/cm^3 and a boiling point of 520 ^{0}C. The salt is used in the manufacture of the ammonium products, as a fertilizer, soldering flux among other applications. Based on its acidifying nature and its ability to maintain pH, the salt is used in anti-rusts products (Clemson.edu, 2021).

2.9.4 Aluminium Chloride

Aluminium chloride also known as aluminium trichloride is a white solid with low melting and boiling points. The compound is largely applied for the production of aluminium metal, synthesis of arene metal complexes and a surfactant. The use of the compound as an inhibition tool is based on its ability to form micelle on the metal compound (iron or its alloys) forming a protective layer on the metal surface after rust removal (Yang and Cheng, 2019), as shown in Figure 2.19.

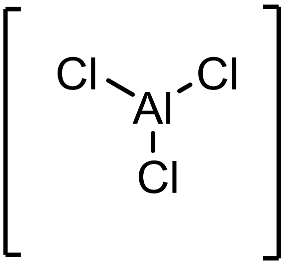


Figure 2.19: Structure of aluminium chloride (Chemspinder.com, 2021).

2.9.5 Grapthol Green

This is a pigment powder widely applied in chemistry for the plastic applications. The pigment was essentially incorporated in the design of the formulations due to its heat stability and its solubility that blended well with the designed formulations.

2.10 Activating Agents

Activating agent is a mineral compound that is surface active and utilized to increase the rate of chemical reaction. It was noticed in the past that the amount of iron dissolved accumulated at the beginning of a typical boiler cleaning (Newman and Rahfield, 1993). The rate increased when ferrous ions was dissolved in the solution. It was noticed that addition of about 0.05% ferrous salts to the rust formulation shortened the total time to perform the boiler cleaning. Apart from iron sulphate, phosphorous compounds have also been utilized in rust removal as an activating agent.

2.10.1 Ferrous sulphate

Iron (II) sulphate or ferrous sulphate represents a range of sulphates with the formula $FeSO_4 \cdot xH_2O$, the compounds existing as heptahydrate. The iron form is applied in industrial applications and for the treatment of iron deficiency. The hydrate applied in industries is blue-green heptahydrate, mainly known as green vitriol (Koenig, 1996). The aquo complex $[Fe\ (H_2O)\ 6]^{2+}$ is formed when iron (II) sulphate dissolves, which is paramagnetic and has octahedral molecular geometry. The structure is as shown in Figure 2.20.

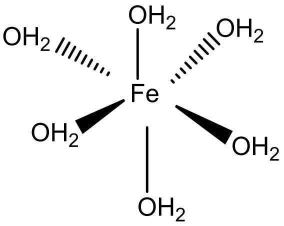


Figure 2.20: Structure of aqua complex (Longstroth, 2016).

Ferrous sulphate is applied in the production of inks. It is also used extensively in wool dyeing as a mordant (Handreck, 2002). Ferrous sulphate is also applied in stain concrete, and some sandstones and limestones to remove yellowish color rust as indicated by Ghaly (2014). It has been utilized in the purification of water by flocculation and for removal of phosphates in municipal and industrial sewage plants treatment (Longstroth, 2016; Koenig *et al.*, 1996).

Iron sulfate is utilized as an activating agent due to its ability to increase the concentration of ferrous ions since the process of descaling takes the form of a redox, leading to faster detaching of iron oxide (scales) from the metal. Other materials utilized in activating the formulation include; potassium hydroxide (KOH) and phosphoric acid (H_3PO_4) (Safitri *et al.*, 2017).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Preparation of rust removal solutions

The reagents and chemicals utilized in the preparation of rust mover solutions were: low-weight organic acids (LMWOs) - acetic, oxalic, hydroxyacetic, and sulphamic (inorganic) acids and the activating agent (ferrous sulphate). Five formulations were prepared having different amounts of LMWOs, inorganic acid and the activating agent. In formulation five, citric acid extracted from a lemon was used. The procedure for the citric acid extraction is provided in section 3.11.

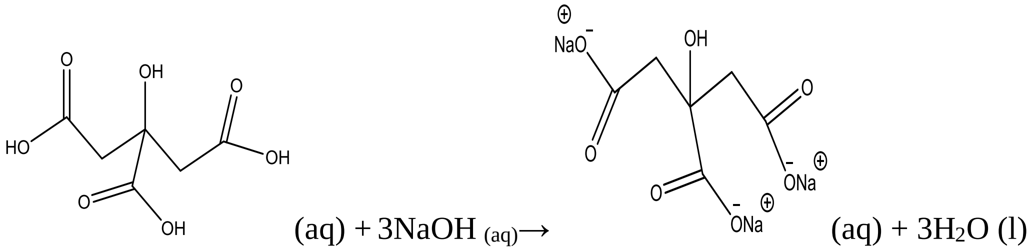
3.1.1 Preparation of rust remover solutions

Five formulations were used in the preparation of rust remover. All the formulations contained the same amount inorganic acid and activating agent however the amounts of the low molecular weight organic acids were varied. The first formulation was prepared as described below.

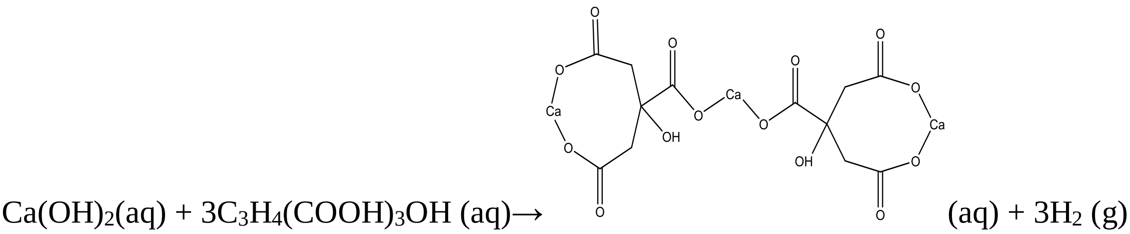
100 mL of distilled water was added to a 1-litre volumetric flask. 61 g oxalic acid was then added in portions to the flask with constant shaking followed by130 g sulphamic acid also in portions with constant shaking. 5.1913 g of iron sulphate (activating agent) was then added with constant shaking and more distilled water was added to volume (1000 mL).

3.1.1.1 Preparation of citric acid extract

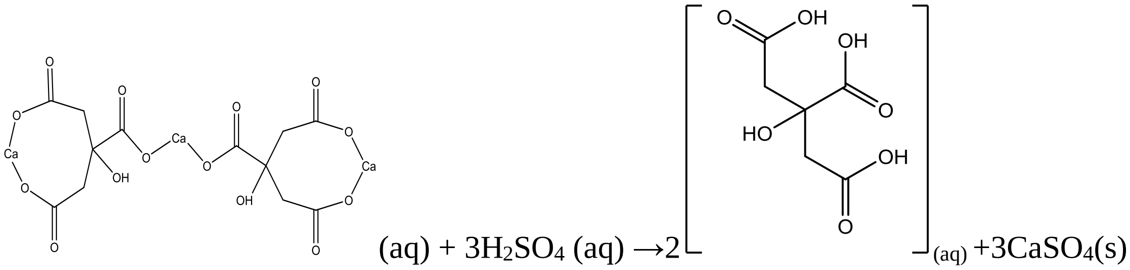
Lemons were bought from Muthurwa market, washed with distilled water and 30 g of the fruits were taken. The lemons were again washed, peeled, and the juice extracted by squeezing to give 300 mL of the juice. 150 mL of 1M of sodium hydroxide (NaOH) was then added to the juice to form trisodium citrate. 40 g of calcium chloride ($CaCl_2$), was then added to give tricalciumdicitrate (Verhoff, 2016). The tricalciumdicitrate was then filtered using a Buckner funnel and washed with 40 mL of hot distilled water. The filtrate was then added to dilute sulphuric acid (0.1M) drop wise until a yellow solution was formed. This was then concentrated by allowing it to evaporate until citrate crystals formed according to Equations 3.1, 3.2, and 3.3.



$$\text{(aq)} + 3NaOH_{(aq)} \rightarrow \text{(aq)} + 3H_2O\ (l) \qquad (3.1)$$



$$Ca(OH)_2(aq) + 3C_3H_4(COOH)_3OH\ (aq) \rightarrow \text{(aq)} + 3H_2\ (g) \qquad (3.2)$$



$$\text{(aq)} + 3H_2SO_4\ (aq) \rightarrow 2\left[\ \right]_{(aq)} + 3CaSO_4(s) \qquad (3.3)$$

The crystals were then washed with hot distilled water and 20 mL hexane was added to remove other impurities. The citric acid crystals were then dried at ambient temperature. The mass of the acid obtained was 40 grams. The procedure was repeated to obtain an adequate amount of citric acid for the preparation of rust remover.

The conceptual diagram (Figure (3.1)) shows the extraction procedure or the extraction of citric acid from the lemon in the laboratory. The procedure involved: peeling, activation, filtration and washing, and crystallization.

Figure 3.1: Laboratory preparation of citric acid.

The procedures for the preparation of various formulations for rust remover solutions are summarized in Table 3.1

Table 3.1: Amounts of the reagents used in the preparation rust remover solutions.

Formulation	LMWOs Weight (g)				Citric acid extract	Inorganic acid Weight (g)	Activating agent Weight (g)	Dissolved in 100 mL then topped to1000 mL
	Citric acid (pure)	Acetic acid	Oxalic acid	Hydroxyacetic acid		Sulphamic acid	Iron sulphate	Distilled water topped to
1	61.00					130	5.19	1000
2		63.24				130	5.19	1000
3				98.85		130	5.19	1000
4			149.00			130	5.19	1000
5					120.00	130	5.19	1000

From Table 3.1 formulation one contained citric acid (61.00 g),sulphamic acid (130.00 g) and iron sulphate (5.19 g). Formulation two contained acetic acid (63.24 g) sulphamic acid (130.00g) and iron sulphate (5.19 g). Formulation three contained hydroxyacetic acid (98.85 g), sulphamic acid (130.00 g) and iron sulphate (5.19 g). Formulation four contained oxalic acid (149.00 g), sulphamic acid (130.00 g) and iron sulphate (5.19 g) while formulation five contained citric acid extract (120.00 g), sulphamic acid (130.00 g) and iron sulphate (5.19 g). All the formulations were made to 1000 mL in a round bottomed flask using distilled water.

The use of iron sulphate with the same weight in all the formulation was based on the calculation of the salt (5.19 grams) which gave 1 ppm in 1 litre solution. The sulphamic acid (inorganic acid) was also used as a constant, as this was the optimal rust remover value, when the acid was used alone, and thus it had to be optimized with the third component which was low weight organic acid (LMWO), and their values proved to be the optimal after performing a series of trial and error optimizations.

South African and Holts (market standard) were used to compare efficiencies of the formulations prepared. The amount of the inorganic acid and the activating agent used was kept the same in all formulations. Only the amounts of LMWOs were varied.

3.2 Formation of rust in different solutions

18 nails were taken and weighed then tied loosely using a thread and then suspended in a 500 mL beaker containing 250 mL of distilled water, with the nails hanging above the solution. The beaker was then covered at the top using aluminium foil, leaving the hanging nails for two weeks for the formation of the rust. After two weeks, the samples were then oven dried at a temperature of $100 - 105$ °C. The new weight (change in mass-increase) of the nail samples, were quantitatively determined, and their new weight recorded, after the samples cooled ($W2$). Similarly, rust was initiated in 5% sodium chloride solution, 10% sodium chloride solution, and in 10% concentration hydrogen peroxide solution.

NB: Each nail was dealt with individually, whereby the initial mass of the mass before was subjected to the rusting condition and was recorded as W1. The new weight of the nail was determined after two weeks of rusting (W2). The new weight (W2) was then utilized to determine the efficiency of the designed anti-rusts. The final weight (W3) was achieved after dipping the W2 nail in the designed anti-rust formulation.

3.3The efficiency of rust removal by the prepared solutions

The prepared rust remover (formulation 1-5) were used to evaluate the rust removal efficiency of the respective rust remover solutions.

3.3.1 Rust removal by the solutions

The efficiency of the solutions (Formulations 1-5) to remove rust was evaluated by dipping the rusted iron nails in the various solutions for a predetermined time.

A known weight (W_2) of rusted iron nail was dipped in 60 mL of the solutions arranged in beakers labeled 1-9, whereby in beakers 1-3 the nails were withdrawn after 30 minutes, beakers 4-6 the iron nails were withdrawn after 60 minutes, and in beakers 7-9 the iron nails were withdrawn after 90 minutes. All the procedures were conducted at room temperature.

The procedure was repeated at a temperature of 40 ^{0}C using the same procedure in an orbital shaker.

After rusting for times stated, the iron nails were removed and dried in an oven at 105 ^{0}C and the weights taken. The weights were recorded as W3 for the iron nails. The solution in which the nails were dipped was retained for further qualitative analysis.

3.4 Qualitative analysis

The prepared formulations and the standards were analyzed using Fourier transform Infrared spectrometer (FTIR) (Model: IR Affinity-IS, Shimadzu) to characterize the functional groups in the formulations.

In the calculation of the % of the rust removed, the formula that has been used is:

% rust removal= $\left.{(W2-W3)}\middle/{(W2-W1)}\right.$*100%

(W_1=Initial weight of nails, W_2=Stained weight of nails, W_3=Weight after dipping in the formulation). Nine measurements were done, three after 30 minutes, three after 60 minutes, and three after 90 minutes. The mean and the standard deviation for the % of removed rust after 30, 60, and 90 minutes were recorded.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Rust removal by formulation 1

The percentage of rust which was removed by formulation one is given in Table 4.1. The formulation was tested at pH=0.5 for 30 minutes, 60 minutes and 90 minutes, at room temperature.

Table 4.1: Percentage of rust removed by formulation 1 at room temperature

No.	Initial weight of rusted iron nail (g)	Corroded nails readings (g)	Weight After rust removal (g)	Time of exposure (min)	Rust Weight (g)	Rust removed (g)	% removed	Mean	Standard deviation
1	2.9621	2.9713	2.9681	30	0.0092	0.0032	34.8	47.6	14.5
2	2.9361	2.9428	2.9398	30	0.0067	0.0030	44.8		
3	2.9571	2.9650	2.9600	30	0.0079	0.0050	63.3		
4	2.9463	2.9524	2.9472	60	0.0061	0.0052	85.2	79.1	7.2
5	2.9523	2.9582	2.9540	60	0.0059	0.0042	71.2		
6	2.9605	2.9663	2.9616	60	0.0058	0.0047	81.0		
7	2.9589	2.9636	2.9600	90	0.0047	0.0036	76.6	83.9	7.6
8	2.956	2.9620	2.9570	90	0.0060	0.0050	83.3		
9	2.7654	2.7727	2.7660	90	0.0073	0.0067	91.8		

NB: Nine tests were performed. Readings 1-3 indicated the % of rust removal after 30 minutes, samples 4-6 indicating % of rust removal after 60 minutes, and 7-9 showing % rust removal by the formulation after 90 minutes. Similarly, the mean and standard deviations were also captured in all the tables after 30, 60, and 90 minutes.

The study showed that after 30 minutes, the percentage of the rust removed ranged from 35-63%, with mean of 47.6%. After 60 minutes and 90 minutes the ranges were 71-85% and 77-

92% with a mean of 79.1% and 83.9% respectively. The study showed that rust removed increased with time at room temperature, with the highest being 92%. The efficiency of the formulation was relatively similar to that of the standards (Holts and South African) as they had the highest efficiency of 94% and 97% respectively. Similarly, the results can be compared with Essa's (2007) results, which showed rust removal efficiency increased with time in citric acid solution, with the efficiency ranging from 77.8% to 99.86% from an hour to 4 hours. The percentage of rust removed when formulation one was used at a temperature of 40 ^{0}C is shown in Table 4.2.

Table 4.2: Percentage of rust removed by formulation 1 at 40 °C

No.	Initial weight of rusted iron nail (g)	Corroded nails readings (g)	Weight after removal (g)	Time of exposure (min)	Rust weight (g)	Rust removed (g)	% of rust removed	Mean	Standard deviation
1	2.9654	2.9700	2.9692	30	0.0046	0.0008	17.4	34.8	24.8
2	2.9605	2.9700	2.964	30	0.0095	0.0060	63.2		
3	2.9554	2.9600	2.9589	30	0.0046	0.0011	23.9		
4	2.9503	2.9700	2.9514	60	0.0197	0.0186	94.4	95.5	1.4
5	2.9546	2.9612	2.9548	60	0.0066	0.0064	97.0		
6	2.7951	2.801	2.7954	60	0.0059	0.0056	95.0		
7	2.9974	3.0000	2.999	90	0.0026	0.0010	38.5	76.9	33.2
8	2.8136	2.8200	2.8138	90	0.0064	0.0062	96.9		
9	2.9437	2.9500	2.9440	90	0.0063	0.0060	95.2		

The study showed that after 30 minutes, the percentage of the rust removed ranged from 17-63%, with a mean of 34.8%. After 60 minutes and 90 minutes the ranges were 94-97% and 39-97%, and with their mean being 95.5% and 76.9%. The formulation indicated that its rust removal efficiency increased with time, and after 90 minutes, it had the same removal efficiency as the Holts (standard).

4.2 Rust removal by formulation 2

The percentage of rust removed by formulation 2 at room temperature is given in Table 4.3. The evaluation of rust removal by formulation two was performed at pH=2.7.

Table 4.3: Percentage of rust removed by formulation 2 at room temperature

No.	Initial weight of rusted iron nail (g)	Corroded nail reading (g)	After removal (g)	Time of exposure (min)	Rust weight (g)	Rust removed (g)	%rust removed	Mean	Standard deviation
1	2.7449	2.7492	2.7480	30	0.0043	0.0012	27.9	42.4	15.9
2	2.6631	2.6641	2.6637	30	0.0010	0.0004	40.0		
3	2.7265	2.7890	2.7518	30	0.0625	0.0372	59.5		
4	2.8150	2.8155	2.8152	60	0.0005	0.0003	60.0	76.7	14.6
5	2.6417	2.6496	2.6430	60	0.0079	0.0066	83.5		
6	2.7739	2.7769	2.7743	60	0.0030	0.0026	86.7		
7	2.8118	2.8131	2.8121	90	0.0013	0.0010	76.9	76.2	3.3
8	2.8832	2.8856	2.8837	90	0.0024	0.0019	79.2		
9	2.9691	2.9713	2.9697	90	0.0022	0.0016	72.7		

The study showed that after 30 minutes, the percentage of the rust removed ranged from 28-60%, with 42.4 mean. After 60 minutes and 90 minutes the ranges were 60-87% and 73-79%, with mean of 76.7% and 76.2% respectively. The amount of rust removed at room temperature increased with time, the highest being after 60 minutes, just like Holts (standard). Similarly, the efficiency of the above results can be compared with Cohly *et al.*, (2013) study, in that they utilized acetic acid to descale. This is whereby they dipped a rusted iron nail (6.4 cm, 8 mg) in a glass beaker containing 80 mL of 5% acetic acid, and the rusted iron nail produced hydrogen gas on its surface becoming shinny. The particles of the rust on the nail began falling off the nails. The amount of rust (%) removed by formulation 2, at pH=2.8 and at a temperature of 40 ^{0}C, at 125 rev/min are shown in Table 4.4.

Table 4.4: Percentage of rust removed by formulation 2 at 40 ^{O}C

No.	Initial weight of rusted iron nail (g)	Corroded nails readings (g)	Mass after removal (g)	Rust weight (g)	Time of exposure (min)	Rust removed (g)	% rust removed	Mean	Standard deviation
1	2.7132	2.7166	2.7145	0.0034	30	0.0021	61.8	70.0	7.7
2	2.8754	2.8815	2.8768	0.0061	30	0.0047	77.0		
3	2.8246	2.8291	2.8259	0.0045	30	0.0032	71.1		
4	2.7153	2.7213	2.7165	0.0060	60	0.0048	80.0	79.6	1.2
5	2.9198	2.9258	2.9211	0.0060	60	0.0047	78.3		
6	2.8836	2.8898	2.8848	0.0062	60	0.0050	80.6		
7	2.8240	2.8296	2.8265	0.0056	90	0.0031	55.4	75.6	17.7
8	2.9208	2.9268	2.9218	0.0060	90	0.0050	83.3		
9	2.8518	2.8627	2.8531	0.0109	90	0.0096	88.1		

The study showed that the amount of rust removed after 30 minutes, ranged from 62-77%, with a mean of 70. After 60 minutes and 90 minutes the ranges were 78-81% and 55-88% with of mean 79.6 and 75.6 respectively. The amount of rust removed, increased, with respect to time and was more after 90 minutes, although its efficiency was relatively low in comparison with market standards (Holts/South African anti-rusts).

4.3 Rust removal by formulation 3

The percentage of rust removed by formulation 3 is given by Table 4.5. The quantitative results for this formulation at the normal condition (pH=0.6) at the room condition (25 ^{0}C) is as given in Table 4.5.

Table 4.5: Percentage of rust removed by formulation 3 at room temperature

No	Initial weight of rusted iron nail (g)	Corroded nails readings (g)	After removal (g)	Rust weight (g)	Time of exposure (min)	Rust removed (g)	% of rust removed	Mean	Standard deviation
1	2.8665	2.8693	2.8670	0.0028	30	0.0023	82.1	81.0	2.9
2	2.7911	2.7923	2.7913	0.0012	30	0.0010	83.3		
3	2.9067	2.9112	2.9077	0.0045	30	0.0035	77.8		
4	2.8176	2.8280	2.8198	0.0104	60	0.0082	78.8	78.0	3.3
5	2.9140	2.9166	2.9145	0.0026	60	0.0021	80.8		
6	2.8710	2.8745	2.8719	0.0035	60	0.0026	74.3		
7	2.8868	2.8884	2.8870	0.0016	90	0.0014	87.5	82.3	4.9
8	2.7047	2.7069	2.7051	0.0022	90	0.0018	81.8		
9	2.8456	2.8465	2.8458	0.0009	90	0.0007	77.8		

The study showed that the percentage of the rust removed after 30 minutes, ranged from 78-83%, with mean of 81%. After 60 minutes and 90 minutes, the ranges were 74-81% and 78-88%, with mean of 78% and 82.3% respectively. The percentage of the rust removed increased to time and was higher after 90 minutes. However, its efficiency was relatively low in comparison with market standards (Holts/South African anti-rusts). The quantitative result for the elevated condition at pH=0.6 (40 ^{0}C at 125 rev/min) was as given in Table 4.6.

Table 4.6: Percentage of rust removed by formulation 3 at 40 ^{0}C

No.	Initial weight of rusted iron nail (g)	Corroded nails readings (g)	Mass after removal (g)	Rust Weight (g)	Time of exposure (min)	Rust removed (g)	% of rust removed	Mean	Standard deviation
1	2.8794	2.8869	2.8812	0.0075	30	0.0057	76.0	77.9	1.9
2	2.9928	3.0012	2.9945	0.0084	30	0.0067	79.8		
3	2.8230	2.8275	2.8240	0.0045	30	0.0035	77.8		
4	2.7325	2.7404	2.7341	0.0079	60	0.0063	79.7	82.7	4.4
5	2.7479	2.7531	2.7489	0.0052	60	0.0042	80.8		
6	2.8575	2.8673	2.8587	0.0098	60	0.0086	87.8		
7	2.7811	2.7864	2.7817	0.0053	90	0.0047	88.7	85.9	3.6
8	2.6949	2.7004	2.6959	0.0055	90	0.0045	81.8		
9	2.8671	2.8764	2.8683	0.0093	90	0.0081	87.1		

The study showed that the percentage of rust removed after 30 minutes, ranged from 76-80%, with mean of 77.9%. After 60 minutes and 90 minutes, the ranges were 80-88% and 82-89% and with a mean of 82.7% and 85.9% respectively. The percentage of the rust removed increased to time and was more after 90 minutes. However, its rust removal efficiency was relatively low, as it had the highest of removal efficiency of 89%, unlike the standards. The South African and Holts standards had the highest rust removal efficiencies of 97% and 94% respectively. The above results also showed the same trend in comparison with Lee *et al*., (1999) research, with their results indicating that the rate of rust dissolution in oxalic acid depended on temperature, in that there is complete dissociation of oxalic acid at a higher temperature.

4.4 Rust removal by formulation 4

The percentage of rust removed by formulation 4 is given by Table 4.7. The quantitative result of the formulation at a pH=0.2, at room temperature (25 ^{0}C) is given in Table 4.7.

Table 4.7: Percentage of rust removed by formulation 4 at room temperature

No.	Initial weight of rusted iron nail (g)	Corroded nails readings (g)	Mass after removal (g)	Rust weight (g)	Time of exposure (min)	Rust removed (g)	% rust removed	Mean	Standard deviation
1	2.9224	2.9310	2.9298	0.0086	30	0.0012	14.0	22.5	7.6
2	2.8373	2.8377	2.8376	0.0004	30	0.0001	25.0		
3	2.8128	2.8142	2.8138	0.0014	30	0.0004	28.6		
4	2.6994	2.7026	2.7006	0.0032	60	0.0020	62.5	46.4	15.1
5	2.9143	2.9174	2.9164	0.0031	60	0.0010	32.3		
6	2.906	2.9096	2.9080	0.0036	60	0.0016	44.4		
7	2.6955	2.6973	2.6971	0.0018	90	0.0002	11.1	13.8	6.0
8	2.9100	2.9172	2.9165	0.0072	90	0.0007	9.7		
9	2.9007	2.9065	2.9053	0.0058	90	0.0012	20.7		

The study showed that the percentage of the amount of rust removed after 30 minutes, ranged from 14-29%, with a mean of 22.5%. After 60 minutes and 90 minutes the ranges were 32-63% and 11-21%, with mean of 46.4% and 13.8% respectively. The percentage of rust removed increased with time increase and was higher after 60 minutes that was 63%. However, the formulation indicated low rust removal efficiency in comparison with the standards (Holts, after 60 minutes, had rust removal efficiency of 92% and the South African standards with 92%).

Table 4.8: Percentage of rust removed by formulation 4 at 40 ^{O}C

No.	Initial weight of rusted iron nail (g)	Corroded nails reading (g)	Weight after removal (g)	Rust Weight (g)	Time of exposure (min)	Rust removed (g)	% of rust removed	Mean	Standard deviation
1	2.7432	2.7582	2.7543	0.0150	30	0.0039	26.0	25.7	4.3
2	2.8117	2.8201	2.8176	0.0084	30	0.0025	29.8		
3	2.7472	2.7538	2.7524	0.0066	30	0.0014	21.2		
4	2.804	2.8097	2.8076	0.0057	60	0.0021	36.8	25.8	7.2
5	2.7749	2.7832	2.7812	0.0083	60	0.0020	24.1		
6	2.7924	2.7981	2.7967	0.0057	60	0.0014	24.6		
7	2.8728	2.8751	2.8744	0.0023	90	0.0007	30.4	41.7	14.7
8	2.6788	2.6812	2.6798	0.0024	90	0.0014	58.3		
9	2.9161	2.9205	2.9189	0.0044	90	0.0016	36.4		

The quantitative result of this formulation at elevated conditions at pH 0.6 (40 ^{O}C and 125 rev/min) was as follows: The study showed that the percentage of the amount of rust removed after 30 minutes, ranged from 21-30%, with mean of 25.7%. After 60 minutes and 90 minutes the ranges were 24-37% and 30-58%, with mean of 25.8 and 41.7 respectively. The percentage of the rust removed increased to time and was higher after 90 minutes that was 58%. However, the efficiency was relatively low in comparison with the standards, (Holts and South African had 93% and 95% had rust removal efficiency after 90 minutes).

4.5 Rust removal by formulation 5

The percentage of rust removed by formulation 5 is given by Table 4.9. The analysis of the derived citric acid was as follows, at the pH= 2.5. The quantitative analysis is as given in Table 4.9.

Table 4.9: Percentage of rust removed by formulation 5 at room temperature

No.	Initial weight of rusted iron nail (g)	Corroded nails readings (g)	Mass after removal (g)	Rust Weight (g)	Time (min)	Rust removed (g)	% of rust removed	Mean	Standard deviation
1	2.8008	2.8276	2.8275	0.0268	30	0.0001	0.3	22.7	38.1
2	2.8033	2.8299	2.8296	0.0266	30	0.0003	1.1		
3	2.8073	2.8079	2.8075	0.0006	30	0.0004	66.7		
4	2.7950	2.8295	2.8290	0.0345	60	0.0005	1.4	1.0	0.8
5	2.8225	2.8226	2.8226	0.0001	60	0.0000	0.0		
6	2.7976	2.8228	2.8224	0.0252	60	0.0004	1.6		
7	2.8028	2.8148	2.8146	0.0120	90	0.0002	1.7	1.4	0.6
8	2.8037	2.8145	2.8143	0.0108	90	0.0002	1.9		
9	2.8122	2.8391	2.8389	0.0269	90	0.0002	0.7		

The study showed that the percentage of the amount of rust removed after 30 minutes, ranged from 0.3-67%, with mean of 22.7%. After 60 minutes and 90 minutes the ranges were 0-1.6 % and 0.7-1.9 %, with mean of 1 and 1.4 respectively. The percentage of the rust removed decreased with the increase to time and was higher after 30 minutes. The removal efficiency by the formulation was the lowest in comparison with the standards, (Holts after 30 minutes had 94% and 97% for the South African).

The results at the pH=2.5, at an elevated temperature of 40 ^{0}C, are shown in Table 4.10.

Table 4.10: Percentage of rust removed by formulation 5 at 40 ^{O}C

No.	Initial weight of rusted iron nail (g)	Corroded nails readings (g)	Mass after removal (g)	Rust Weight (g)	Time (min)	Rust removed (g)	% of rust removed rust	Mean	Standard deviation
1	2.9167	2.9223	2.9223	0.0056	30	0.0000	0.0	4.9	6.4
2	2.6530	2.6608	2.6606	0.0078	30	0.0002	2.6		
3	2.6462	2.6503	2.6498	0.0041	30	0.0005	12.2		
4	2.6394	2.6461	2.6457	0.0067	60	0.0004	6.0	6.1	3.2
5	2.6925	2.6989	2.6983	0.0064	60	0.0006	9.4		
6	2.6721	2.6787	2.6785	0.0066	60	0.0002	3.0		
7	2.6583	2.6645	2.6640	0.0062	90	0.0005	8.1	24.5	15.5
8	2.7035	2.7065	2.7057	0.0030	90	0.0008	26.7		
9	2.7035	2.7120	2.7087	0.0085	90	0.0033	38.8		

After 30 minutes, the percentage of the rust removed ranged from 0-12% with a mean of 4.9%. After 60 minutes and 90 minutes the ranges were 3-9 % and 8-39 %, with mean of 6.1% and 25% respectively. The standard commercial antirust product from the market, named Holts was used for the rust removal purposes and its results achieved at the normal condition were as given in Table 4.11.

Table 4.11: Percentage of rust removed by market standard (Holt) formulation at room temperature

No.	Initial weight of rusted iron nail (g)	Corroded nails readings (g)	After removal (g)	Rust Weight (g)	Time of exposure (Min)	Rust removed (g)	% rust removed	Mean (%)	Standard deviation
1	2.8393	2.8602	2.8416	0.0209	30	0.0186	89.0	83.4	13.8
2	2.9598	2.9834	2.9613	0.0236	30	0.0221	93.6		
3	2.9678	2.9981	2.9776	0.0303	30	0.0205	67.7		
4	2.8196	2.8498	2.8276	0.0302	60	0.0222	73.5	75.0	15.9
5	2.8240	2.8554	2.8366	0.0314	60	0.0188	59.9		
6	2.7561	2.7918	2.7591	0.0357	60	0.0327	91.6		
7	2.9683	3.0086	2.9712	0.0403	90	0.0374	92.8	80.4	13.3
8	2.7377	2.7735	2.7441	0.0358	90	0.0294	82.1		
9	2.8408	2.8700	2.8506	0.0292	90	0.0194	66.4		

The study showed that the percentage of rust removed after 30 minutes, ranged from 68-94 %, with mean of 83.4%. After 60 minutes and 90 minutes the ranges were 60-92 % and 66-93 %, with mean of 75% and 80.4% respectively. The amount of rust removed increased with respect to time, and was higher after 90 minutes.

The standard commercial antirust product from the market, named Holts was used for the rust removal purposes and its results achieved at 40 ^{o}C are given in Table 4.12.

Table 4.12: Percentage of rust removed by market standard (Holts) formulation at 40 ^{O}C

No.	Initial weight of rusted iron nail (g)	Corroded nails readings (g)	After removal (g)	Rust Weight (g)	Time of exposure (Min)	Rust removed (g)	% rust removed	Mean (%)	Standard deviation
1	2.8187	2.8245	2.8200	0.0058	30	0.0045	77.6	84.5	11.1
2	2.8159	2.8170	2.8161	0.0011	30	0.0009	81.8		
3	2.8080	2.8321	2.8114	0.0241	30	0.0207	85.9		
4	2.8259	2.8290	2.8264	0.0031	60	0.0026	83.9	80.3	3.4
5	2.8100	2.8183	2.8119	0.0083	60	0.0064	77.1		
6	2.8076	2.8081	2.8077	0.0005	60	0.0004	80.0		
7	2.7962	2.8053	2.7974	0.0091	90	0.0079	86.8	88.9	6.8
8	2.7939	2.8286	2.7951	0.0347	90	0.0335	96.5		
9	2.8134	2.8158	2.8138	0.0024	90	0.0020	83.3		

The study showed that the percentage of the amount of rust removed after 30 minutes, ranged from 78-86 %, with mean of 84.5%. After 60 minutes and 90 minutes the ranges were 77-84 % and 83- 97 %, with mean of 80.3% and 88.9% respectively. The amount of rust removed increased with respect to time, and was higher after 90 minutes. Analysis for the results are as given in Table 4.12.

The standard commercial antirust product from the South Africa was used for the rust removal purposes and its results achieved at the normal condition were as given in Table 4.13.

Table 4.13: Percentage of rust removed by South Africa anti-rust formulation at room temperature

No.	Initial weight of rusted iron nail (g)	Corroded nails readings (g)	Weight after removal (g)	Rust Weight (g)	Time (min)	Rust removed (g)	% of rust removed	Mean (%)	Standard deviation
1	2.7541	2.7795	2.7550	0.0254	30	0.0245	96.5	94.0	2.5
2	2.7617	2.7781	2.7631	0.0164	60	0.0150	91.5		
3	2.7647	2.7778	2.7654	0.0131	90	0.0124	94.7		

The study showed that the percentage of rust removed after 30 minutes, was 97%. After 60 minutes and 90 minutes, the rust removed were 92 % and 95 % respectively, with the formulation having an average removal of 94%. The percentage of the rust removed increased with time, and was higher after 90 minutes. Notably, the anti-rust efficiency of this performance was not replicated, based on the available quantity. However, this formulation emerged to be superior in comparison with other formulations that were designed, as it showed the tendency to act with the same power as the market anti-rust product (Holt).

4.6 Qualitative analysis

The results of the FTIR analysis of the formulation 1 (one) sample before and after the reaction are presented in Figures 4.1 and 4.2.

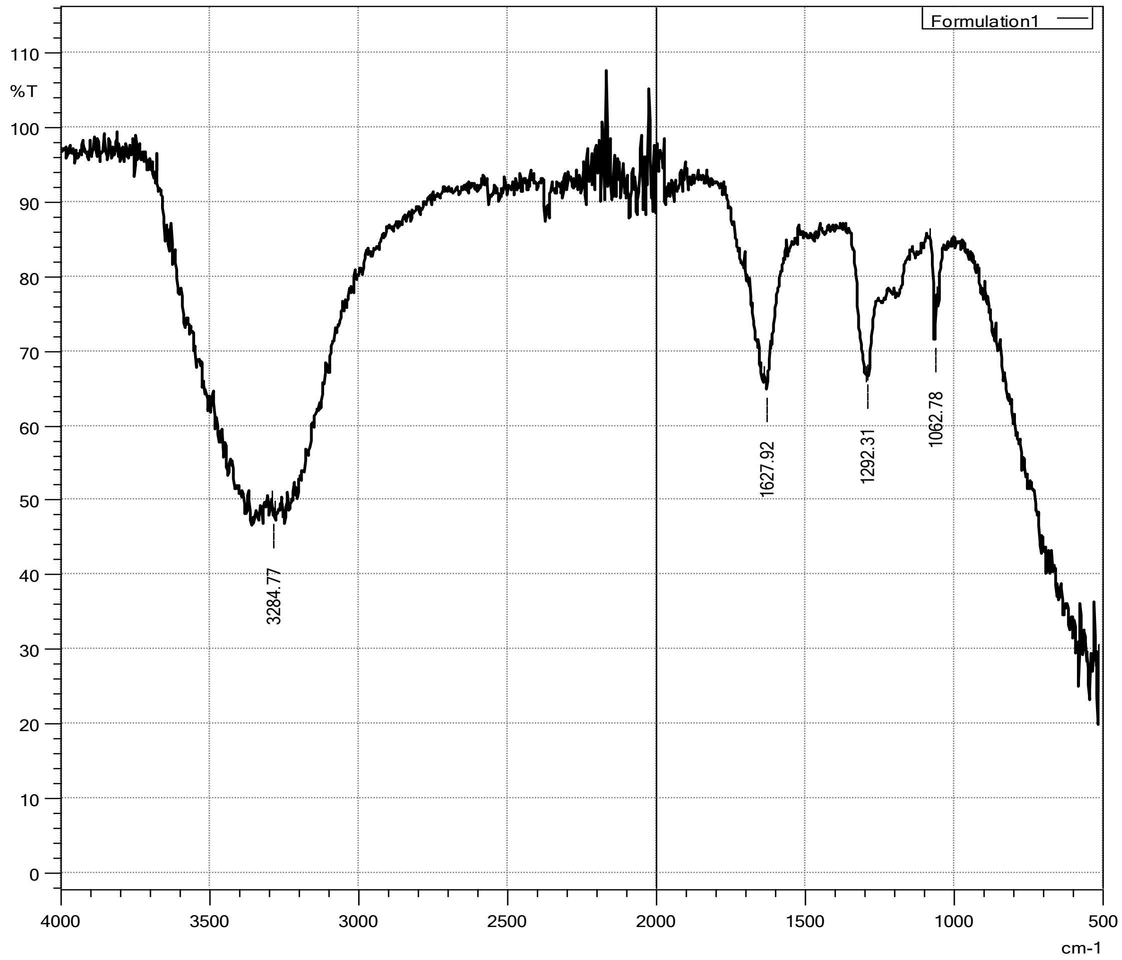


Figure 4.1: FTIR data for formulation 1 before reaction

The main peaks which were noticed by the formulation after running it in the FTIR included N-H stretch of the NH_2 that was attached to the sulfonic group at 3284 cm^{-1}. The C=O stretch of –COOH group of citric acid at 1634cm^{-1}, O-H stretch vibration from the carboxylic group at 1292 cm^{-1}, and C-C absorption from the citric acid, at 1062 cm^{-1}. The data after the reaction is shown in Fig. 4.2.

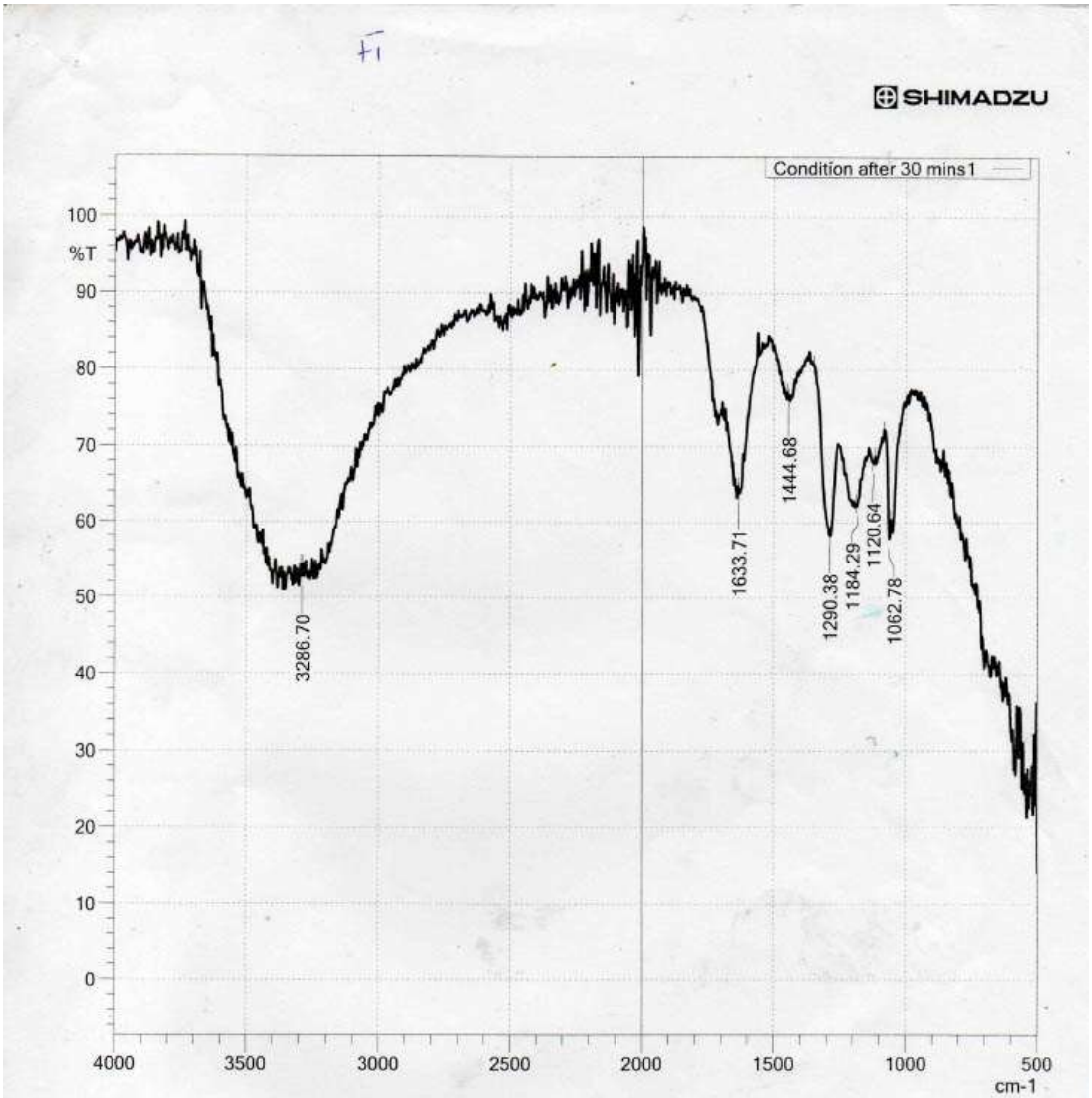
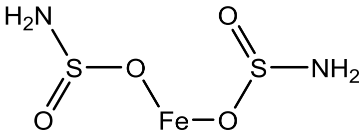


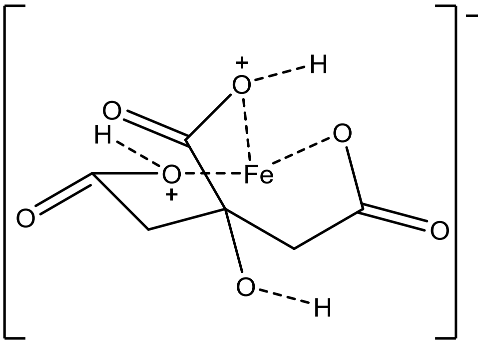
Figure 4.2: FTIR data for formulation 1 after the reaction.

The formulation indicated the presence of new absorptions formed at 1185 cm^{-1}, due to the formation of iron (II) citrate complex, C-H scissoring due to formation of cyclic iron (II) complex at 1445 cm^{-1}, and C-C due to the formation of cyclic iron (II) complex at around 1121 cm^{-1}. The other groups remained the same as before. The proposed formed complexes are shown in equations 4.1 and 4.2.

$Fe^{2+}_{(aq)} + 2H_3NSO_3^{-}{}_{(aq)} \rightarrow$



(s) + H_2 (g) (4.1)

$Fe^{2+}_{(aq)} + C_6H_5O_7^{3-}_{(aq)} \rightarrow$  (aq) + H_2 (g) (4.2)

The qualitative determination for formulation 2 was also done through analysis of the sample by the FTIR. The FTIR data before the reaction is as shown in Figures 4.3.

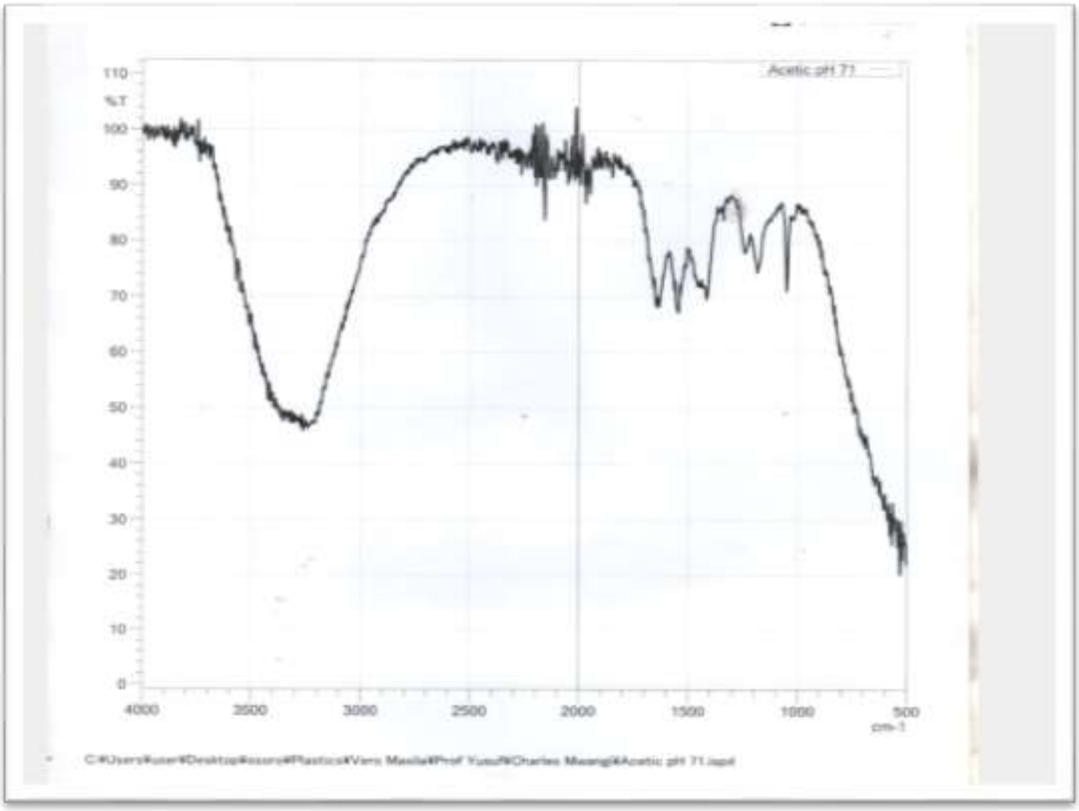


Figure 4.3: FTIR data for formulation 2 before the reaction.

Before the reaction, the FTIR spectra indicated there was the presence of absorption at 1100 cm^{-1} (C-O) of –COOH group of acetic acid. The presence of C=O stretch at 1700 cm^{-1} of the citric acid (COOH), the sulfoxide of the sulphamic acid absorbed (S=O) at 1350 cm^{-1} and an amide (N-H) bend at around 1620 cm^{-1} attached to S-NH_2, and N-H of sulphamic acid absorbed at 3300 cm^{-1}. The FTIR data after the reaction was as follows as indicated in Figure 4.4.

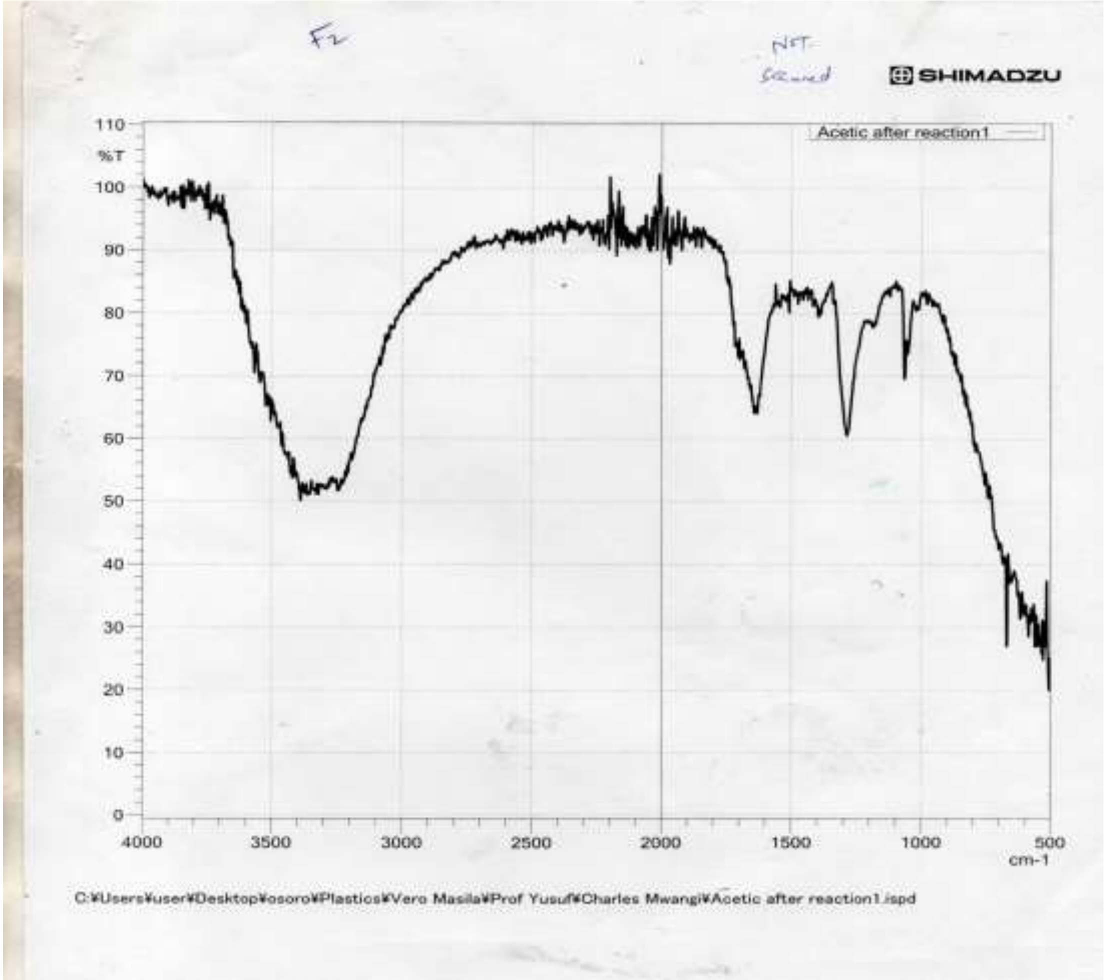
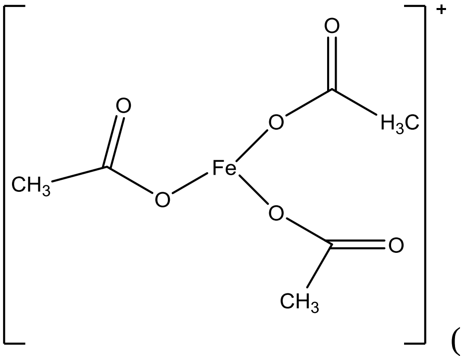


Figure 4.4: FTIR data for formulation 2 after the reaction.

After the reaction, the new bonds emerged at 700 cm^{-1} and 1680 cm^{-1}. The C-O bond appeared at 1300 cm^{-1}, increasing in cm^{-1}, an indication of the formation Fe-O bond with COOH group of the acetic acid, due to formation of iron (II) acetate complex. The –C-O bond at 1100 cm^{-1} of (COOH) from the acetic acid and the sulfoxide bond (S=O) at 1300 cm^{-1}, did not change. The proposed complex formed is as given by equation 4.3.

Fe^{2+}(aq)+ 3CH_3COO^- (aq) →



(aq) (4.3)

The qualitative determination for the formulation 3 was also done through analysis of the sample by the FTIR machine. The spectrum before the reaction was as shown in Figure 4.5.

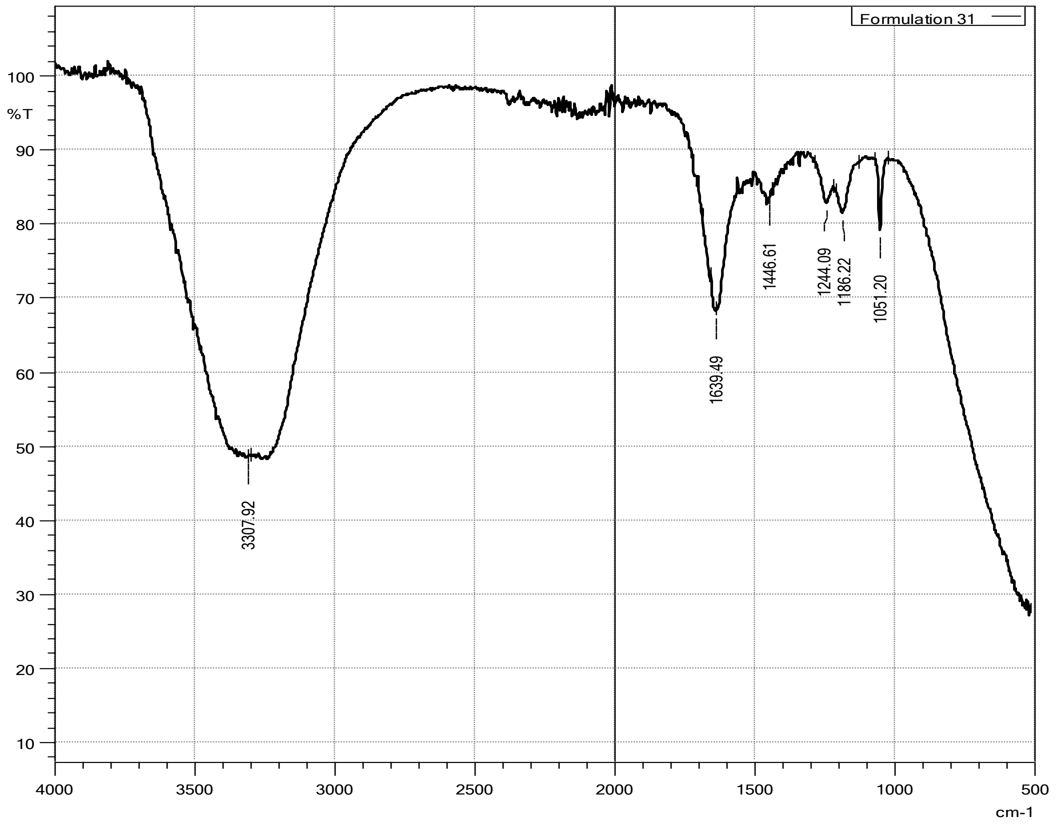


Figure 4.5: FTIR data for formulation 3 before the reaction

Before the reaction the major groups which were present included; -O-H stretch at 3308 $cm^{-1}$of glycolic acid, -C-O- bond at 1639 cm^{-1} from glycolic acid. Further, there was C-H bending at 1447 cm^{-1} from the glycolic molecule, strong C-O stretch at 1245 cm^{-1} (glycolic acid). The FTIR data after the reaction was as shown in Figure 4.6.

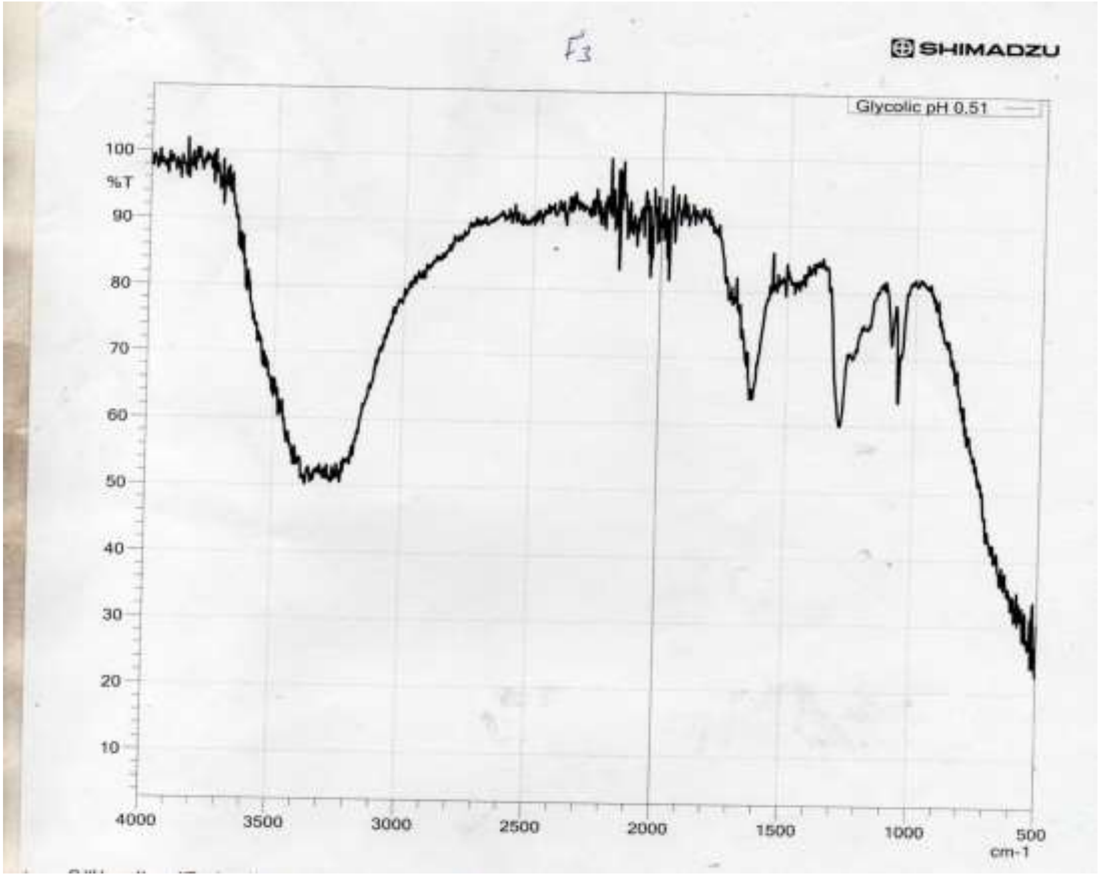
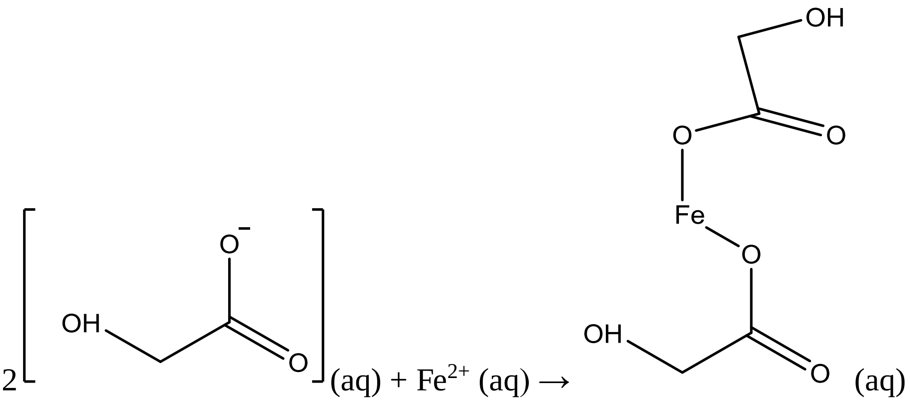


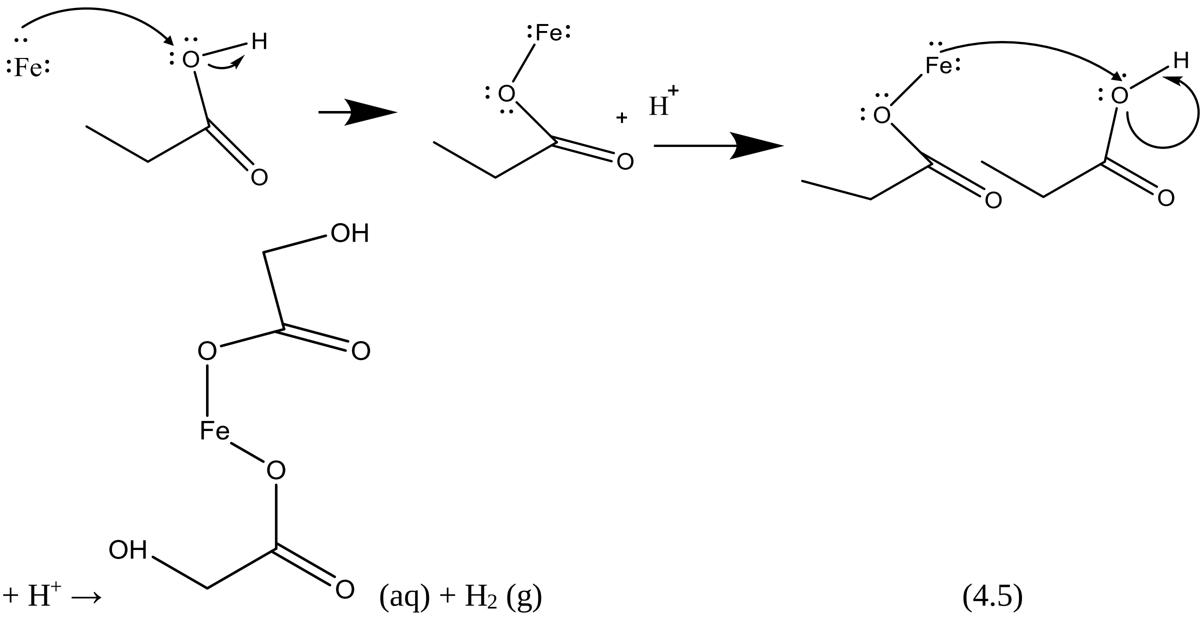
Figure 4.6: FTIR data for formulation 3 after the reaction

After the reaction, the FTIR spectra formed emerged at 1250 cm^{-1}, indicating the presence of S=O stretch, O-H bond at 3250 cm^{-1}, and C-H bending at 1650 cm^{-1} as a result of the formed iron (II) acetate complex. The proposed complexes formed are as equations 4.4.



(4.4)

The prevailing mechanism of the formation of the above complex is that the Iron (II) metal is coordinated with the glycolate ions. This is whereby the Fe^{2+} accepts pairs of nonbonding electrons from the oxygen in the glycolate molecule. Iron (II) glycolate complex (blue-green color) is formed, with the release of the hydrogen proton. The proposed reaction is shown by equation 4.5.



+ H^+ → (aq) + H_2 (g) (4.5)

The qualitative analysis of the formulation 4 was done and its spectrum before the reaction is shown in Figure 4.7.

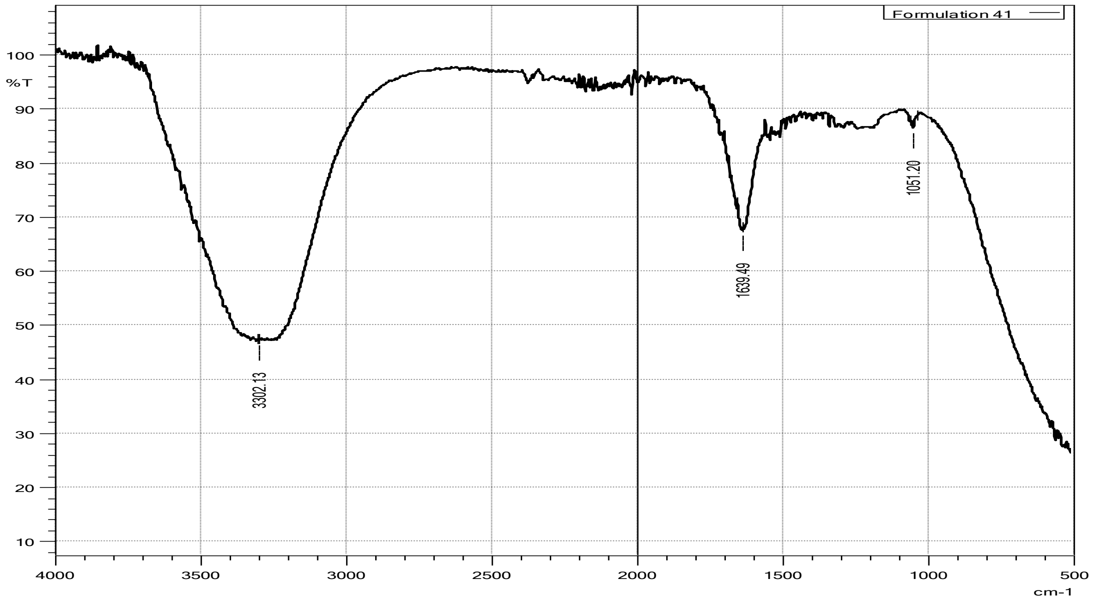


Figure 4.7: FTIR data for formulation 4 before the reaction

Before the reaction, the peaks emerged at 3302 cm^{-1} indicating, the presence of NH stretch from the sulphamic acid. A peak at 1640 cm^{-1}, indicating the presence of C=O stretch from the oxalic acid COOH, and a peak at 1050 cm^{-1}, indicating the presence of S=O from the sulphamic acid. The qualitative analysis of the formulation after the reaction is shown in Figure 4.8.

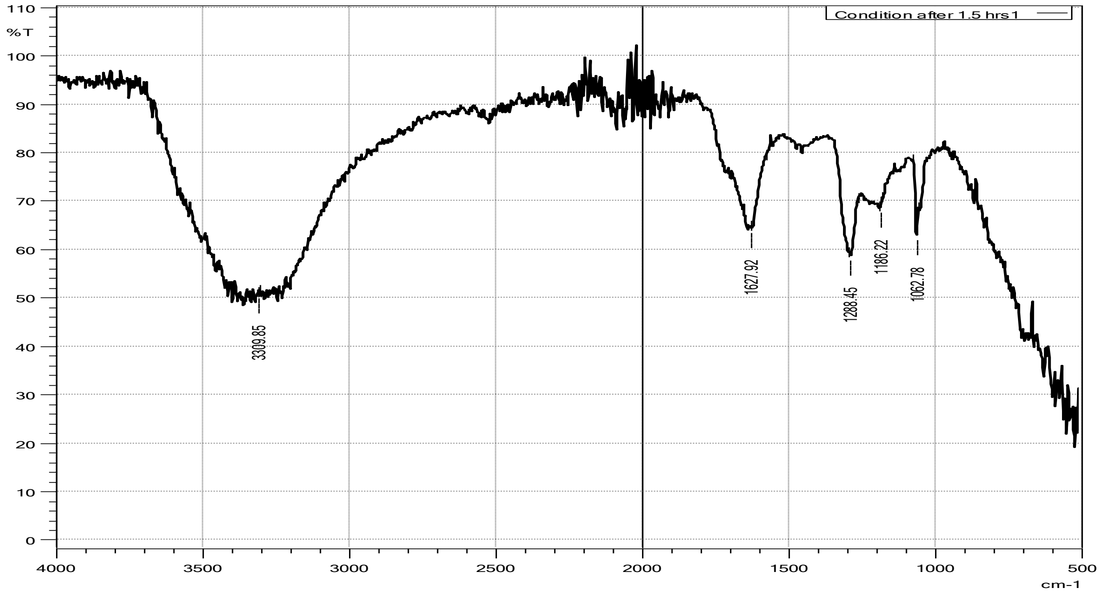
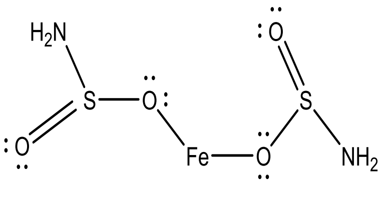


Figure 4.8: FTIR data for formulation 4 after the reaction.

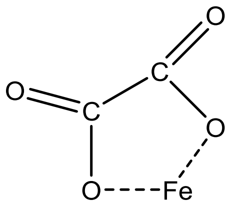
After the reaction new-formed functional groups generated at 1186.22 cm^{-1}, 1288.45 cm^{-1}, and 1627.92 cm^{-1}. At 1286.22 cm^{-1}, the bond can be linked with strong C-O, and C=O bond at 1639 cm^{-1} formed due to the formation of iron (II) oxalate complex. The N-H (bending) generated due to ferrous iron (II) sulphamate complex at 3302 cm^{-1} formed as proposed indicated by equations 4.6 and 4.7.

Fe^{2+} (aq) + 2 $H_3NSO_3^-$(aq) →



(aq) + H_2 (g) (4.6)

Fe^{2+} (aq) + $C_2O_4^{2-}$ (aq) →



(s) (4.7)

The qualitative analysis for the formulation 5 (extracted citric acid) was also performed before the reaction, and the main functional groups that were detected by FTIR were composed of: -C-O- bond at around 1224 cm^{-1}, C=O- bond stretching at around 1688 cm^{-1}, and –OH stretching at around 3383 cm^{-1} from the citric group. At 885 cm^{-1} C-H bending is realized, attributed to citric acid in the formulation. The FTIR data before the reaction is shown in Figure 4.9.

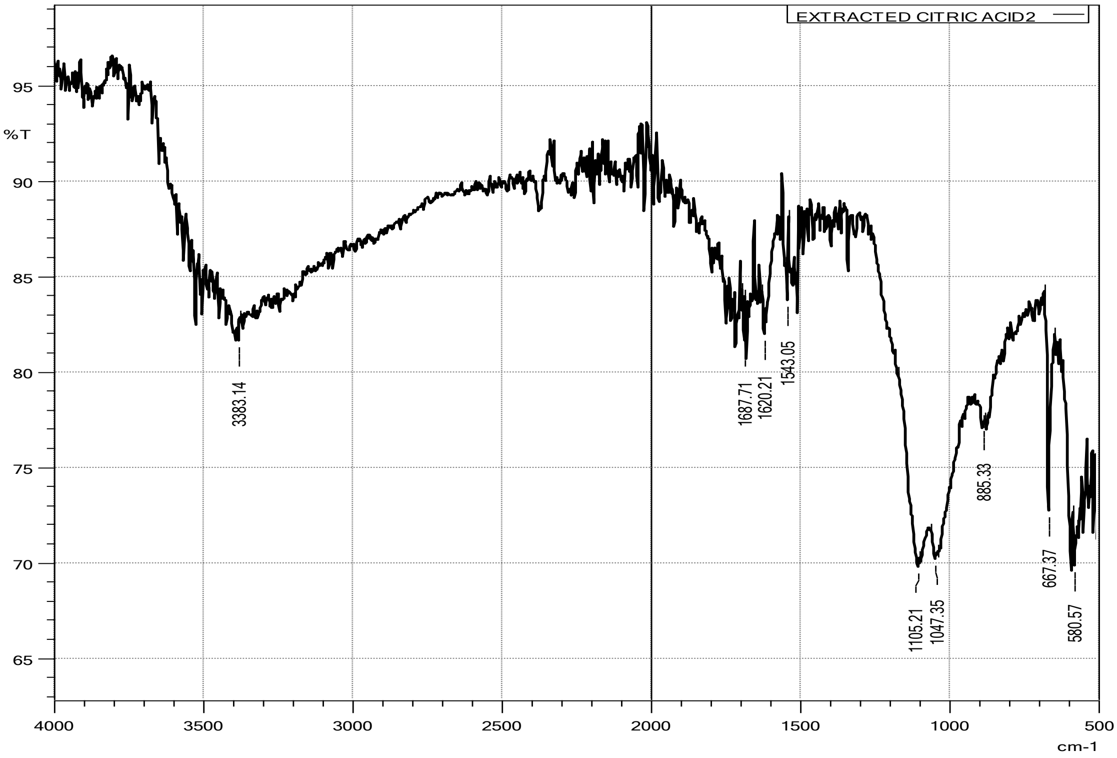


Figure 4.9: FTIR data for formulation 5 before the reaction.

The qualitative analysis of the formulation after the reaction is shown by the FTIR Figure 4.10.

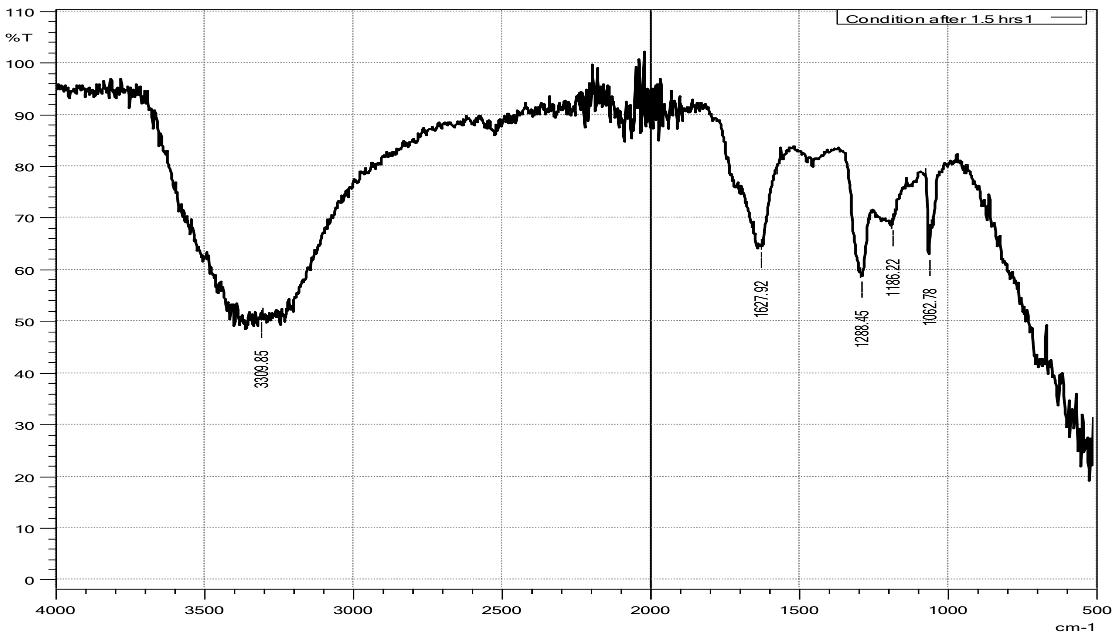
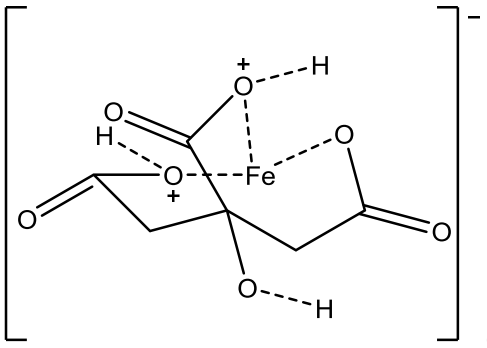


Figure 4.10: FTIR data for formulation 5 after the reaction.

After the reaction, peaks appeared at 1288 cm^{-1} associated with C-O stretching from the iron (III) citrate complex formed, a peak at 1063 cm^{-1} (O-H bending) as a result of the formed iron (III) citrate complex, O-H peak at 3309 cm^{-1}, and at 1640 cm^{-1}.The formed complex is as indicated by equation 4.8.

Fe^{2+} (aq) + $C_6H_5O_7^{3-}$(aq) →



(aq) + H_2 (g) (4.8)

In conclusion, the performance of the derived citric acid, emerged to be less effective compared with the commercial citric acid, which can be attributed to the existence of impurities that may have reduced its performance in the rust removal. Figure 4.11 shows the market anti-rust, which was utilized as a standard.

Figure 4.11: Holt anti rust (Unipro Limited).

The anti-rust product sold in the market as "Holts" was used as a standard. Its FTIR spectra after reaction is presented in Figure 4.12.

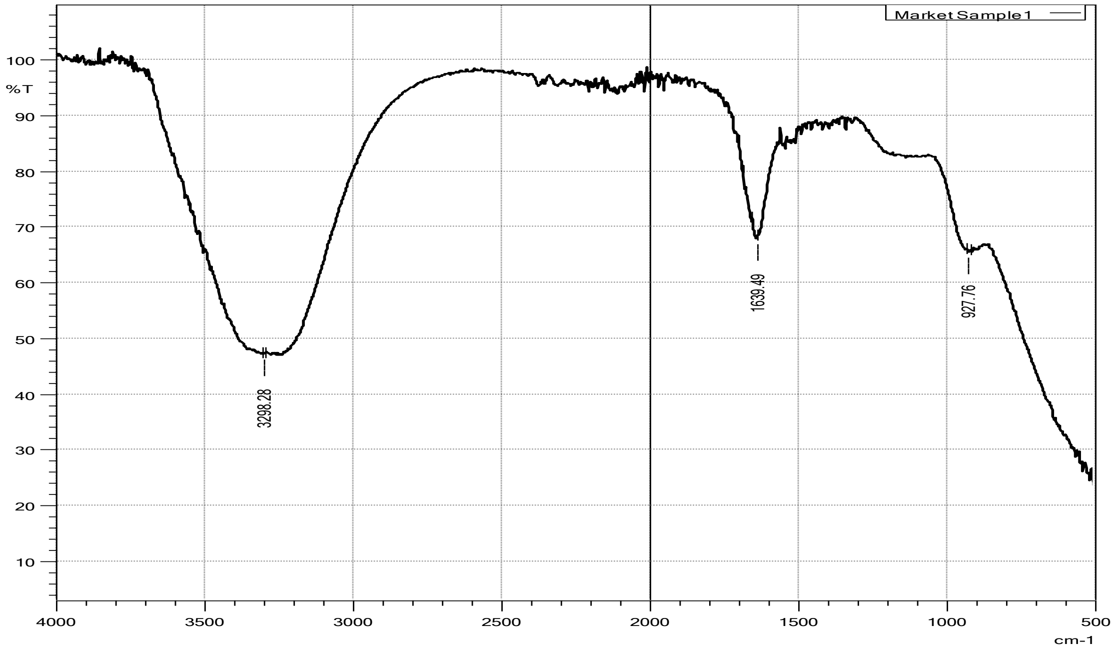


Figure 4.12: Holt anti-Rust FTIR after reaction.

Also, the FTIR spectrum for the South Africa standard after rust removal was also performed and is as shown in Figure 4.13.

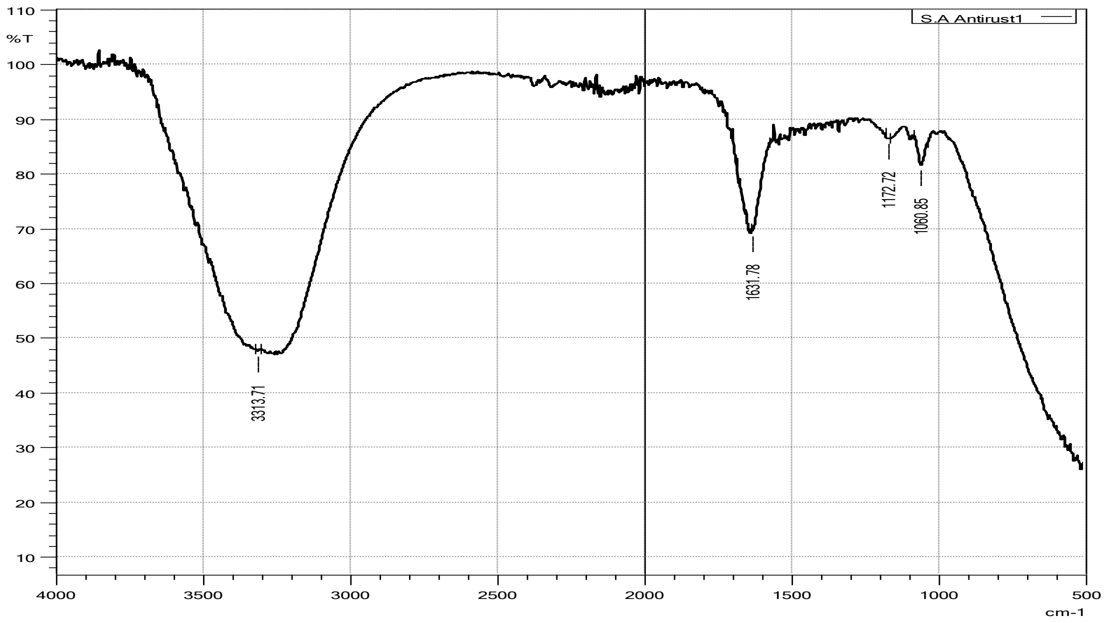


Figure 4.13: South Africa anti-Rust FTIR after reaction

After the reaction, the market sample according to the FTIR, there was detection of the –O-H stretching at around 3313 cm^{-1}. A C=C- cis stretching bond at 1631 cm^{-1}, -C-H bending bond around 1172 cm^{-1}, and –C-O bond around 1060 cm^{-1}. The other standard, which was used for comparison purposes, was anti rust from South Africa.

The function functional groups realized from the FTIR by the South African anti-rust, prevailed at 3314 cm^{-1}, 1660 cm^{-1}, 1173 cm^{-1} and 1061 cm^{-1}. O-H stretching at 3314cm^{-1}predicting the presence of carboxylic group, C=O stretching at 1660 cm^{-1}, predicting the presence of the carboxylic group in the formulation, and C-O stretching at 1061 cm^{-1}.

Notably, the South African and market anti-rusts standards were run after reacting with the iron nails samples based on their low quantities.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The study showed that formulation one which contained citric acid, sulphamic, and iron sulphate at room temperature had % efficiency in rust removal of 77-92% after 90 minutes, whereas, formulation two which was composed of acetic acid, sulphamic acid and iron sulfate had % efficiency of 60-87% after 60 minutes. Formulation three, which contained hydroxyacetic acid, sulphamic acid, and iron sulphate, had a % efficiency of 78-88% after 90 minutes. Formulation four that was composed of oxalic acid, sulphamic acid, and iron sulfate, and formulation five of extracted citric acid, sulphamic acid, and iron sulphate, had % efficiencies of 32-63% and 0.3- 67% after 60 and 30 minutes respectively. The market standard (Holts), which was used for comparison with the prepared formulations, had its efficiency after 30, 60, 90, at 68-94 %, 60-92 %, and 66-93 %, respectively with its optimum efficiency prevailing after 30 minutes. The overall optimal formulation after 30 minutes was formulations 3 with an average of 81%, followed by formulation 1 at 47.6% and formulation 2 at 42%.

In assessing the functional groups in formulation 1, this was done after the reaction of the formulations which formed C-O bond at 1185 cm^{-1}, (formation of iron (II) citrate complex), (C-H scissoring (formation of cyclic iron (II) complex) at 1145 cm^{-1}. In formulation 2 the formation of C-O bond at 1300 cm^{-1} (broad), which suggested the formation of the Fe-O bond of the COOH group of the acetic acid. Formulation 3**,** also generated new spectra after reacting with the sample that emerged at 1350 cm^{-1} suggesting the presence of S=O stretch (Iron (II) glycolate complex). Formulation 4, showed the formation of new peaks at 1186.22 cm^{-1} and 1288.45 cm^{-1}, suggesting N-H bending vibrations, (formation of iron (II) sulphamate complex). Also, at 1286.22 cm^{-1} C-O bond was generated of an iron (II) oxalate complex. Finally, formulation 5 showed the emergence of new bonds at 1288 cm^{-1} (C-O stretch from iron (III) citrate complex), and a new peak at 1063 cm^{-1} (O-H bend, resulting from the formation of iron (II) citrate complex).

5.2 Recommendations

The recommendations from this study were:

1. An anti-rust efficiency studies on other low-weight organic acids like malic acid, fumaric acid, butyric acid, and lactic acid should be undertaken.
2. That research should be extended by studying the rust products formed using XRD analysis.
3. That studies on other activating agents on rust removal be done.

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