



**Comparative studies of electrochemical corrosion behaviour of mild steel
in some agro-fluids**

by

ANTHONY CHIKERE OGIZI

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SUPERVISOR: PROF A S AFOLABI

CO-SUPERVISOR: DR A S ABDULKAREEM

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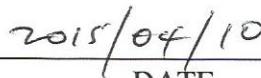
DECLARATION

Student number: **4810-707-7**

I declare that '*Comparative Studies of Electrochemical Corrosion Behaviour of Mild Steel in some Agro-Fluids*' is my own work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references.



SIGNATURE



DATE

Mr Anthony Chikere Ogazi

DEDICATION

This work is dedicated to my son Success Chidera Ogazi and to all members of my beloved family who are my great source of inspiration.

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PUBLICATIONS

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2. **Anthony C. Ogazi**, Ayo S. Afolabi and Ambali S. Abdulkareem (2013) Comparative weight loss analyses of mild steel in agro fluid media. *Proceedings of the "International Conference on Chemical, Mining and Metallurgical Engineering (CMME'2013)" Nov. 27-28, 2013, Johannesburg South Africa, Vol. III*, pp 217 – 220, (ISBN: 978 – 93 – 82242 50 – 5).

ABSTRACT

The electrochemical corrosion behaviour of mild steel in apple, grape, mango, orange and the mixture of these juices was investigated in this study. Open circuit potential and weight loss analytical techniques were employed to establish the comparative corrosion rates of this material in the agro media over the interval of five days for a sixty-day immersion period at an ambient temperature. The chemical compositions of both mild steel and the agro media were determined to ascertain corrosion mechanism for the reaction. Polarization behaviour of mild steel in the agro media were determined by Tafel extrapolation curves. The analysis showed that cathodic polarisation curves were almost identical irrespective of the concentration of the various media while the anodic polarization curves exhibited varying active and passive corrosion behaviour due to passivating oxide films. The analysis of the results further showed that the corrosion rate of the metallic sample decreased with longer immersion periods which could be attributed to a gradual decline in acidity of these media as revealed by the pH results. Hence, the evolution of hydrogen gas and reduction of dissolved oxygen molecules from the reacting system were presumed to be major factors retarding corrosion of the solution involved. Similarly, the presence of suspended particles on the surface of the test steel sample could have also led to the impediment to corrosion rates from the surrounding atmosphere. Microscopic analysis of the corroded mild steel specimens revealed uniform and localised corrosion with Fe_2O_3 spotted as the main corrosion product. The result obtained from the electrochemical study showed that the corrosion rate of the mild steel sample was highest in the orange medium (1.53mm/yr), followed by grape medium (1.40 mm/yr), mixture of these media (0.67mm/yr), mango medium (0.40mm/yr) while the metal corroded least in the apple medium (0.30mm/yr) over the duration of immersion.

Key terms: Corrosion; Mild steel; Agro juices; Weight loss; Electrochemical; Corrosion rates; Polarisation curves; Passivating oxide films; Microscopic analysis; OCP

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LIST OF ABBREVIATIONS

Acm ⁻²	ampere per square centimetre
ASTM	American Society for Testing and Materials
ads	adsorption
ba	anodic Tafel slope
bc	cathodic slope
CR	corrosion rate
°C	degree Celsius
EDS	energy dispersive spectroscopy
EIS	electrochemical impedance spectrometer
E _{corr}	corrosion potential
g	grams
g/cm ³	grams per cubic centimetre
g/l	grams per litre
HPLC	high pressure liquid chromatography
I _{corr}	corrosion current density
I _{crit.}	Critical passivation current density
LM	light microscopy
M	metal

MOH	metallic hydroxide
m	number of moles of reacting species
mm	millimetre
mmpy (mm/year)	millimetre per year
mVolt	milli-volt (10^{-3} volt)
n	number of electrons
OCP	open circuit potential
pH	potential of hydrogen
ρ	density
SEM	scanning electron microscopy
SVE	scanning vibrating electrode
TEM	transition electron microscopy
t	thickness
%	percentage
uv	ultra violet
μm	micro-meter
Vdec^{-1}	volt per decimetre
v/s	voltage per second
W	weight loss

WIE	wire beam electrode
>	greater than
<	less than
X	magnification range
XRD	X-ray diffraction
% wt	percentage weight

CHAPTER 1

1.0 INTRODUCTION

1.1 Background and motivation

Corrosion is a gradual physiochemical destructive attack on metals through interaction with the environment (Kadry, 2008; Ogunleye *et al.*, 2011). In broad aspect, corrosion is a process of destructive alteration of metal or an alloy by chemical reaction with any solid, liquid or gaseous substance (ASM *International*, 2000). The pattern of attack is largely dependent on combined influences of several factors relating to the metal, service condition and nature of intimate environment. Corrosion is conveniently classified according to the manner in which it manifests itself (Fontana, 1986; Ogundare *et al.*, 2012) and is regularly encountered in the chemical, petrochemical, oil and food processing industries.

There are numerous forms of corrosion. One of such categories includes chemical and electrochemical corrosion (Kim *et al.*, 2006). Chemical corrosion is the direct result of exposure of a material to a chemical and is governed by the kinetics of chemical reactions (Uhlig, 1985). Faraday (1791-1867) established a quantitative relationship between chemical action and electric current (Walsh, 1991). Similarly, Whitney in 1903 provided a scientific basis for electrochemical corrosion which involves dissolution of a metal through oxidation process thereby resulting to formation of oxide films a metallic surface (Evans, 1972). Oxidation and reduction reactions occur simultaneously and are interdependent. Corrosion occurs only at the site of oxidation. The loss of metals and the cost implications of corrosion are quite high in any society. This is because metals and their alloys form the essential bases for modern technological civilization. Corrosion leads to huge economic waste especially in

the processing and manufacturing industries (Oluwole *et al.*, 2012). Studies carried out have shown that corrosion is recognized as one of the most serious problems facing the modern world resulting to losses worth of billions of US dollars each year; approximately ranging from one to five percent of Gross National Product (GNP) in countries like United Kingdom, Germany, United States of America and Japan (Batchelor *et al.*, 2002; Oluwadare and Agbaje, 2007). The cost estimate of corrosion is very crucial in drawing attention to wasteful depletion of resources due to negligence especially in the developing nations where funds are rarely available. Indeed, corrosion studies have become fundamental academic and industrial concerns which remain global scientific problem as it affects the metallurgical, oil, chemical and food processing industries (Callister, 1997; Onen, 2004). The phenomena of corrosion can be traced from the structural features of the metal involved, the nature of the environment and the reactions that occur at the metal- environment interface (Shreir, 2010). To ensure appropriate selection of metals/alloys, a number of factors should be considered. These include understanding their physical and chemical properties, and their interaction with the environment as well as cost implications (Frankel, 2008). Material selection should base on life span and must be equitable to the expected return on investment which however depends on the purpose of its application (*ASM International*, 2000).

The specific environment which this study has investigated is that of agro fluids since mild steel is widely used in the industrial processing of materials (Singh and Singh, 1995; Kangas, 1998). The study of chemical composition of mild steel and more importantly the agro fluid environment is crucial as this will to large extent determine the corrosion reaction and subsequently provide the corrosion mechanism of this metal in the selected agro media. Studies showed that mild steel is an alloy containing iron and other constituents (Vera *et al.*, 2003; Singh and Gupta, 1996). However, mild steel as a construction material is vulnerable to

corrosion (Shreir, 2010). Previous studies revealed that when mild steel corrodes, there is usually metal loss to a solution in the form of oxidation (Shreir, 2010; ASM *International*, 2000). Corrosion occurs at anodic sites and the metal is oxidized to metallic ions as electrons are produced. On the other hand, anodic areas occur at cracks in the oxide coating at boundaries between phases or around impurities (Ita and Offiong, 1997).

Most research studies on agro media focused on inhibition of metals in these media (Ibrahim and Habbab, 2011; Ebenso *et al.*, 2004; Ita and Eden, 2000; Oguzie *et al.*, 2006; Onen, 2004). Similarly, the corrosion effects of mild steel immersed in some agro media such cocoa and cassava extracts (Afolabi, 2007), palm fruit, tomato pulp, cassava pulp (Adetunji *et al.*, 2011); orange juice (Oladele and Okoro, 2011; Badmos and Ajimotokan, 2009) have also been studied. Most agro fluids are acidic (Mc Swane *et al.*, 2003; Bailey and Bailey, 1995; Reger *et al.*, 2009). Organic acid present in the agro fluid is the most important corrosion agent (Ofoegbu *et al.*, 2011). The effect of this medium on metal can be influenced by the environmental conditions such as flow rate, temperature, viscosity and presence of stresses in the system. The exact analysis of the constituent of agro fluid is a challenge due to their very complex composition (Ofoegbu *et al.*, 2011). Since mild steel is active in acidic medium, it may be susceptible to corrosion in juice processing media.

1.2 Research problems

This research is set to address corrosion behaviour of mild steel in the selected agro-fluids as little or no existing data were found that studied electrochemical corrosion behaviour of mild steel in the agro fluids:- mango, orange, grape and apple environments. Mild steel is selected for this study because of its availability, cost advantage, strength, malleability, amenability to heat treatment to vary its mechanical properties and has been chosen for similar studies (Bolton, 1994; Smith and Hashemi, 2006; Singh and Gupta, 1996; Khaled and Amin 2009). It is also used in the fabrication of reaction vessels and storage tanks by industries which either manufacture or use organic acids as reactants for industrial processes (Singh and Singh, 1995). Since agro juices contain organic acids (Anthony and Offiong, 1998; Niu *et al.*, 2008) which are industrially processed by metals (Oladele and Okoro, 2011), the need to investigate and document the corrosion behaviour of mild steel in these agro fluids may be encouraged to predict the integrity of this metal in these environments.

1.3 Aim and objectives

The aim of this study is to investigate and compare the electrochemical corrosion behaviour of mild steel in agro fluids such as orange, grape, mango and apple. Other specific objectives of the study include to:

- a. Determine the chemical compositions of the mild steel sample that will be used and the selected fruit juices- mango, apple, orange and grape.
- b. Investigate corrosion behaviour of the mild steel sample in these agro media using a weight loss measurement method.

- c. Investigate electrochemical behaviour of the mild steel sample in the agro environments and the mixture of these media using a 3-electrode electrochemical cell.
- d. Examine the microstructure of corroded steel samples by SEM and EDS.
- e. Study corrosion mechanism of the mild steel sample in these agro media.

1.4 Scope of the research

This study focuses on the determination of electrochemical corrosion behaviour of mild steel in orange, mango, grape and apple juices. It also investigates the weight loss analyses to ascertain the various rates of corrosion at room temperature. The scope includes the microstructural examination of corroded mild steel samples, comparison and deduction of corrosion mechanism of mild steel in equivalent mixture of these media. Although the study is limited to the aforementioned scope using mild steel and four agro juices, its findings may be applicable to other metals/alloys under similar environments. Further specific areas for follow-up research are pointed out in the recommendation.

1.5 Expected contribution to knowledge

This research study will also present good data on the comparison of corrosion rates and weight loss analyses of the mild steel samples in the various agro environments studied. Other specific contributions include the provision of data on:

- Corrosion behaviour of the mild steel sample in the selected agro media using a weight loss measurement.
- Electrochemical behaviour of mild steel sample in the agro juices and in the mixture of these environments.

- Comparison of corrosion mechanism of the mild steel sample in the agro media studied.
- Microstructural analyses of corroded mild steel samples immersed in apple, grape, mango, orange and the mixture of the agro media using SEM and EDS.

1.6 Structure of the dissertation

Chapter one provides the introduction, background and motivation for conducting this research and states the aim and objectives of the study. It also states the scope and expected contribution to knowledge.

Chapter two is the literature review of the study which covers the general corrosion concept and provides electrochemical corrosion behaviour of metallic materials. It examines the characteristics of agro fruits environments and corrosion mechanism of mild steel. In addition, this chapter reviews microscopic analyses of mild steel in the agro media.

Chapter three explains the research materials and methodology used for experimentation which involves the logical sequence of operations outlined in the objectives of this study. It also describes sample preparation, procedures and techniques by which the experiments are conducted to obtain the results.

Chapter four reports the experimental results and discussion on the weight loss measurements, electrochemical studies and characterisation of the corroded mild steel samples.

Chapter five states the conclusions based on the analyses of the results with recommendations for further studies.

CHAPTER 2

2.0 LITERATURE REVIEW

2.1 Concept of corrosion

The corrosion is the destruction or the deterioration of metallic materials by direct chemical, electrochemical or biochemical reactions with different environments (Wang *et al.*, 2011; Ofoegbu *et al.*, 2011). Corrosion processes are very broad and complex phenomena which can be uniform, localized and many more. Historically, corrosion has been observed in all civilizations since the inception of technology and is widely dependent on the use of metals and alloys. Indeed all metals except for some noble metals such as gold are subject to corrosion (Shreir, 2010). It usually begins at the surface of a material and occurs because of the spontaneous tendency of the materials to return to their thermodynamic stable state or to one of the forms in which they were originally found, (Schutz, 2000). Metals are generally prone to corrosion because most of them occur naturally as ores, which is the most stable state of low energy and there is a net decrease in free energy from metallic to oxidized state (Shreir, 2010).

According to MESA, (2000); the primary driving force of corrosion in all alloys of iron is the transformation of iron from its natural state to steel. Steel is essentially an unstable state of iron because energy is required to form it. Mild steel therefore corrodes easily when exposed to agro fluid or used to package juice to a great extent during service. Corrosion may as well be considered as an oxidation process in which an oxide coating is formed on the surface of the metal undergoing the process (Onen, 2000). The exposure of steel to an industrial atmosphere would result to formation rust of an approximate composition, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and being loosely adherent (Ababio, 2005). This does not form a protective barrier to isolate the

metal/alloy from the environment; thus the reaction proceeds at an approximately linear rate until the metal/alloy is completely consumed. Fontana and Staehle (1990) acknowledged that corrosion includes the reaction of metals, glasses, ionic solids, polymeric solids and composites with environments that embrace liquid metals, gases, non-aqueous electrolytes and other non-aqueous solutions. While in the context of corrosion engineering, it is considered as the reaction of an engineering constructional material (metals or non metals) with their environments with consequent deterioration in properties of the materials (Onen, 2000).

2.2 Types of corrosion

There exist various kinds of corrosion which can affect the metal in a variety of ways depending on its nature and the precise environmental conditions prevailing, and a broad classification of the various forms of corrosion (Shreir 2010). Five major types have been identified by Shreir (2000) and Uppal and Bhatia (2001) as uniform, localized, pitting, selective dissolution and conjoint action of corrosion and a mechanical factor. Thus, an 18Cr-8Ni stainless steel will corrode locally during intergranular attack, crevice corrosion or pitting. Shreir (2010) observed that in certain circumstances selective attack along an active path in conjunction with a tensile stress may lead to transgranular fracture. According to Shreir (2010) there are different types, characteristics and examples of corrosion as summarized in Table 2.1.

Table 2.1 Types, characteristics and examples of corrosion (Source: Shreir, 2010)

Type	Characteristics	Examples
Uniform (or almost uniform)	All areas of the metal corrode at the same or similar rate.	Oxidation and tarnishing; active dissolution of acids; anodic oxidation and passivity; chemical and electrochemical polishing; atmospheric and immersed corrosion in certain cases.
Localized	Certain areas of the metal surfaces corrode at higher rates than others due to heterogeneities in the metal, the environment or in the geometry of the structure as a whole. Attack ranges from slightly localized to pitting.	Crevice corrosion; fill form corrosion; deposit attack; bimetallic corrosion; intergranular corrosion and weld decay.
Pitting	Highly localized attack at specific areas resulting in small pits that penetrate into the metal and may lead to perforation.	Pitting of passive metals such as the stainless steels, aluminium alloys, e.t.c. in the presence of specific ions e.g. Chloride ions.
Selective dissolution	One component of an alloy (usually the most active) is selectively removed from the alloy.	Dezincification, dealuminification, graphitization.
Conjoint action of corrosion and mechanical factor	Localized attack or fracture due to the synergistic action of a mechanical factor and corrosion.	Erosion-corrosion, fretting corrosion; impingement attack, cavitations damage; stress corrosion cracking (SCC); hydrogen cracking and corrosion fatigue.

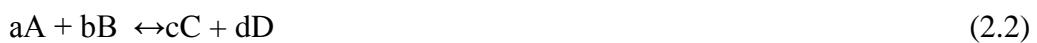
2.3 Corrosion as a reaction at a metal/environment interface

Most metallic corrosion result from electrochemical effects. When this occurs, corrosion is initiated by the flow of electrons between the electrode sites of different potentials in contact with an aqueous electrolytic solution (Genesca *et al.*, 2002; ASM *International*, 2000; Frankel, 2008). The metals dissolve at the anodic site on the surface of the metal where the electrons are released as represented by Equation 2.1, (Bentiss *et al.*, 1999).



Meanwhile, it has been established that metals corrode when exposed to the atmosphere as well as in acidic solutions (Bentiss *et al.*, 1999; Bajah and Godman, 1992; Fontana and Staehle, 1990). According to these researchers, corrosion involves the transfer of electrons along the surface of the metal under the influence of a potential difference. Sharma and Sharma, (1999) observed that metals /alloys do not corrode in dry air or in water completely free of air. Corrosion therefore, requires oxygen and water to occur. Corrosion is accelerated by acids or by contact with less active metals such as copper or lead. Certain salt solutions also accelerate corrosion, not only because they are acidic by hydrolysis, but also because of specific catalytic effects or reactions of the anions. Therefore, there is effective collision of particles which affect corrosion rate (Khaled and Amin, 2009).

According to Shreir *et al.*, (2000), corrosion may be regarded as a heterogeneous redox reaction at metal/non metallic interface in which the metal is oxidized and the non metal is reduced. This can be expressed by the simple chemical reaction given as shown in Equation 2.2:



where A is the metal and B, the non- metal (environment) are reactants. C and D are the reaction products. C is the oxidized form of the metal (corrosion product), while D is the reduced form of the non-metal which is another corrosion product. In the simplest form, the above reaction will be transformed to Equation 2.3:



for example, $4Fe + 2Fe_2O_3 \leftrightarrow 2Fe_3O_4$

Notably, reactions of this type which do not involve water or aqueous solutions are referred to as dry corrosion reactions. The corresponding reactions in aqueous solutions are called wet reactions (Shreir *et al.*, 2000), and the overall reaction(s) can be expressed as indicated in Equation 2.4:



Thus, in all corrosion reactions, one or more of the products will be oxidized form of the metal, aqueous cations such as $Fe^{2+}_{(aq)}$, $Fe^{3+}_{(aq)}$; and the anions, e.g. $HFeO_2^-_{(aq)}$, $FeO_4^{2-}_{(aq)}$ or solid compounds (Bentiss *et al.*, 1999). According to Shreir *et al.*, (2000) when metal reacts with a specific non-metallic substance under distinct environmental conditions, the physical and chemical properties of the reaction products and that of the environmental conditions (temperature, pressure, velocity, viscosity, humidity, etc) will be very crucial ascertaining the rate and extent of the corrosion reaction. Talbot and Talbot (1998) observed that a corroding system is driven by two spontaneous coupled reactions which take place at the interface between the metal and an aqueous environment. The exchange of electrons between the two reactions constitutes an electronic current at the metal surface (Marcus and Maurice, 2001).

Corrosion process is therefore seen as a complete electric circuit with the following component parts: an anodic reaction, cathodic reaction, electron transfer between the anodic and cathodic reactions and an ion current in the electrolyte (ASM *International*, 2000; Talbot and Talbot, 1998).

2.4 Environments in corrosion process

There are diverse environments by which corrosion process can occur (ASM *International*, 2000). Factors responsible for varying degrees of corrosion effect include: concentration, pH, velocity, temperature, atmosphere, natural waters, sea water, chemicals, fused salts, liquid metal(s), flue gas, bacteria e.t.c., (De-La Fuente *et al.*, 2011; Martino *et al.*, 2004). During corrosion, the kinetics of the cathodic and anodic partial reactions controls the rate of overall corrosion reaction. Shreir *et al.*, (2000) considered environmental factors such as concentration, velocity and temperature on the assumption that either the anodic or cathodic reaction is rate controlling. Thus, if a metal is corroding under cathodic control, it becomes apparent that velocity of the solution will be more significant when diffusion of the cathodic reactant is rate controlling, though temperature may have an effect (Kasal *et al.*, 2009). If the cathodic process requires high activation energy, temperature will have the most significant effect (Shreir *et al.*, 2000; Kasal *et al.*, 2009). These studies assert that effects of concentration, velocity and temperature are complex and it will become evident that these factors can frequently outweigh the kinetic and thermodynamic considerations. An increase in hydrogen ion concentration will raise the redox potential of the aqueous solution with a consequent increase in corrosion rate (Singh and Gupta, 1996). If however, there is an increase in the rate of the cathodic process, there will be a decrease in corrosion rate when the metal exhibits an active/passive transition (Pud *et al.*, 1999). When metals are subjected to high velocity and temperature, these complex environmental conditions may not necessarily

apply. Metals are more frequently exposed to the atmosphere than any other corrosive environment. Atmospheric corrosion is also the oldest corrosion problem known to man yet not fully understood (Vera *et al.*, 2003). The main reason for this inconsistency lies in the complexity of the variables which determine the kinetics of the corrosion reactions. Thus, corrosion rates vary from place to place, hour to hour and from season to season. The rate of transportation of reducible ions and molecules to the anode may control the polarization of metal. However, polarization resistance increases with extending emersion time (Calle and MacDowell, 2003; Chao *et al.*, 2012). This complexity sometimes makes meaningful results from laboratory experiments very difficult to obtain. In atmospheric corrosion, emphases are often placed on metals like iron and steel; zinc, copper, lead aluminium and chromium whose corrosion is of economic importance. Atmospheric corrosion is classified as dry oxidation, damp corrosion and wet corrosion (Shreir *et al.*, 2000).

2.4.1 Characteristics of agro fruits environment

Fruit juices are liquid, non alcoholic products with different degrees of clarity and viscosity, obtained through pressing or breaking up of fruits with or without sugar or carbon dioxide addition (Costescu *et al.*, 2006). Agro fruits exhibit high level carboxylic acidity which would have corrosive effect on metals at different rates. Tran *et al.*, (2013), emphasized that organic acids enhance corrosion rates of metallic alloys by accelerating cathodic reaction through direct reduction at the metal surface or by buffering effect which involves dissociation of the hydrogen ions near the corroding surface. Organic acids also play an important role in the growth, maturation and acidity of the fruit, and affect the shelf life of the fruit by influencing the growth of microorganisms (Wu *et al.*, 2007; Niu *et al.*, 2008). Organic acids are mostly responsible for corrosive effects of agro juices (Oladele and Okoro, 2011; Oluwole and Olawale, 2010). However there is minute presence of phenolic content, fatty acids and amino

acids (Wu *et al.*, 2007) in the various juices. The citric, malic, oxalic and tartaric acids ranging from 0.1 to 30 g/L were found in orange, grape, mango and apple juices. However, there is a considerable difference in the organic acid content found in various types and brands of fruit juice (Ajila *et al.*, 2010). For example, Minute Maid contains higher levels of oxalic and citric acids when compared to all other orange juices tested. According to Toalodo *et al.*, (2013), analysis of grape juices from *Vitis Labrusca L.* showed it contains significant amount of gallic acid, in addition to phenolics, monomeric anthocyanins and antioxidant from its seeds. Apple concentrate was found to have higher amount of malic acid than other carboxylic acids (Wu *et al.*, 2007). Brae burn apples contained the highest amount of citric acid in apples; however Granny Smith apples were the overall most acidic apples tested.

According to Awwiri, (2004), an autocatalytic mechanism has been proposed to explain the high rates of corrosion in acids with primary displacement of H⁺ ions from solution; followed by acid reduction rather than hydrogen evolution as acid reduction leads to a manifest decrease in free energy. Citrus fruits are mostly classified as acid fruits because they very soluble solids (Nour *et al.*, 2010). Corrosion in orange medium for instance, is very substantial because of varying amounts of citrus acid present in the fluid as indicated to be above 70%. These include folic acid, pectin, flavonoids, malic, tartanic benzoic, succinic, oxalic and formic acids. Nitrogenous compounds are also present to some extent of about 0.05-1.0%, mostly as free amino acids: asparagines, histidine, betine, cystein, praline, serine and stachydrine (Anthony and Effiong, 1998; Abiola *et al.*, 2004). Similarly, analysis from USDA Nutrient Database (2011), of typical mango specie (*mangifera indica*) showed it contains wide range of citrus acids: ascorbic acid 27.2/mg, pantothenic acid 0.16/mg, saturated fatty acids 0.066/g, monosaturated fatty acid 0.101/g and polyunsaturated fatty acid. Others include amino acids: tryptophan 0.008/g, threonine 0.019/g, valine 0.026/g, alanine

0.051/g, aspartic acid 0.06/g, glycine 0.021/g, serine 0.022/g and many more (Bally, 2006).

Despite being a weak acid, carboxylic acid exhibits corrosive effect in solution. This leads to transcrystalline stress cracking of mild steel under stress even at room temperature.

Grapefruit is an excellent source of many nutrients and photo-chemicals that contribute to healthy diet. Yet it contains wide range of citric acids which pose threat to metals under certain conditions. Review of previous work on chemical and nutritional value per 100/g of a grapefruit composition showed that it contains among others: - pantothenic acid 0.283/mg, folate 10/ug, ascorbic acid 33.3/mg, thiamine 0.037/mg, riboflavin 0.020/mg and niacin 0.269/g (USDA Nutrient Database, 2011). Natural apple juice extract also contains organic acids mainly: hydroxysuccinic acid (2.5%w/w), ascorbic acid (8%w/w), mineral salts, vitamin A (beta carotene), vitamin B1, vitamin B2, dye and phenolic compounds (Nagy, 1993; Karadenitz and Eksi, 2002). Indeed, agro juices are chemically quite complex, different complementary tests will be required to determine their chemical composition (Restek Corporation, 2003). These may include minerals, sugar profile, sorbitol content and anthocyanin pigments, and many more. Varying techniques have been adopted to analyze and quantify the composition of organic acid content in agro fruits; one of such is high performance liquid chromatography (HPLC) (Ajila *et al.*, 2010; Li *et al.*, 2011). According to Nour *et al.*, (2010), the process is complex and could be carried out either by direct determination of the constituent elements or by the analysis of derivatized products of the agro fruits.

2.5 Corrosion of mild steel in agro juices

Corrosion studies on mild steel in organic acid solutions are rare when compared with similar studies in mineral acids (Sekine *et al.*, 1987; Singh and Singh, 1995). Agro juices contain high degree of carboxylic acids, such as citric acids, malic acid, tartaric and fumic acids (Anthony and Offiong, 1998; Niu *et al.*, 2008; Liu *et al.*, 2011). Organic acid is one of the most important reagents used in the production of different chemicals in various manufacturing industries such as food, plastic and fibres, pharmaceutical and drugs (Singh and Singh, 1995; Kangas, 1998; El-Maksoud, 2008). The reactive carboxyl group makes organic acids a basic building block for many compounds (Ababio, 2005). Mild steel is used in fabrication of reaction vessels and storage tanks by industries which either manufacture or use organic acids as reagents for industrial processes (Singh and Singh, 1995). However, at relatively high temperatures, the acids can dissociate, forming more aggressive ions which can cause faster corrosion than might otherwise be expected (El-Maksoud, 2008). The usage of mild steel in acidic environment is therefore restricted because of its susceptibility to corrosion (Singh *et al.*, 2011). Studies showed that corrosion kinetics of mild steel would differ significantly in various agro juices (Ahmed *et al.*, 2012).

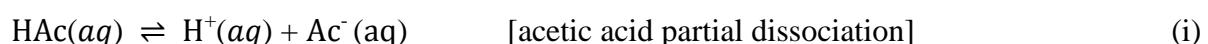
2.5.1 Weight loss

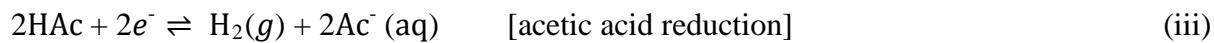
Weight loss method is widely used to evaluate corrosion effects of mild steel in agro media (Afolabi, 2007; Singh and Gupta 1996; Ogunleye *et al.*, 2011). This method has proved to be reproducible and dependable. Corrosion rates of mild steel depend significantly on the concentrations of dominant carboxylic acids species in the agro juices environments (Li *et al.*, 2011; Toado *et al.*, 2013) of apple, grape, mango and orange. According to Robin (2004), the constituents of carboxylic acids are major sources of oxygen and hydrogen which could accelerate the oxidation in the medium thus promoting corrosion of the material. Studies

showed that increase in concentration and temperature of the carboxylic acid would increase corrosion effect on mild steel (Ogunleye *et al.*, 2011; Singh and Gupta, 1996). However decrease in corrosion rates could be contributed by the inhibitive effects of the juices concerned by forming protective film layer due to fermentation and other physical factors (Oluwole and Olawale, 2010; Ogunleye *et al.*, 2011). The weight loss of mild steel per surface area would have a decreasing tendency (Oladele and Okoro, 2011) with increase in immersion time. This may be because of reduction in the concentration of the agro juice environment. The conductance and degree of dissociation of hydrogen ions from the acid medium could be influenced by kinetic energy of the reacting molecules (Singh *et al.*, 2011).

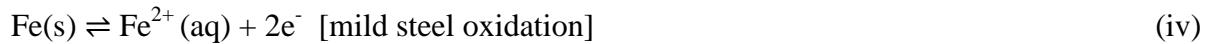
2.5.2 Corrosion mechanism

The mechanism of corrosion of mild steel in agro environment depends mostly on the dominant carboxylic group (Ababio, 2005; El- Maksoud, 2008) and corrosion products formed within the period of immersion (Vander Voort, (2002); De-La Fuente *et al.*, 2011; Wang *et al.*, 2012). Studies showed that organic acid enhances the corrosion rate of mild steel by increasing cathodic reaction (Garsany *et al.*, 2002; George, 2003). However, the exact mechanism remains unclear whether the adsorbed carboxylic molecules are reduced at the surface in addition to any reduction of hydrogen ions. Researchers had proposed a mechanism to explain corrosion rate of mild steel in the presence of acetic acid (CH_3COOH , or HAc) which is the main source of hydrogen ions (Garsany, *et al.*, 2002; Matos *et al.*, 2010). This mechanism is referred to as “direct reduction”. Acetic acid is reduced at the metal surface according to following reaction mechanism in Equations (i) – (iii):





The dissolution of iron (anodic reaction) occurs simultaneously at the metal surface (Uhlig, 2000; Matos *et al.*, 2010) as shown in Equation (iv):



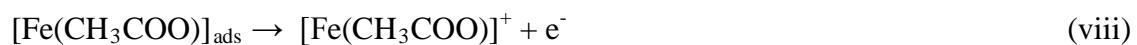
Dissociation of acetic acid could be swift with increase in temperature, thus making it difficult to experimentally distinguish between the reduction of acetic acid and that of hydrogen ions (Matos *et al.*, 2010). Organic acid could dissociate to provide additional source of hydrogen ions near the steel surface. The mechanism is referred to as “buffering effect” (George, 2003, Matos *et al.*, 2010). The role of acetic acid is to act as a “buffer,” which provides more hydrogen ions when the latter are consumed by the corrosion reaction at the surface (equation ii). The study showed that direct reduction of acetic acid in equation (iii) is not significant and can be omitted from the analysis so that only the reduction of hydrogen ions is taken into account (Garsany *et al.*, 2002).

Similar corrosion mechanism was proposed by Gulbrandsen and Nogueira, (2011) where the dissociation of adsorbed acetic acid is followed by a Volmer-Heyrovsky step as shown in chemical Equations (v) and (vi):

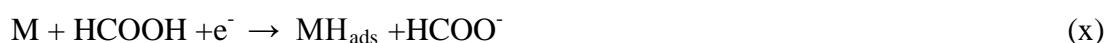


According to Garsany *et al.*, (2002), direct reduction of acetic acid at the surface of mild steel would increase the corrosion rate with increasing carboxylic acid concentration at the same

pH. This is independent of the controlling step of either charge or mass transfer control (Garsany *et al.*, 2002). If cathodic reaction is that of reduction of hydrogen ions (buffering effect), the corrosion rate could be limited to certain acetic acid concentration. The reaction control would shift from mass transfer to charge transfer control (Garsany *et al.*, 2002; Dougherty, 2004). The mechanism for diffusion of anodic dissolution of mild steel in acetic acid solution had been proposed by Singh and Gupta (1996) as illustrated in Equations (vii)-(ix).



Equations (x) and (xi) further show the proposed mechanism for hydrogen evolution at the mild steel cathode during electrochemical process in formic acid solution (Singh and Gupta, 1996).



Two hydrogen atoms adsorbed at adjacent sites would combine to liberate hydrogen gas. The rate of hydrogen evolution is proportional to the concentration of the organic acid molecules in the solution. The total concentration of undissociated carboxylic acid molecules would increase with increase in the amount of acid present in the solution irrespective of its conductance (Singh and Gupta, 1996).

2.5.3 Electrochemical and microscopic analyses

Studies on electrochemical polarization behaviour of mild steel in organic acids have been investigated by some researchers. Open circuit potential is widely adopted in determining polarization behaviour of mild steel in most acidic media (Zhang *et al.*, 2009; Wang *et al.*, 2013; Vimala *et al.*, 2012). Polarization of mild steel in organic acids has been investigated at various concentration and temperatures (Pud *et al.*, 1999; Singh *et al.*, 2011). The values of corrosion of corrosion parameters :- corrosion rate (CR), corrosion densities (I_{corr}), corrosion potential (E_{corr}), Tafel slopes of anodic curve (B_a) and cathodic curve (B_c) are determined from polarization curves (Singh *et al.*, 2011).

According to Kasai *et al.*, (2009); Singh *et al.*, (2011) electrochemical corrosion behaviour of mild steel in organic acidic environment corrosion potential (E_{corr}) would increase steadily with time, while both the anodic current of metal oxidation and cathodic current of oxygen reduction would decrease. The effect of different concentration of carboxylic on anodic and cathodic polarization behaviour of mild steel at fixed temperature is illustrated in Figure 2.1

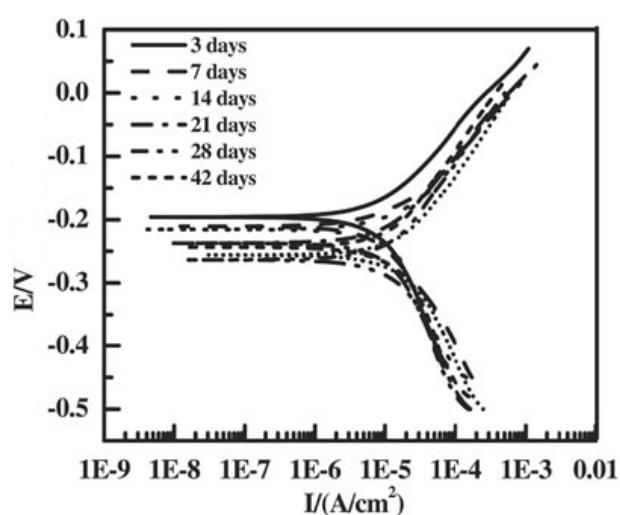


Figure 2.1 Polarization curves of mild steel in organic acid medium (Kasai *et al.*, 2009)

The almost identical nature of the cathodic polarization curves obtained from different concentrations indicates that the mechanism for the cathodic reaction does not change when either the concentration or the temperature is varied (Singh and Gupta, 1996). The feature of these curves shows transition from active to active-passive and transpassive regions (Marcus and Maurice 2001; Saha *et al.*, 2011; Singh *et al.*, 2011). Studies showed that corrosion rate decreased due to the protective film on the metal surface (Alain Robin, 2004; Saha *et al.*, 2011). According to Kasai *et al.*, (2009) a positive shift of E_{corr} was observed after 42 days in the acid medium while the I_{corr} declined (Figure 2.1). However, the decrease in anodic current was greater than that in the cathodic current (Saha *et al.*, 2011). Cathodic Tafel slopes (B_c) showed no visible trends, while anodic Tafel slopes (B_a) increased tremendously. This behaviour shows that the transfer of electrons is more difficult from anodic sites (Saha *et al.*, 2011; Hsu *et al.*, 2005). Oxide layers formed on metal surface during any polarization process could make the diffusion of a reactant or a product to be the rate-determining step (Singh *et al.*, 2011).

The microstructure of corroded mild steel samples in organic acid media can be investigated using scanning electron microscope (SEM), transmission electron microscope (TEM), light microscope (LM), energy disperse spectroscopy (EDS) and X-ray diffraction (XRD) methods (De-La Fuente *et al.*, 2011; Amin *et al.*, 2009; Chao *et al.*, 2012). According to Vander Voort, (2002), all studies of microstructures and fractures of metals should begin at lowest magnification level, the unaided human eye and progress upward, first using the stereomicroscope for structures and the LM for fracture path before using electron metallographic equipment such as SEM, XRD and EDS. Amin *et al.*, (2009) suggested that mild steel could suffer selected or localized corrosion in some acidic media depending on the concentration of molecules but corrosion effect could be suppressed in the presence of an

inhibitor which acts as adsorbent to the corrosion media. SEM examination of corroded mild steel immersed in organic acid solution (*centella asiatica* extract) by Shivakumar and Mohana, (2012) revealed that corrosion products appeared very uneven and lepidoteral-like morphology. The surface layer was however rough in the absence and presence of optimum concentration of *CE* extracts at 30 °C for a period of six hours. Yahya *et al.*, (2013) investigated micrographic images of mild steel immersed in solution with and without aqueous lignin through SEM as shown in Figure 2.2. According to the study, specimen immersed without lignin showed a tiny ball-like structure of corrosion products homogeneously distributed overall of the inspection surface after 7 days. The immersion for 21 days showed agglomeration of tiny ball-like structures of the corrosion products followed by formation of long and sharp coral-like structures of corrosion products since the immersion time has been extended to 42 days (Yahya *et al.*, 2013). Immersion of the specimen in lignin showed a flake of lignin layer which covered the metal surface after 7 days, spalling after 21 and 42 days respectively.

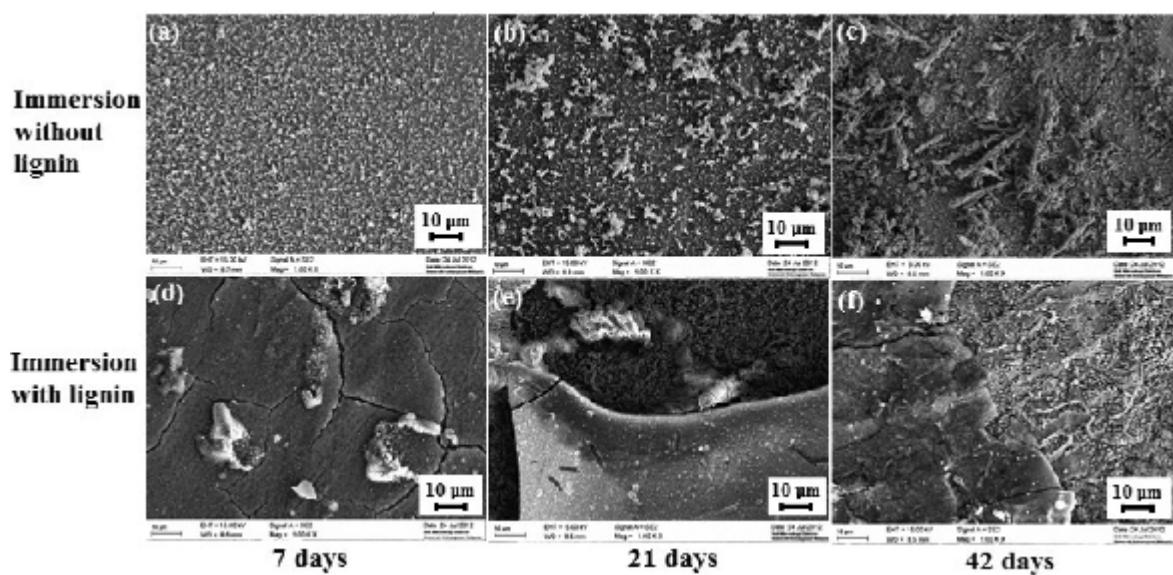


Figure 2.2 SEM micrographs of mild steel surfaces after 7, 21 and 42 days of immersion in solution with and without lignin (Yahya *et al.*, 2013).

The elemental compositions of the mild steel specimens immersed in organic acid medium could be determined by EDX examined at specific regions (Hussin and Kassim, 2010). Elemental analysis showed that specimens without lignin had high percentage of oxygen (O) and iron (Fe) elements compared to carbon (C) due to the corrosion products properties than that with lignin in the study conducted by Yahya *et al.*, (2013).

Electrochemical corrosion of mild steel in agro juices is indeed a very complex study. The above literature revealed that corrosion of the metal to wider extent is a function of its immediate environment and chemical properties of the steel alloy. Characteristics of the agro juices and corrosion mechanism of the mild steel would be essential in determining corrosion rates. Weight loss, electrochemical analyses and microscopic studies were widely adopted by most researchers in determining the extent of corrosion of mild steel in agro media.

CHAPTER 3

3.0 MATERIALS AND METHODS

3.1 Preparation of materials

Commercial mild steel obtained from ArcelorMittal South Africa which was analysed by optical emission spectroscopy technique using PMI-Master Pro equipment (UK) was used in this study. The chemical composition of the mild steel sample is presented in table 3.1. The steel sample was cut into sixty specimens of 60 x 30 x 6 mm for weight loss examination using PE-M500 Laser precision metal cold-cutting lubricating device (Hubei, China) to ensure uniform crystalline structure of the metal. They were later surface-prepared using emery papers with 80, 120 and 220 grit sizes.

Table 3.1 Chemical composition of mild steel sample

Elements	Iron (Fe)	Carbon (C)	Manganese (Mn)	Phosphorus (P)	Sulphur (S)	Silicon (Si)
Composition (wt %)	97.57	0.25	1.60	0.04	0.04	0.50

Additional sixty square-base mild steel test specimens (10mm x 5mm thickness) were used for electrochemical studies. They were mounted in cold-curing polyester resin to reveal a flat surface in contact with the corrosion media. The terminals of the test specimens were linked by insulated stripes of copper wire. Mild steel specimens were abraded using 220, 600 and 1200 grit emery papers mounted on IMPTECH (20 PDVT) grinding and polishing machine at average speed/force of 300 rpm/30N over the duration of 4 minutes according to Advanced

Laboratory specifications. The specimens were polished with diamond abrasive pastes of 3 micron, 1 micron and 50/nm grit sizes at average speed 150/rpm force of 25 N for 3 minutes. The cross sections of the electrodes were degreased with acetone, rinsed with distilled water and dried at ambient temperature.

3.2 Preparation of agro media

Corrosion media investigated include fruit species of freshly harvested orange (*citussinensis*), mango (*chok Anan*), grape (*vitisvinifera L.*), apple (*delicious*) juices and their mixture. These agro media were prepared by squeezing out the juices from their freshly harvested fruits. Because of variation in the concentration and composition of organic acid in different agro media (Wu *et al.*, 2007; Ajila *et al.*, 2010), it became necessary to determine the chemical composition of these acids in each medium. The analysis of the organic acid content in the agro media was studied at University of Johannesburg chemical laboratory using high pressure liquid chromatography (HPLC) method. HPLC has been acknowledged to be very efficient chromatographic technique in determining chemical composition of organic acids in agro juices although absolute precaution is required (Ajila *et al.*, 2010, Li *et al.*, 2011; Niu *et al.*, 2008). The chemical constituents of the agro media were identified and quantified (as shown in Table 3.2) with the aid of ultra violet (UV) detector with a wavelength of 250 nm attached to a model K-2502 KNAUER equipment by comparing their retention times and peak heights with standard organic acid solutions. Table 3.2 shows the composition of the agro media used for the study. The percentage composition of the dominant carboxylic acids did differ slightly from similar analyses (Li *et al.*, 2011; Ajila *et al.*, 2010). This might be contributed by variation in the agro species used for the study.

Table 3.2 Chemical composition of agro juices

Apple(<i>delicious</i>) (g/l)	Grape (<i>vitisvinifera</i>) (g/l)	Mango (<i>chok Anan</i>) (g/l)	Orange(<i>citussinensis</i>) (g/l)
Citric 0.06	Citric 0.07	Citric 2.94	Ascorbic 0.65
Malic 2.84	Malic 3.50	Malic 7.52	Citric 14.01
Shikimic 0.02	Succinic 0.01	Tartaric 0.98	Malic 1.52
Succinic 0.21	Tartaric 7.14	Succinic 2.09	Lactic 1.91
Tartaric 0.02			Tartaric 0.38
Quinic 0.61			Oxalic 0.11

3.3 Methods

3.3.1 Weight loss measurement

A total immersion test method was employed in the weight loss analysis of the mild steel specimens because of its good reproducibility (Singh and Gupta, 1996; Saha *et al*, 2011; Bastidas *et al*, (1996). There were sixty immersed samples of the mild steel in the five various agro juice environments, twelve per each corrosion medium. Only one specimen was investigated for each exposure time. The steel samples were fully immersed in five different thermoplastic containers containing 4 litres of each agro medium without replenishment: apple, grape, mango, orange and mixture containing 1 litre of each agro juice as shown in Figure 3.1.

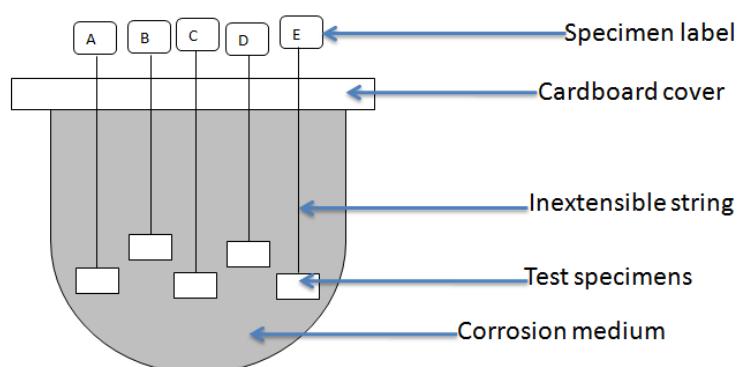


Figure 3.1 experimental set-ups of mild steel specimens in corrosion media

The study was conducted at room temperature for the entire immersion period while the pH values of the competing agro media were obtained for every immersion period to indicate any change in their concentration using a standard portable ISTEK Multi 90i, (Soul KOREA) pH meter. The pH values of the agro media were recorded before and after the exposure time to establish difference in their acidic level.

The specimens were rinsed with distilled water before and after immersion period and subsequently dried with acetone at ambient temperature. The various metallic specimens were labelled, weighed with digital analytical balance SHIMADZU AUW 220D (USA) to obtain their initial weights and completely suspended in the various agro media with aid of polypropylene strings. The weight loss and microscopic analyses were conducted at the Chemical Engineering laboratory of the University of Johannesburg, while the electrochemical corrosion study was determined at the Metallurgical Engineering laboratory of the Tshwane University of Technology, Pretoria. The average corrosion rates from weight loss measurements environments were calculated using corrosion rate formula (Equation 3.1) cited by Sculling (1984); Adetunji *et al.*, (2011).

$$CR = \frac{87.6W}{\rho AT} \quad 3.1$$

where CR is the corrosion rate in millimetre per year; W is the weight loss in mg, ρ is the density of the metal in g/cm³, A is area of the test specimen in cm² and T is exposure time in hours respectively. Each measurement was repeated thrice and the average readings taken to ensure reproducibility (Singh and Gupta 2006, Ogunleye *et al.*, 2011; Adetunji *et al.*, 2011). The average results are tabulated in the Appendices.

3.3.2 Electrochemical corrosion measurement

The electrochemical measurements of the immersed mild steel specimens were conducted using a three-electrode electrochemical cell. Autolab PGSTAT 30 Potentiostat (Metrohm, USA) linked to computer desktop fully installed with GPES 4.9 autolab software was engaged for the electrochemical corrosion measurement. About 200 ml of each of the test agro medium was poured into a glass beaker and measured for every experiment. The working electrode was the mild steel, whereas saturated silver/silver chloride (Ag/AgCl) in 3 mol of potassium chloride (KCl) was the reference electrode, while the counter electrode was platinum rod. All the three electrodes were connected together to allow free flow of electrons before the commencement of electrochemical measurement. Sixty coupons were immersed in the five corrosion media (twelve for each agro medium) while the potential and current distribution were monitored and measured by the autolab corrosion software from the PGSTAT potentiostat which controlled the scan rates. Experimental measurements were taken every five days for a sixty-day immersion period. During potential distribution measurement, the cell enabled of the potentiostat was switched off, while all the electrodes were temporarily disconnected from the corrosion media to avoid altering the open circuit potential (OCP) results. This was in accordance with the procedure used by Wang *et al.*, (2012). The experimental set-up for the electrochemical measurement is illustrated in Figure 3.2. It schematically shows the basic apparatus involved for the determination of polarization curves in the open circuit potential method and their connections.

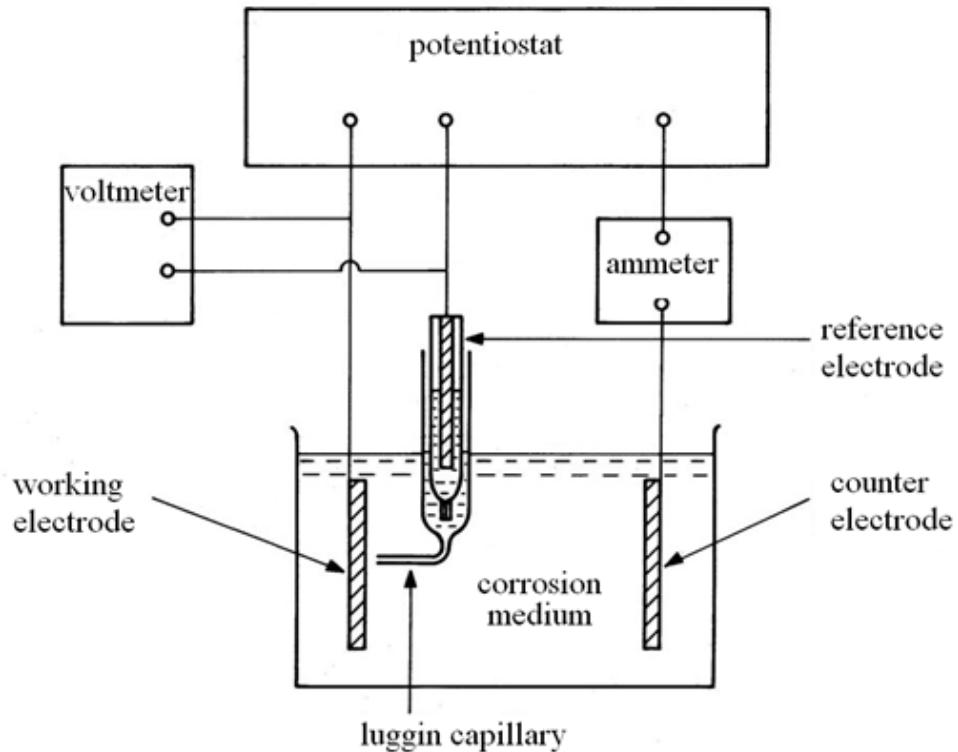


Figure 3.2 Schematic apparatus for the determination of polarization curves

Polarization curves at various immersion time were controlled and measured by the open circuit potential (OCP) and recorded potentiodynamically with scan rate (potential sweep) of 0.002 (V/s). Corrosion potential measurement commenced from -1.0 volts and ended at 2.0 volts. Corrosion current densities (I_{corr}) and corrosion potential (E_{corr}) were evaluated from the intersection of linear anodic and cathodic branches of the polarization curves in accordance with Tafel extrapolation method as adopted by Poorqasemi *et al.*, (2009). The pH values of the various agro juices were also measured for each exposure time using a standard portable MBI model-3D (Montreal, Canada) pH meter. Other corrosion parameters such as anodic and cathodic Tafel slopes analyses and evaluation of corrosion properties were determined from the polarization curves.

3.3.3 Microstructural examination

Microscopic examination involves the inspection of corroded metallic materials or their alloys to ascertain the extent of corrosion (Vander Voort, 2002; Fonseca *et al.*, 2007). Microscopic analysis of the corroded mild steel samples was carried out to study their surface morphologies and to determine the extent of corrosion on the corroded specimens in the agro media. The techniques used to evaluate corrosion products after electrochemical studies were scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The metallographic analysis was based on the procedures described by Vander Voort, (1999). The SEM shows the morphological studies of the corroded mild steel specimens, while EDS reveals the elemental analysis of the surface and cross section of corrosion product films. SEM/EDS studies were conducted from TESCAN WEGA 3SB (USA)compact scanning electron microscope equipped with OXFORD Instrument (UK) link system electron microprobe as shown in Figure 3.3. The Oxford instrument has X-Max detector for superior imaging quality.

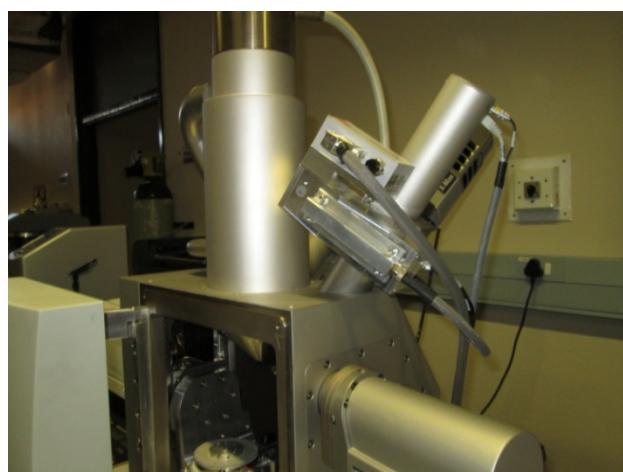


Figure 3.3 TESCAN WEGA 3SB scanning equipment

The results were monitored and controlled through a computer networking system. SEM analysis of the mild steel specimens was carried out on the corroded surfaces considering the skyward facing side to expose the surface morphology. The SEM reading was taken at the 1500X magnification which revealed more distinguishable characteristics. The spectrum processor of the EDS was set to depict variation in the composition of the surface elements. At the end of microstructural examination, the specimens were carefully removed from the scanning equipment.

CHAPTER 4

4.0 EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Weight loss results and analysis

Weight loss involves the study of the variation in the masses of the mild steel samples immersed in the apple, grape, mango, orange and mixtures of these media over the exposure time. The experimental results are tabulated in Appendix A and presented in Figure 4.1. The graphs show gradual increase in the weight loss of the steel samples over the duration of the study.

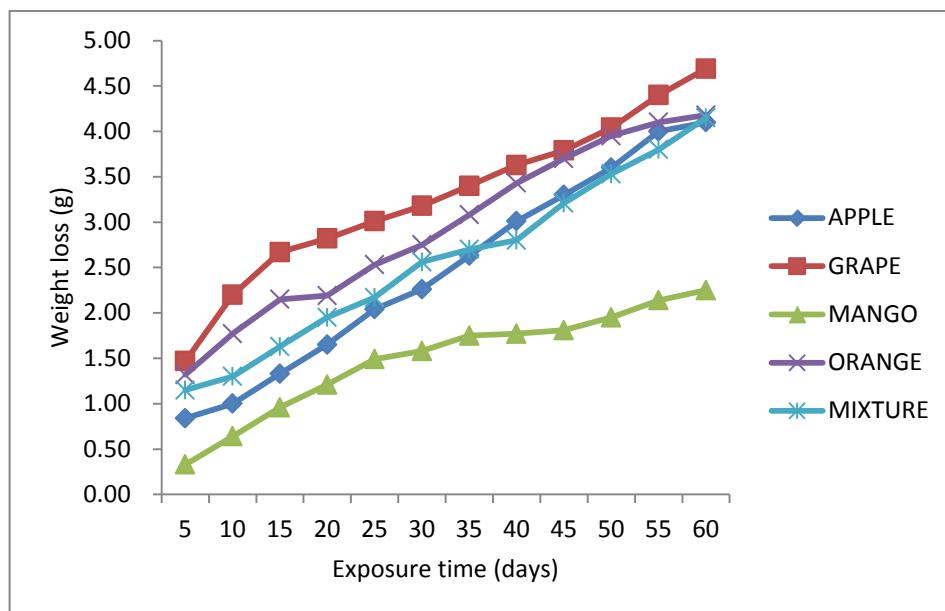


Figure 4.1 Weight loss analysis of mild steel in the agro media

Figure 4.1 shows that mild steel sample in the grape medium lost more weight than in other agro media and closely followed by specimen in the orange medium and that in the apple medium from the 5th day of immersion. This behaviour probably suggests greater corrosive effect on the steel sample in the grape medium than other contending media. Mango medium

shows mild effect of corrosion on mild steel sample (Figure 4.1) and subsequently had less weight loss. The sample in the mixture medium exhibited distinct characteristics from other media as its weight loss measurement is being separated by two most corroding media (orange and grape) and the least corroding media (mango and apple media) respectively. The rates of weight losses of the mild steel samples in grape, mango and mixture media showed almost similar results on the 60th day of immersion. This behaviour might indicate the similarity in corrosivity of these three competing agro media towards the end of immersion period.

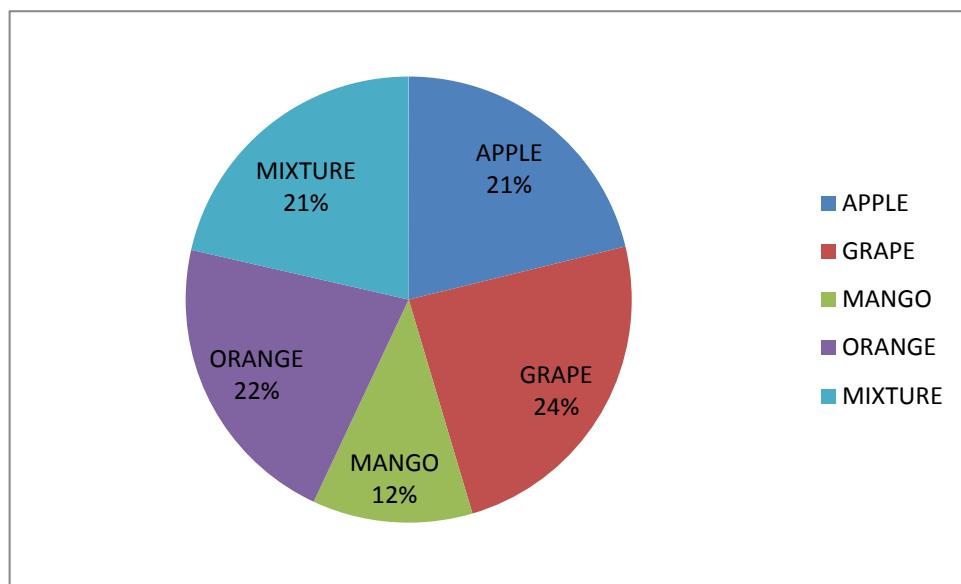


Figure 4.2 Summary of % weight loss analysis of mild steel on the 60th day of immersion

The weight loss results in Appendix A show that 4.69 g of the mild steel sample were lost in grape juice, 4.18 g in orange juice, 4.15 g in mixture, 4.10 g in apple and 2.25 g in mango juices within 60 days of immersion. The overall results showed relatively high weight loss of the mild steel in the agro media within the exposure time which could have been attributed by

the chemical properties of the metal and the surrounding physical environment. The summary of percentage weight loss of the mild steel samples is illustrated in Figure 4.2. The steel samples in the mixture and apple media indicate approximately equal percentage weight loss of 21%, while sample in orange medium lost 22%. The percentage weight loss in mango and grape media are 12% and 24% respectively. The variation of corrosion rates of mild steel specimens with exposure time in the various agro juices is shown in Figure 4.3. The corrosion rates of the steel samples in the various media declined with increase in immersion period. This behaviour is in conformity with the findings suggested in previous studies (Singh and Gupta 1996; Oladele and Okoro, 2011).

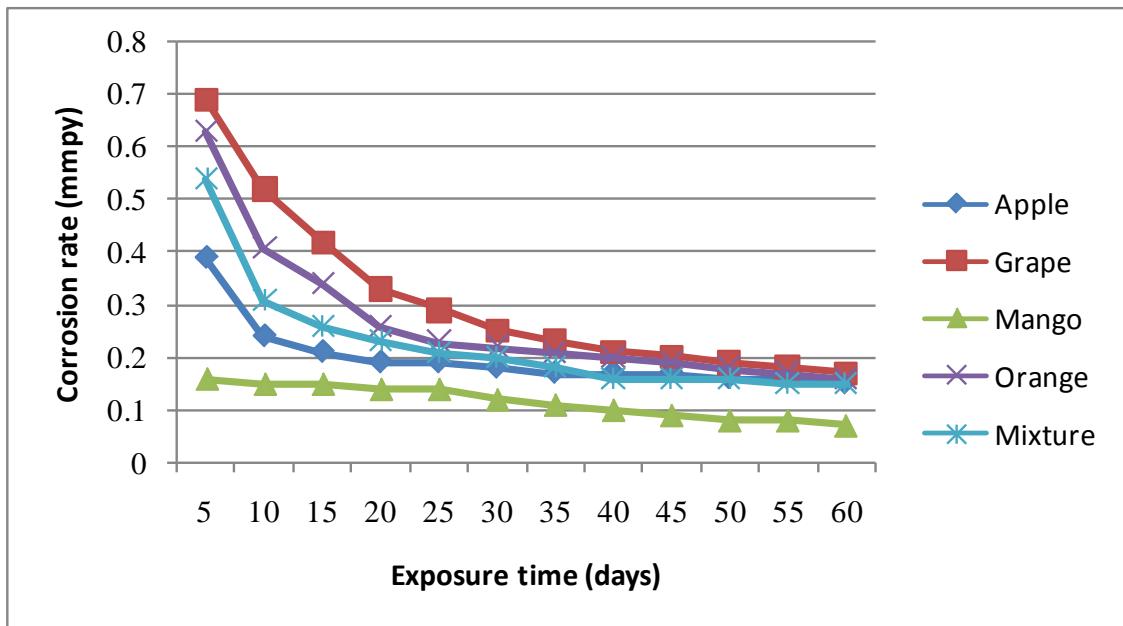


Figure 4.3 Corrosion rates of mild steel specimens

The corrosion rates of mild steel sample in the grape medium shows more aggressive attack than in other media as can be deduced from the curves (Figure 4.3) throughout the duration of immersion followed by the samples in orange and apple media respectively. The least

aggressive medium was mango juice, which showed gentle attack on the mild steel sample. In comparison, the corrosion rate of mild steel sample on the 5th day was highest in grape juice (0.69 mmPy) while the sample in mango juice had the lowest corrosion rate of 0.16 mmPy. The mixture medium showed corrosion rate of 0.54 mmPy (Appendix B). The curve of corrosion rate from the mixture medium is positioned between the two more and less corrosive media possibly suggesting the competitive nature of chemical reaction among the participating ions in the combined solution. However, from 25th day of immersion and onward, all the slopes declined gently and appear to have converged towards the end of exposure period apart from the specimen in mango medium. This behaviour does not indicate the termination of corrosion process as supported by Singh and Gupta, (1996).

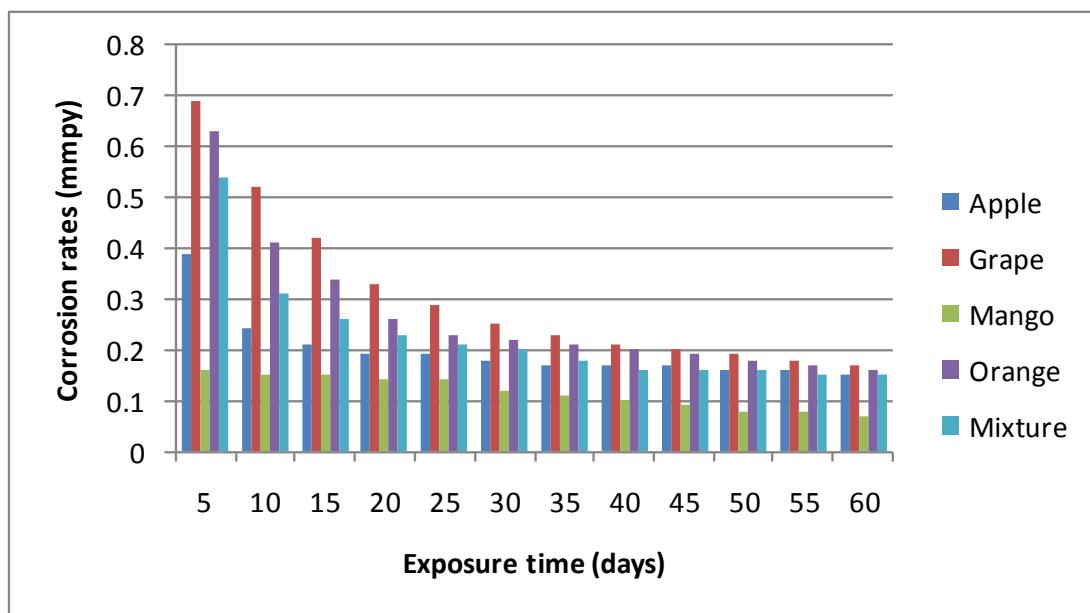


Figure 4.4 Component representations of corrosion rates of mild steel specimens

The analysis of corrosion rates is further illustrated in Figure 4.4. The bar charts show distinctive characteristic of corrosion rates of mild steel samples in the agro media. Corrosion rates on the 60th day indicate that both apple and mixture of the juices have the similar

corrosion effects on the mild steel sample with 0.15 mm^{py} corrosion rate, while specimens in grape, orange and mango corroded at the rates of 0.17 mm^{py}, 0.16 mm^{py} and 0.07 mm^{py} in that order as shown in Appendix B. The reduction in corrosion rates of the mild steel samples might have been influenced by the presence of suspended particles from the agro juices due to fermentation process. The surface areas of the steel specimens were covered by precipitates which could have also contributed to the gradual decline in the volume of agro media with longer immersion periods thereby impeding future exposure to these media. Figure 4.5 shows photographic images of the corroded mild steel samples in the agro media after 60 days of immersion from the weight loss analysis.

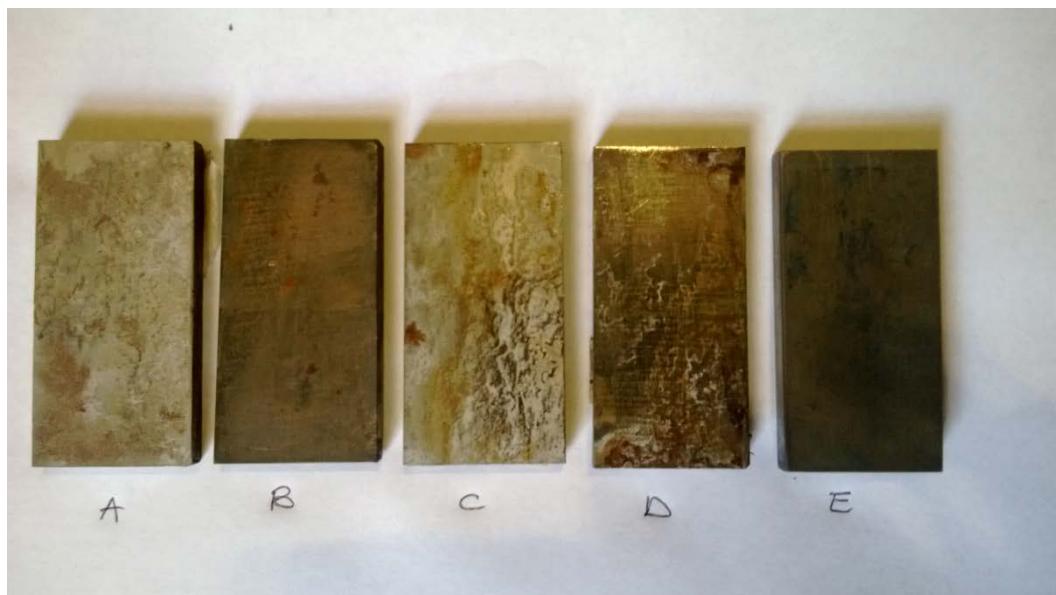


Figure 4.5 Images of corroded mild steel in (A) apple, (B) grape, (C) mango, (D) orange and (E) mixture media (weight loss measurement)

The images depict different surface appearances. Physical observation showed that images in Figure 4.5 (A) and (C) appeared brighter than images in Figure 4.5 (B), (D) and (E). These characteristics might have been attributed by the intensity of corrosion effects on these mild

steel samples. The darker images could reveal greater effects of corrosion on the samples which also correspond to the results of the corrosion rates.

4.2 pH analysis of agro media for weight loss measurement

The pH values of the agro media indicated differences in acid concentrations of the agro media during the exposure period. Figure 4.6 illustrates the variations of acidic content of the agro environments over the immersion period taken from the results in Appendix E. The graph shows a general increase in the pH values of all the competing agro media. Hence it was suspected that evolution of hydrogen gas to the atmosphere decreased with longer exposure times following the decline in the pH values of the agro juices.

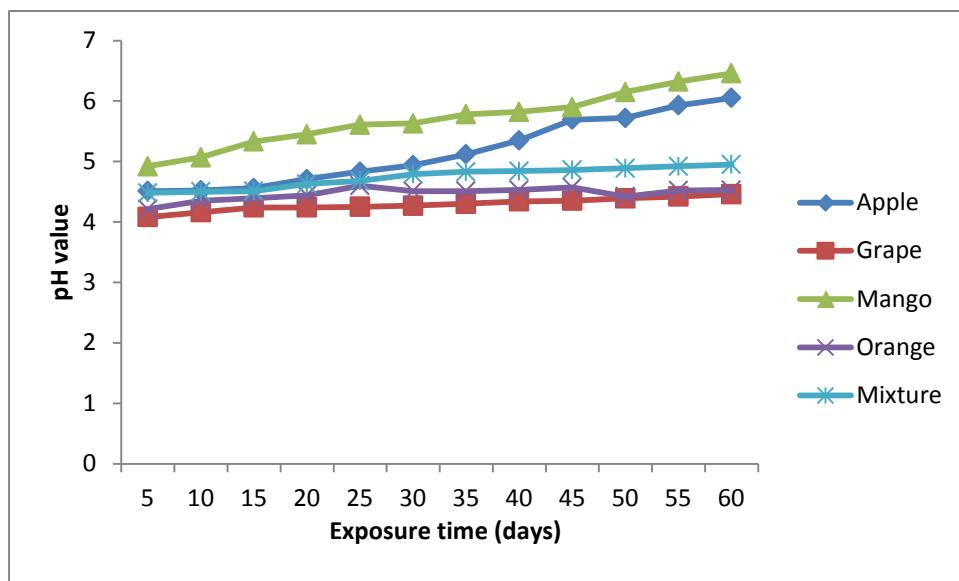


Figure 4.6 pH values of agro media (weight loss analysis)

Figure 4.6 depicts that mango medium exhibited the highest range of pH values from the 5th day to 60th day of immersion. This might be an indication of greater reduction of hydrogen

ion concentration in the medium which could cause less corrosion impact on the immersed mild steel sample. The pH range of the apple medium was slightly less than that of the mango medium as shown in Figure 4.6. This might indicate greater concentration of hydrogen ion in the apple medium and possibly more corrosive attack on the mild steel specimen. Both the grape and orange media revealed similar pH behaviour from the 50th day onwards (Figure 4.6), however the concentration of hydrogen ion in grape medium was greater from the 10th day of immersion until 45th day (Appendix E). Figure 4.6 also shows that the pH range of the mixture medium was flanked by the two highly concentrated acid media (orange and grape) and that of two less concentrated acid media (mango and apple).

4.3 Electrochemical behaviour of mild steel in agro media

Electrochemical behaviour of the mild steel involves dissolution of the metal in the various agro media by the action of electrochemical cells (De-Giorgi, 1992). The electrochemical scans were obtained by monitoring the behaviour of the mild steel in the agro media at both cathodic and anodic regions of the electrochemical cell. Hence, Tafel regions of the polarization curves were extrapolated at the intersections of the E_{corr} and I_{corr} of each scan to show other corrosion data required for the analyses of the study in accordance with standard procedures (Amin *et al.*, 2010). The corrosion potential (E_{corr}), corrosion current density (I_{corr}) and corrosion rates and values of electrolyte parameters such as anodic Tafel (ba) and cathodic Tafel (bc) slopes were determined as functions of immersion time (MacCafferty, 2005; Amin *et al.*, 2011).

Figures 4.7 to 4.18 show the cathodic and anodic polarization curves for the mild steel specimens. The shapes of these curves look very similar suggesting that the main reactions at the metal-solution interface may be identical. But there exists huge differences when closely

observed because the test samples were corroding at different rates in these media. Analyses of the corrosion behaviour of mild steel specimens in the agro media can be best described from corrosion parameters presented in Appendix D-1 to D-12. These data were obtained by extrapolating the anodic and cathodic polarization curves (Fig. 4.7 - 4.18).

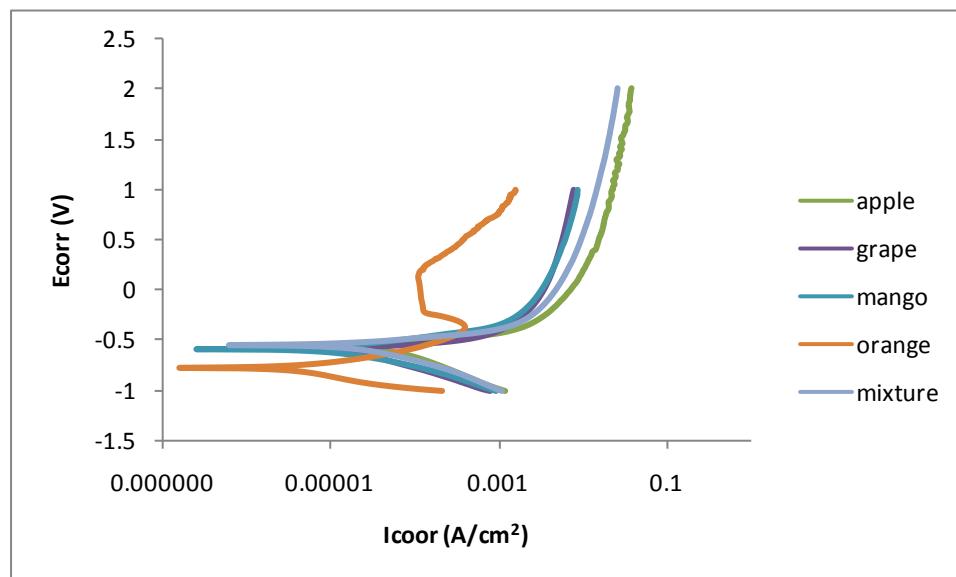


Figure 4.7 Polarization curves of mild steel specimens on 5th day immersion period

The polarization curves in Figure 4.7 show that the corrosion of the mild steel specimen in orange medium has passivated more than in the other agro juices which show little or no sign of passivation to their polarisation curves. Appendix D-1 (extracted from Tafel extrapolation in Figure 4.7) shows that mango medium exhibited the highest corrosion current density (I_{corr}) with a value of 6.621 Acm^{-2} at 0.127 V dec^{-1} anodic Tafel slope (ba) and 0.09 V dec^{-1} cathodic Tafel slope (bc) respectively. This is followed by the steel specimen immersed in mixture, apple, orange and grape media. The data also revealed that apple

medium utilized the highest corrosion potential of -552 mV, while the least came from orange medium (-763mV).

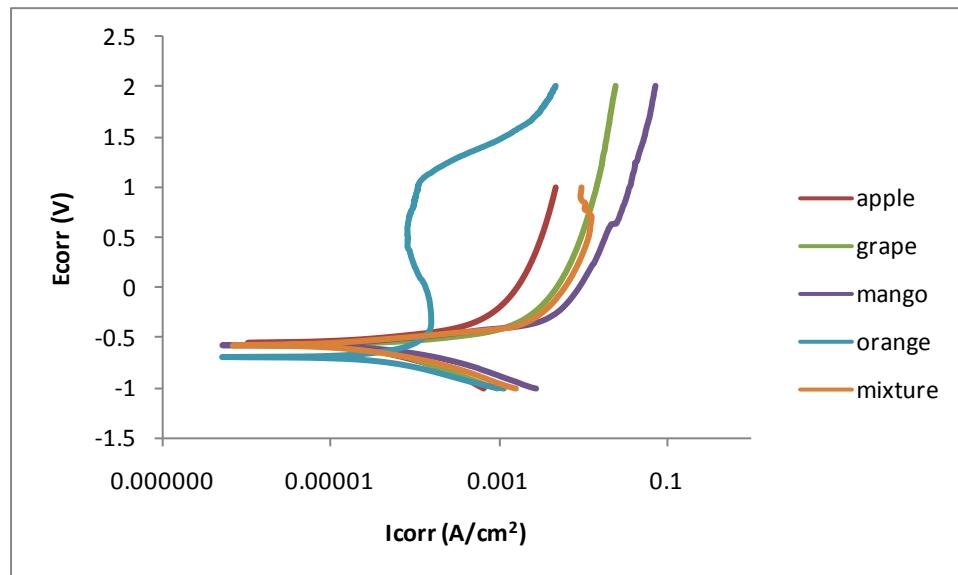


Figure 4.8 Polarization curves of mild steel specimens on 10th day immersion period

Summary of linear Tafel extrapolation data obtained from Figure 4.8 is tabulated in Appendix D-2. It can be deduced that mild steel sample in orange medium exhibited a unique distinct characteristic of passivation from other corrosion media on the 10th day immersion period. Corrosion potential of the mild steel sample is lowest in the orange medium (-694mV), while specimen in apple exhibited the highest E_{corr} (-546 mV). Cathodic Tafel slope (b_c) is greatest in the orange medium and lowest in grape medium. However grape juice utilized greater anodic Tafel slope (b_a) of 0.292 V/dec than any other medium. Appendix D-2 shows that mixture medium contains the highest corrosion current density of I_{corr} (5.108 Acm^{-2}) whereas apple contains the lowest I_{corr} (1.165 Acm^{-2}) respectively.

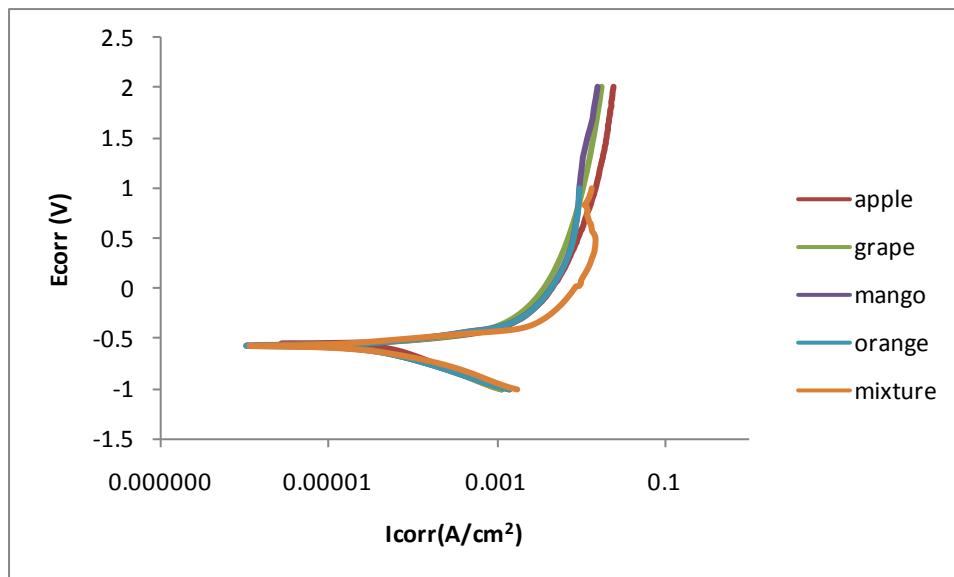


Figure 4.9 Polarization curves of mild steel specimens on 15th day immersion period

Polarization behaviour of the mild steel specimens in Figure 4.9 is depicted in Appendix D-3. There is virtually no sign of passivation of the steel sample in all the competing agro media, which could suggest swift corrosion measurement. According to the graph, E_{corr} is almost identical in all the agro media which could suggest similar corrosion behaviour. However the parameters show that orange juice contains the lowest corrosion potential (-680 mV), whereas apple juice shows the highest E_{corr} (-542 mV). Analysis of I_{corr} shows that steel sample in the mixture medium consumed more current than in other agro media with a current density of 7.926 Acm^{-2} and lowest in mango medium (1.151 Acm^{-2}). Anodic Tafel slope of the mild steel sample in apple medium was highest (0.338 Vdec^{-1}) on the 15th day immersion period, whereas orange juice exhibited the least (0.070 Vdec^{-1}). Cathodic Tafel slope is greatest in grape medium (0.091 Vdec^{-1}) and lowest in mango juice (0.067 Vdec^{-1}).

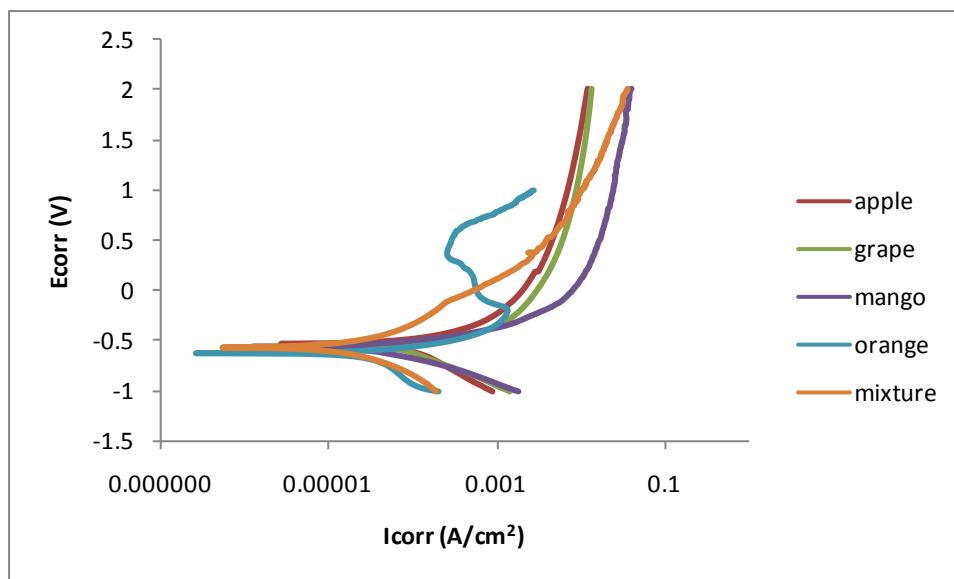


Figure 4.10 Polarization curves of mild steel specimens on 20th day immersion period

Among the competing agro media, it is evident that passivation of oxide film on mild steel specimen was almost sustained in the orange juice on the 20th day of immersion period (Figure 4.10) than in other competing media. The polarization process of the steel sample in orange medium is completed at 1.0 volts while other agro media stopped at 2.0 volts as controlled by the potentiostat. Tafel extrapolation data (Appendix D-4) shows that mild steel sample in orange juice contains the lowest E_{corr} (-617mV), while apple medium has the highest E_{corr} (-535 mV).

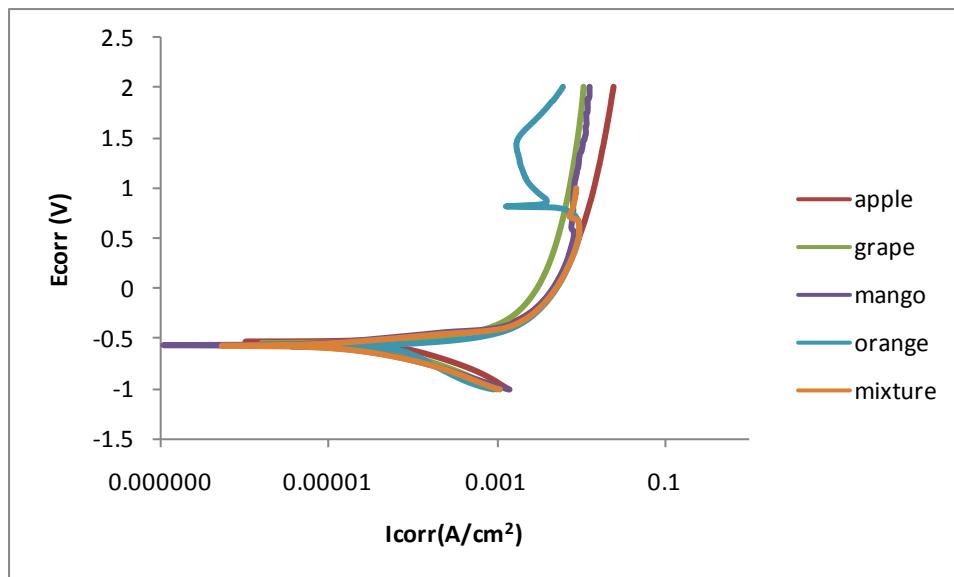


Figure 4.11 Polarization curves of mild steel specimens on 25th day immersion period

Steel sample exposed to orange medium passivated than other competing agro media (Figure 4.11) possibly because of the presence of more oxide layer inhibiting corrosion process. From Appendix D-6, I_{corr} is greatest in the orange medium (6.922 Acm^{-2}) and least in the grape medium (1.661 Acm^{-2}). But the reverse is the case for E_{corr} where orange medium exhibits least values of -547 mV and grape medium shows the highest value(-532mV). b_a is greatest in the apple juice (0.181 Vdec^{-1}) and least in mango juice (0.091 Vdec^{-1}) while b_c is highest in the mixture medium (0.161 Vdec^{-1}) but lowest in the mango juice (0.067 Vdec^{-1}).

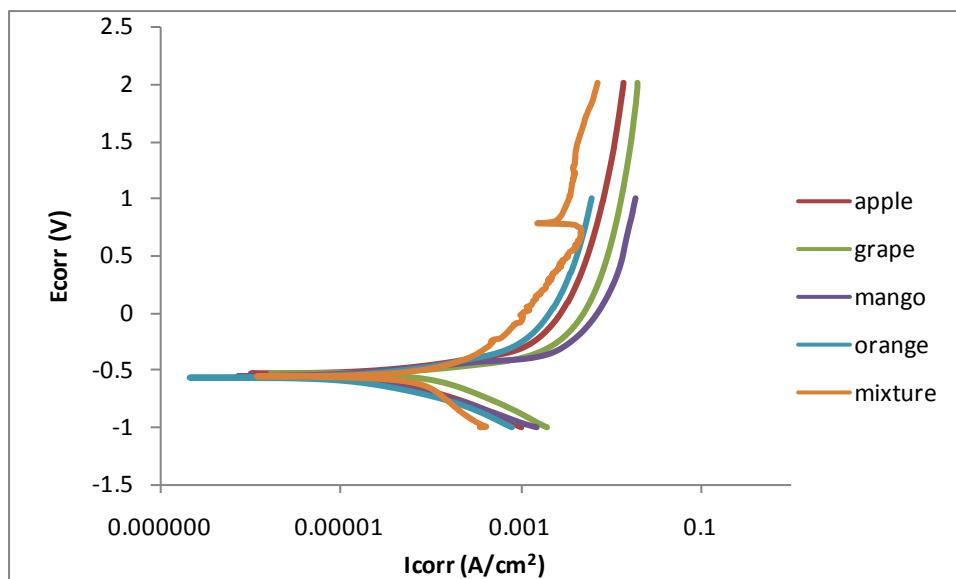


Figure 4.12 Polarization curves of mild steel specimens on 30th day immersion period

Passivation of steel specimen in the mixture medium is observed between 0.5 to 1.0 V in Figure 4.12. This possibly could be caused by the presence of more oxide layer on the metal inhibiting corrosion process. Other mild steel samples did not show sign of passivation as could be observed from the polarization curves. Considering the extrapolation data in Appendix D-6, apple medium shows the highest E_{corr} of -527mVolts, while orange medium indicates the least(-565 mV). However, apple juice contains the lowest I_{corr} of 1.496 Acm^{-2} at the linear extrapolation curve whilst orange medium contains the highest (6.389 Acm^{-2}). b_a was most in apple medium on the 30th day (0.181 Vdec^{-1})and lowest in the mango juice (0.091 Vdec^{-1}). The highest b_c occurs in mixture medium (0.106 Vdec^{-1}) while the lowest b_c is observed in mango medium (0.067 Vdec^{-1}).

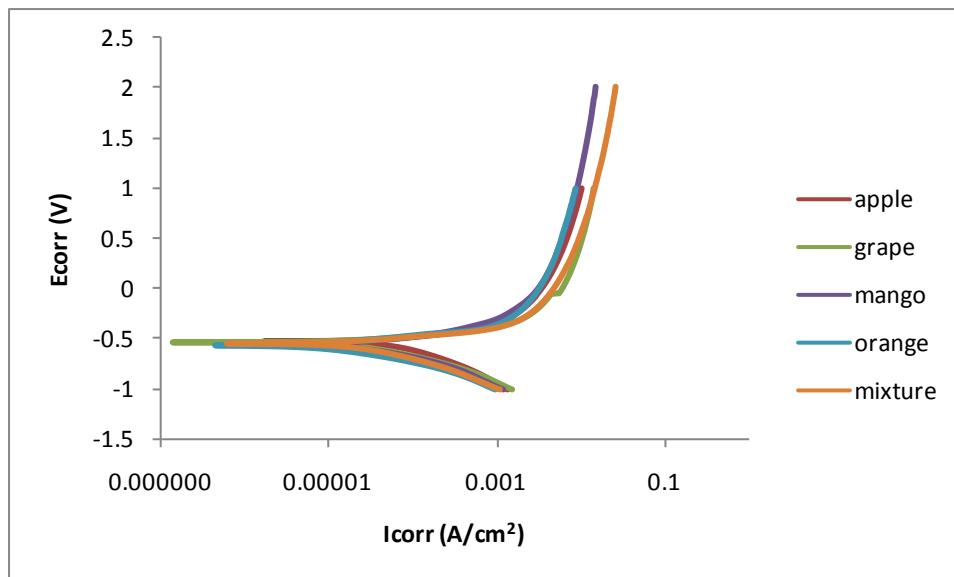


Figure 4.13 Polarization curves of mild steel specimens on 35th day immersion period

The data obtained from Figure 4.13 suggests that mild steel samples in apple and orange media might have stopped their electrochemical processes sooner than other media. There is no notable passivation by corroding steel samples throughout the duration polarization process. The corrosion potential of the mild steel sample is greatest in the apple medium (-525 mV), while that in the orange medium shows the least E_{corr} (-559mV). Cathodic Tafel slope (bc) of the specimen is greatest in the mango juice (0.070 Vdec^{-1}), while mixture medium contains the least bc at 0.037 Vdec^{-1} (Appendix D-7). However the metal specimen in orange juice shows greatest anodic Tafel slope (ba) of 0.292 V/dec among the test media. The sample in grape juice contains highest corrosion current density I_{corr} (6.254 Acm^{-2}) while the least comes from apple medium (1.778 Acm^{-2}).

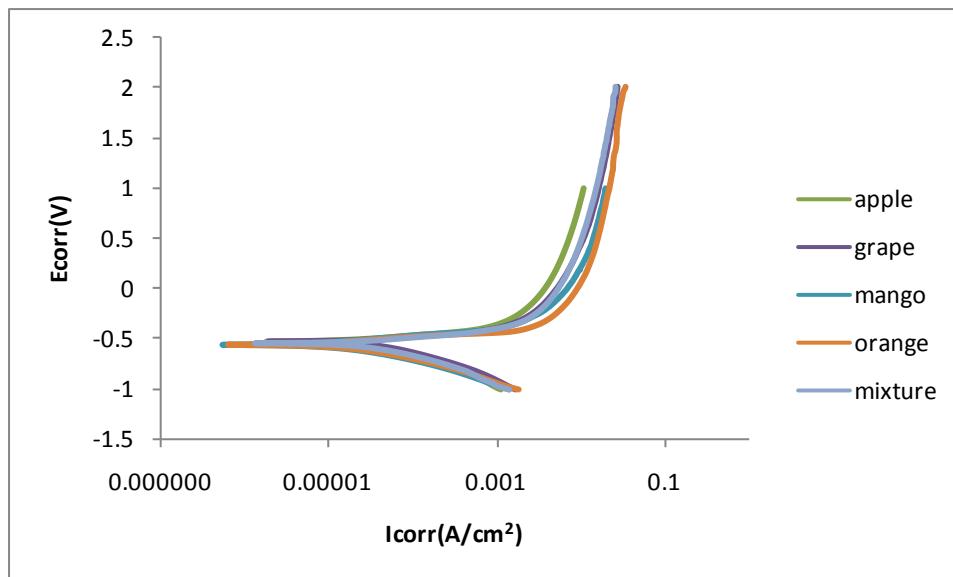


Figure 4.14 Polarization curves of mild steel specimens on 40th day immersion period

Polarization characteristics of the steel specimens in Figure 4.14 did not show passivation on the anodic site, which may suggest speedy corrosion rate. The parameters show that mild steel sample in mango juice exhibited the lowest corrosion potential (-552 mV), whereas that in apple medium shows the highest E_{corr} (-520 mV). Analysis of I_{corr} indicates that the steel specimen in orange medium was consuming more current than in any other agro juice with a current density of 6.027 Acm^{-2} and apple has the lowest (1.346 Acm^{-2}). Anodic Tafel slope of the mild steel sample in mixture medium was highest (0.157 Vdec^{-1}) on the 40th day immersion period, while that in orange juice exhibited the least b_a (0.095 Vdec^{-1}). Cathodic Tafel slope of the mild steel specimen was greatest in mango medium (0.086 Vdec^{-1}) and lowest in orange medium (0.062 Vdec^{-1}).

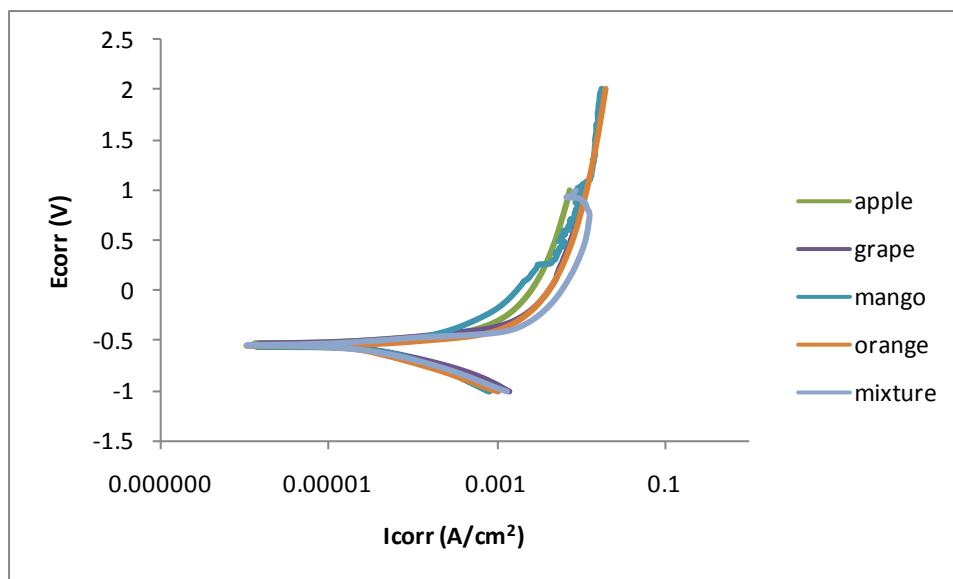


Figure 4.15 Polarization curves of mild steel specimens on 45th day immersion period

Electrochemical corrosion behaviour depicted in Figure 4.15 shows that mild steel samples immersed in mango and orange media increased beyond 1.0 volts of the E_{corr} . This suggests that these specimens took longer time to complete their polarization than in other competing agro media. Passivation was not observed from corroding mild steel samples except for that in mango medium which showed slight resistance to polarisation. Tafel slope analysis presented in Appendix D-9 indicates that I_{corr} was greatest in mixture medium (6.506 Acm^{-2}) and least in apple medium (1.155 Acm^{-2}) respectively. E_{corr} was highest in apple medium (-515 mVolts) and least in mango juice (-548 mVolts). Both b_a and b_c were greatest in orange (0.172 V dec^{-1}) and mango (0.093 V dec^{-1}) media but least in mixture (0.086 V dec^{-1}) and orange (0.036 V dec^{-1}) juices.

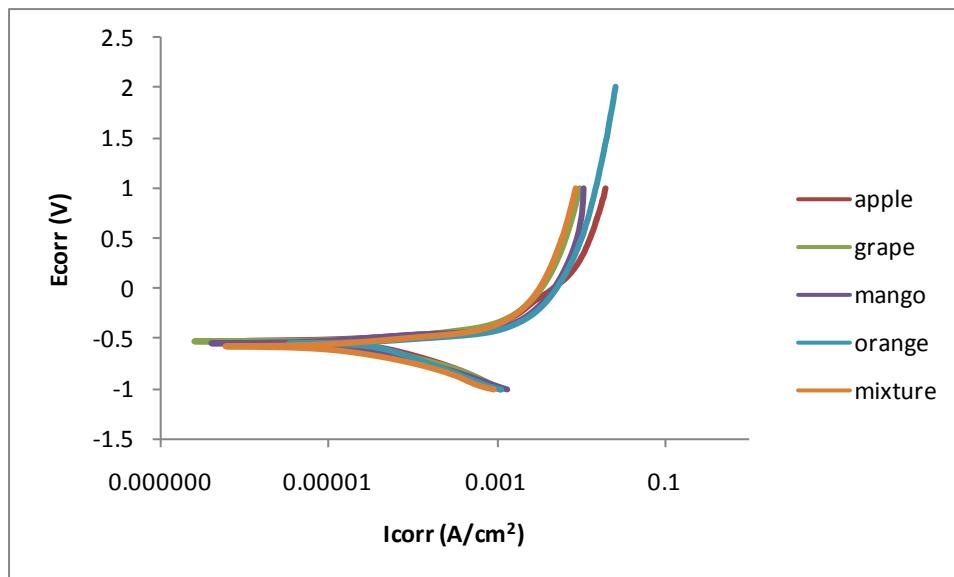


Figure 4.16 Polarization curves of mild steel specimens on 50th day immersion period

Tafel extrapolation curves of the steel samples in Figure 4.16 exhibit similar characteristics with little exception and no passivation was observed from the polarization curves. Polarization of the steel specimen in orange medium extended up to 2.0 volts while others completed at 1.0 volts. Data collected on the 50th day is presented in Appendix D-10. It shows that mild steel sample in orange medium had the lowest E_{corr} (-541 mV) while specimen in apple juice presented the maximum value (-511 mV). I_{corr} was highest in grape medium with current density of 8.322 Acm^{-2} whereas mixture medium had the lowest (1.179 Acm^{-2}). b_a and b_c were highest in the orange (0.32 Vdec^{-1}) and mixture (0.067 Vdec^{-1}) media respectively but lowest in the mango (0.070 Vdec^{-1}) and grape (0.047 Vdec^{-1}) media respectively.

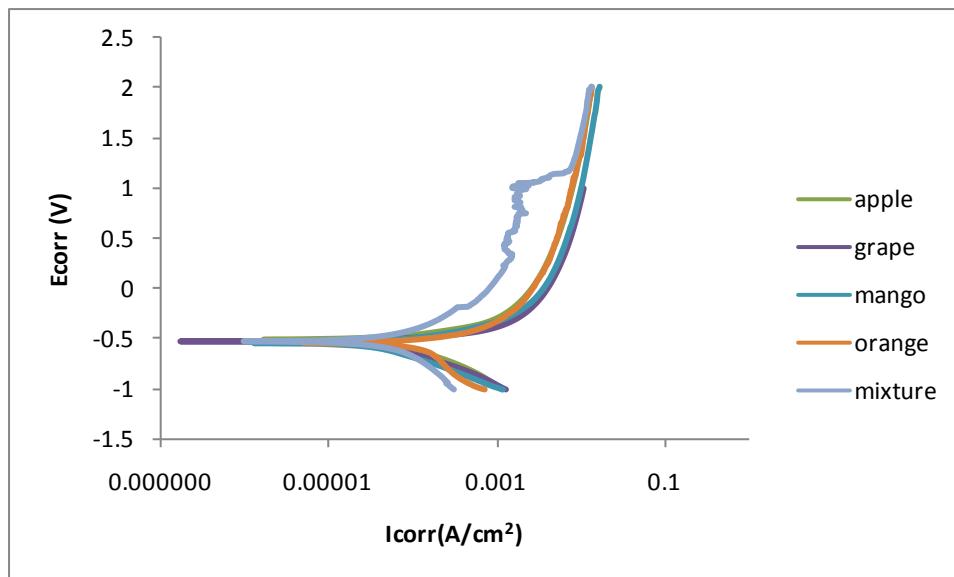


Figure 4.17 Polarization curves of mild steel specimens on 55th day immersion period

Mild steel specimen in mixture medium showed the characteristics of passivation while exhibiting the lowest cathodic Tafel slope (0.138 Vdec^{-1}) as observed in Appendix D-11 and Figure 4.17. Meanwhile other steel samples did not passivate in their various agro media. Mango juice shows the highest bc (0.245 V dec^{-1}) while anodic tafel slope was highest in mango juice (0.245Vdec^{-1}) and lowest in apple medium (0.122 Vdec^{-1}). Corrosion current density of the mild steel sample was highest in orange medium (3.920 Acm^{-2}) and lowest in grape juice (1.506 Acm^{-2}). E_{corr} was highest in apple medium and lowest in mango medium correspondingly on the 55th day of immersion period.

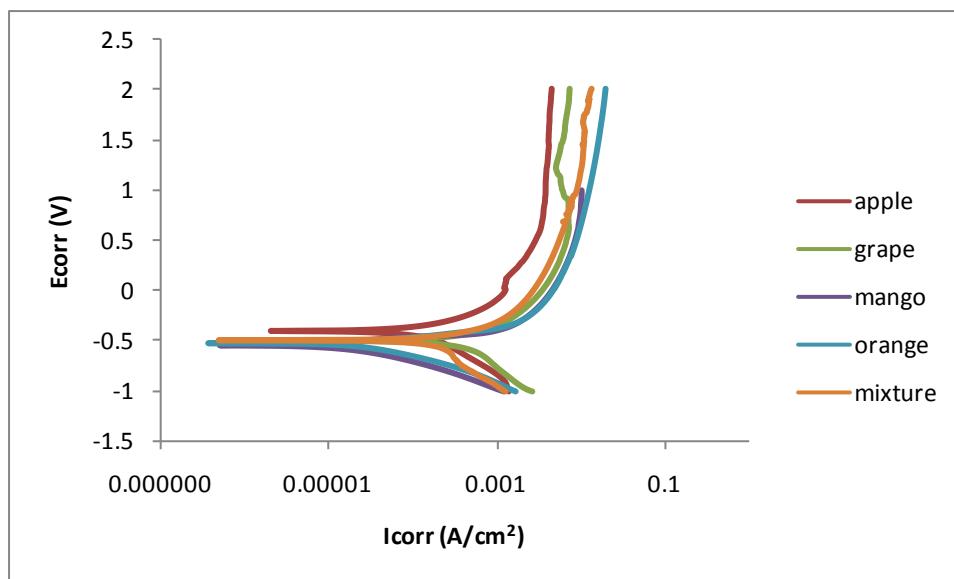


Figure 4.18 Polarization curves of mild steel specimens on 60th day immersion period

Polarization behaviour in Figure 4.18 shows that all the mild steel samples in the agro media had insignificant passivation. Comparison of electrochemical corrosion parameters on 60th day (Appendix D-12) shows that E_{corr} was highest in apple juice (-402mV) while mango had the lowest the value of -530 mV. The highest I_{corr} emerged from sample in mango medium ($6,667 \text{ A/cm}^2$) as observed from the data. Steel specimen in grape juice exhibited the lowest I_{corr} value of 1.034 A/cm^2 . The maximum anodic Tafel slope (b_a) of the mild steel sample was exhibited in apple juice (0.169 V dec^{-1}) while the lowest was in grape juice (0.115 V dec^{-1}). Steel sample in apple medium maintained the highest cathodic Tafel slope of 0.153 Vdec^{-1} while that in orange medium had the lowest value (0.062 V dec^{-1}).

Corrosion rates (CR) of the mild steel specimens in the various agro media are illustrated in Figure 4.19. The data shows a steady decline in the rate of corrosion throughout the duration

of the study which might be associated with gradual reduction in the electrochemical process.

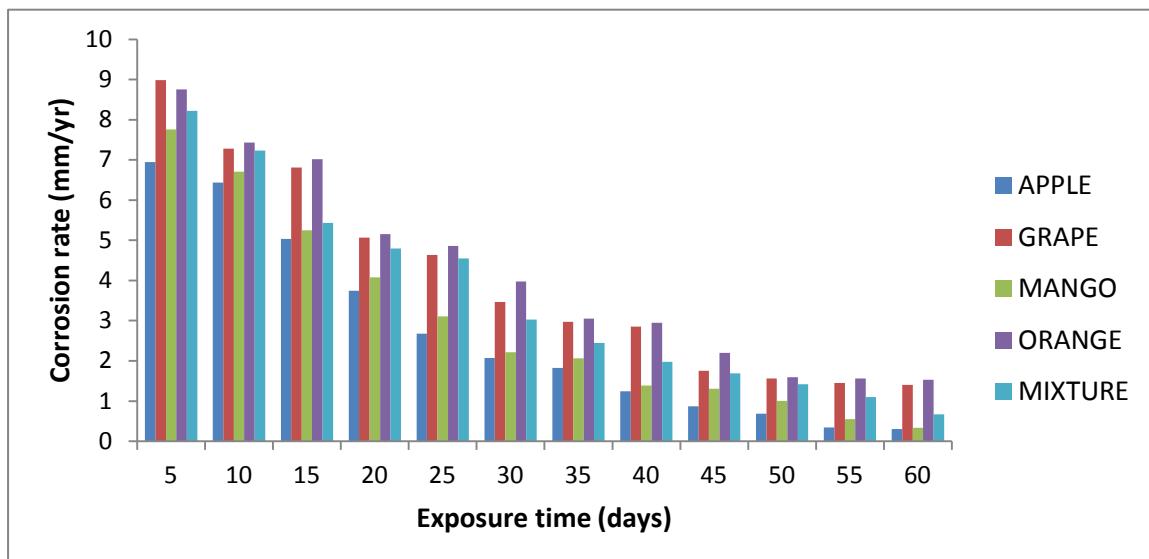


Figure 4.19 Summary of electrochemical corrosion rates of mild steel specimens from Tafel extrapolation data in Appendix C

Grape medium showed the most corrosive effect on the mild steel sample on the fifth day of immersion. However orange medium exhibited higher corrosion rate than other agro media from day 10 onwards and closely followed by grape medium, mixture and mango media respectively (Figure 4.19). The value of CR of the mild steel was lowest in apple medium compared with the rest test agro media. From immersion period of 50 days onwards, corrosion rates in grape and orange media narrowed closely probably suggesting similar corrosion behaviour. However the value of CR in orange medium still exceeded that of grape medium with a very slim margin.

Figure 4.20 shows the stereographic images of corroded mild steel samples after the 60th day of immersion in the electrochemical corrosion tests.



Figure 4.20 Images of corroded mild steel samples in (A) apple, (B) grape, (C) mango, (D) orange and (E) mixture media (electrochemical measurement)

Visual observation show different surface appearances of the five corroded steel samples as recommended by Vander Voort, (2002). A uniform corrosion effect is partly observed in Figure 4.20(A) and (C). Figure 20(B), (D) and (E) showed more of localised corrosion on corroded mild steel specimens. However the scale of corrosive effects on the mild steel specimens cannot be distinguished easily from these pictures. The surface micrographs from SEM and EDX elemental analysis of the corroded mild steel images have been discussed to give vivid distinction on the corrosion effects in the various agro media.

4.4 pH analysis of agro media for electrochemical measurement

The pH values of the corrosion media from electrochemical study is tabulated in Appendix F and graphically presented in Figure 4.21. The concentrations of acid in the various agro media decreased linearly with increasing immersion times possibly because of greater loss of

hydrogen ions displaced from the various agro media due to corrosion of the mild steel samples.

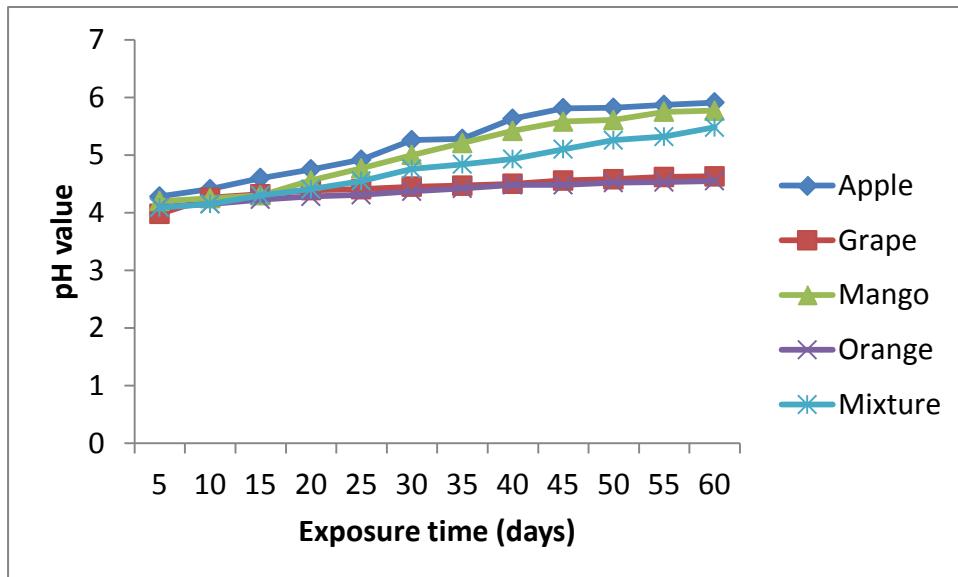


Figure 4.21 pH values of agro media (electrochemical)

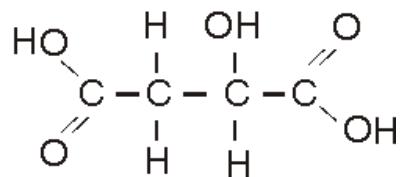
The data in Figure 4.21 shows more significant increase in the pH values of apple, mango, and mixture media when compared with the grape and orange media. However apple medium contained the greatest pH range from the 5th day onwards followed by mango and mixture media and subsequently exhibited least acidity. The pH values of orange and grape media showed mild increase over the duration of the study with less difference in their results (Figure 4.21). Nevertheless grape medium exhibited slightly greater pH values than orange medium from 10th day of immersion of the mild steel samples (Appendix F). It is important to stress that hydrogen ion $[H^+]$ concentration in the agro media might have played important role in enhancing corrosion rate. This is because CR is a function of concentration of the organic acids and may depend on the pH values of the reacting agro species as agreed by similar investigations (Singh and Gupta, 1996; Adetunji *et al.*, 2011, Tran *et al.*, 2013). Therefore, orange medium might have contained more acidic ions with low pH values than

other media and subsequently exhibited more corrosive effect on the mild steel sample followed by grape medium, mixture medium, mango and apple media respectively.

4.5 Corrosion mechanism of mild steel in agro media

The mechanism of corrosion processes involves the electrochemical interactions between the anode (mild steel specimen) and the electrolyte (agro media). Sequel to the studies on reaction mechanism of some metallic alloys on aqueous acidic solution (El-Maksoud, 2008; Ababio, 2005; ASM *International*, 2000); possible equations for chemical reactions during the electrochemical corrosion processes of the mild steel specimen in the agro media under study may be proposed. The corrosion mechanism of the mild steel sample can be determined using dominant acid component of each agro medium and may be deduced as follow:

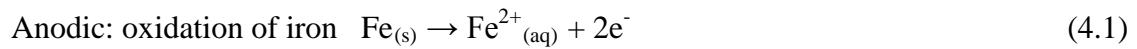
4.5.1 Reaction mechanism in the apple and mango media (both agro juices have malic acid as dominants)



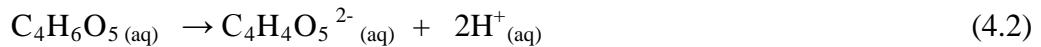
Scheme 4.1 Structural formula of malic acid ($C_4H_6O_5$)

Apple and mango media contained malic acid as their dominant species. The structural formula in Scheme 4.1 shows that malic acid is dicarboxylic and can only dissociate partially to release two hydrogen ions [$2H^+$] per molecule of the acid. Subsequently one mole of

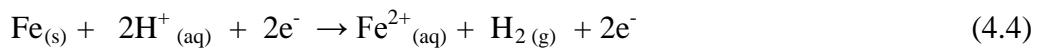
hydrogen gas is evolved per mole of malic acid during electrochemical reactions (Equations 4.2 and 4.3).



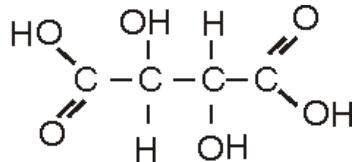
Cathodic: dissociation of malic acid and subsequent evolution of hydrogen gas



Overall reaction:

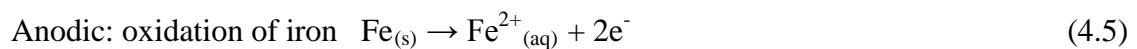


4.5.2 Reaction mechanism in the grape medium (tartaric acid)

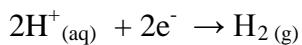
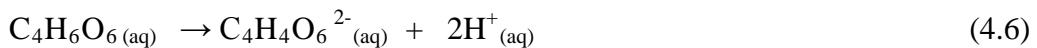


Scheme 4.2 Structural formula of tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$)

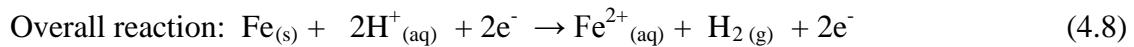
Tartaric acid is also dicarboxylic as shown in Scheme 4.2 as the major dominant in grape juice and can only evolve two hydrogen atoms of hydrogen per molecule of the compound during electrochemical processes. Hence, one mole of iron displaces two atoms Hydrogen gas from the agro medium to be oxidized to iron (II) oxide (Equations 4.5-4.6).



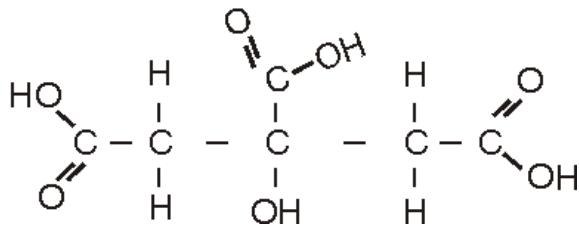
Cathodic: dissociation of tartaric acid and subsequent evolution of hydrogen gas



(4.7)

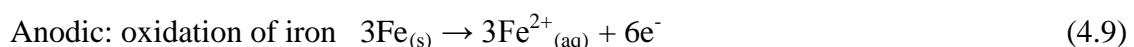


4.5.3 Reaction mechanism in the orange medium (citric acid)

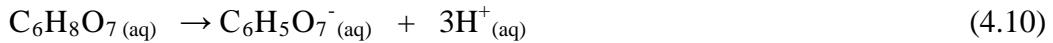


Scheme 4.3 Structural formula of citric acid ($\text{C}_6\text{H}_8\text{O}_7$)

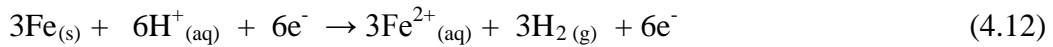
The structural formula of citric acid in orange medium (Scheme 4.3) shows three groups of carboxylic acid per molecule. Hence it is tricarboxylic acid and exhibits more complex structure than malic and tartaric. The dissociation of citric acid causes displacement of 3 moles of hydrogen gas from 2 molecules of the acid as illustrated in Equations 4.10 and 4.11.



Cathodic: dissociation of citric acid and subsequent evolution of hydrogen gas



Overall reaction:



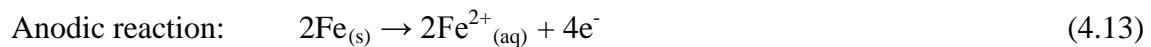
Distinctions can be drawn from the overall reaction mechanism (Equations: 4.4, 4.8 and 4.12) to show which medium would have most corrosive effect to the mild steel per molecule without considering other prevailing factors. One mole of $\text{Fe}_{(s)}$ was displaced from malic and tartaric acids while 3 moles of $\text{Fe}_{(s)}$ were lost in citric acid medium. Sequel to the number of evolved hydrogen atoms per molecule of each acid medium, citric acid possibly might have been more corrosive on the mild steel sample than malic and tartaric acids respectively. Therefore orange medium was suspected to be corroding more than other agro media as supported by electrochemical corrosion study.

4.5.4 Mechanism of passivation

Passivation of the mild steel samples was observed regularly during the electrochemical processes. The chemical reactions between mild steel specimens and dissolved oxygen from the surrounding atmosphere might have brought about formation of iron (II) oxide as supported by (Ababio, 2005). Further oxidation of $\text{FeO}_{(s)}$ could possibly result to the formation of iron (III) oxide. This oxide $[\text{Fe}_2\text{O}_3]_{(s)}$ might be responsible for passivation of further corrosion of the mild steel specimens at the anode and subsequently resulted to the

formation of passive oxide layers on the surfaces of the immersed steel samples. The reaction mechanism may be proposed as follows:

(a) Formation of iron (II) oxides: Oxygen molecules in the agro media could drift to the metallic surface to promote oxidation and corrosion of the mild steel sample as illustrated in Equations 4.13 to 4.15.



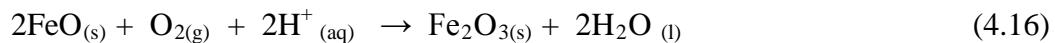
Cathodic reaction: dissolved oxygen reduction from the aerated agro acidic environments



Overall reaction: formation of iron (II) oxide



(b) Formation of iron (III) oxides: The formation of iron (III) oxides from iron (II) oxide could be the product of corrosion on iron in the agro environments as shown in Equation 4.16.



The main cathodic reactions in the aqueous agro environment could therefore be the reduction of oxygen molecules and hydrogen ions from the bulk of the agro media to the metal/solution interface as the reaction proceeded. This is in conformity with similar investigation conducted by Robin, (2004); Singh and Gupta, (1996).

4.6 Scanning electron microscopic analysis

SEM examination provides important data on the morphology of the corroded mild samples in the agro environments (Vander Voort, 2002). The surface micrographs of the steel samples at 1500X magnification are presented in Figure 4.22 to show the structures of oxide layer deposits.

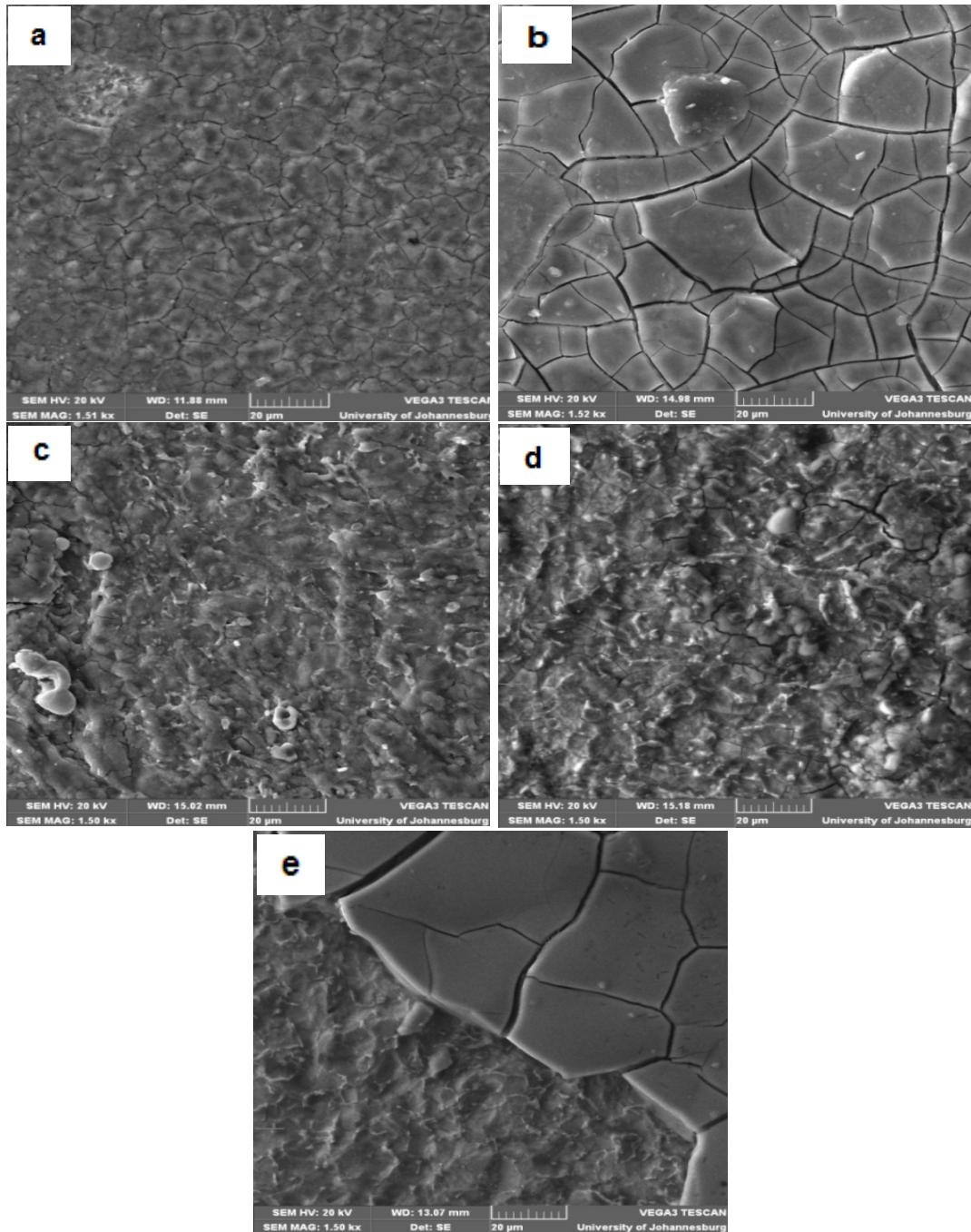


Figure 4.22 SEM micrographs of corroded mild steel samples from (a) apple medium; (b) grape medium; (c) mango medium; (d) orange medium and (e) mixture medium

The samples show different degrees of oxide scales incurred in the various agro media after 60th day exposure period. The SEM image in Figure 4.22 (a) shows uniform multiple web-like cracked oxide scales on the corroded steel sample. The surface cracks appeared to be developing which could be an indication of less corrosion impact on the metal immersed in apple medium. The surface micrograph in Figure 4.22(b) depicts image of the corroded sample in grape medium. The structure of the oxide layer appeared to be much dense with more visible surface cracks which could be an indication of greater corrosion impact on the steel sample than in Figure 4.22(a). The image shown in Figure 4.22(c) depicts no sign of cracks across the surface oxide layer of the mild steel sample but shows uneven oxide deposit with complete closed structure. This possibly suggests mild impact of corrosion on the steel sample. Figure 4.22(d) shows combined effects of few elevated open cracks and more closed surface structures of oxide films which could indicate non-uniform corrosion across the mild steel sample in orange medium. The SEM image in Figure 4.22(e) shows a fractional breakdown of the oxide layer with dense surface cracks which could signify localized corrosion across the surface of mild steel sample. It can be suggested that the wider the oxide cracks the more the corrosive effect of the agro medium.

4.7 Energy dispersive x-ray spectroscopic analysis

EDS analysis provides basic information on the chemical elements present on the features of the corroded mild steel samples being examined by SEM in the agro media. The relative amounts of elements detected are usually classified as either major, minor or trace values depending on the percentage weight composition.

Table 4.1 EDS analysis of the corroded mild steel samples in agro media

Elements	% weight composition				
	apple	grape	mango	orange	mixture
Fe	72.75	59.39	68.54	51.17	38.30
C	15.26	17.49	16.38	26.63	36.21
O	11.25	19.11	14.44	20.19	24.29
K	-	1.45	0.23	0.71	0.41
Zn	-	2.20	-	-	0.37
Na	0.29	-	-	0.46	-
Mn	0.35	0.36	0.41	0.30	0.32
S	-	-	-	0.14	-
Si	-	-	-	0.16	-
Al	-	-	-	0.24	-
Balance	Rb, Ca	-	Si		Ca, Si

The elemental characterization of the EDS shown in Figure 4.23(a-e) is tabulated in Table 4.1 to specify the percentage weight deposit of each spotted element. The major elements detected by EDS in Figure 4.23(a) include Fe, C and O; while minor elements are Na and Mn with traces of Rb and Ca as presented in Table 4.1. Therefore possible main oxide scales on the corroded steel sample could be Na_2CO_3 , MnO_2 , and Fe_2O_3 . Analysis of metal sample in Figure 4.23(b) reveals the presence of Fe, O and C as major elements. The minor constituent elements detected include K, Zn and Mn. The probable oxide film deposits on the corroded mild steel sample could be MnO_2 , Fe_2O_3 , ZnO and K_2CO_3 respectively. The EDS analysis also detected Fe, O and C as major elements on the corroded specimen in Figure 4.23c. The minor elements revealed include K and Mn with a trace of Si.

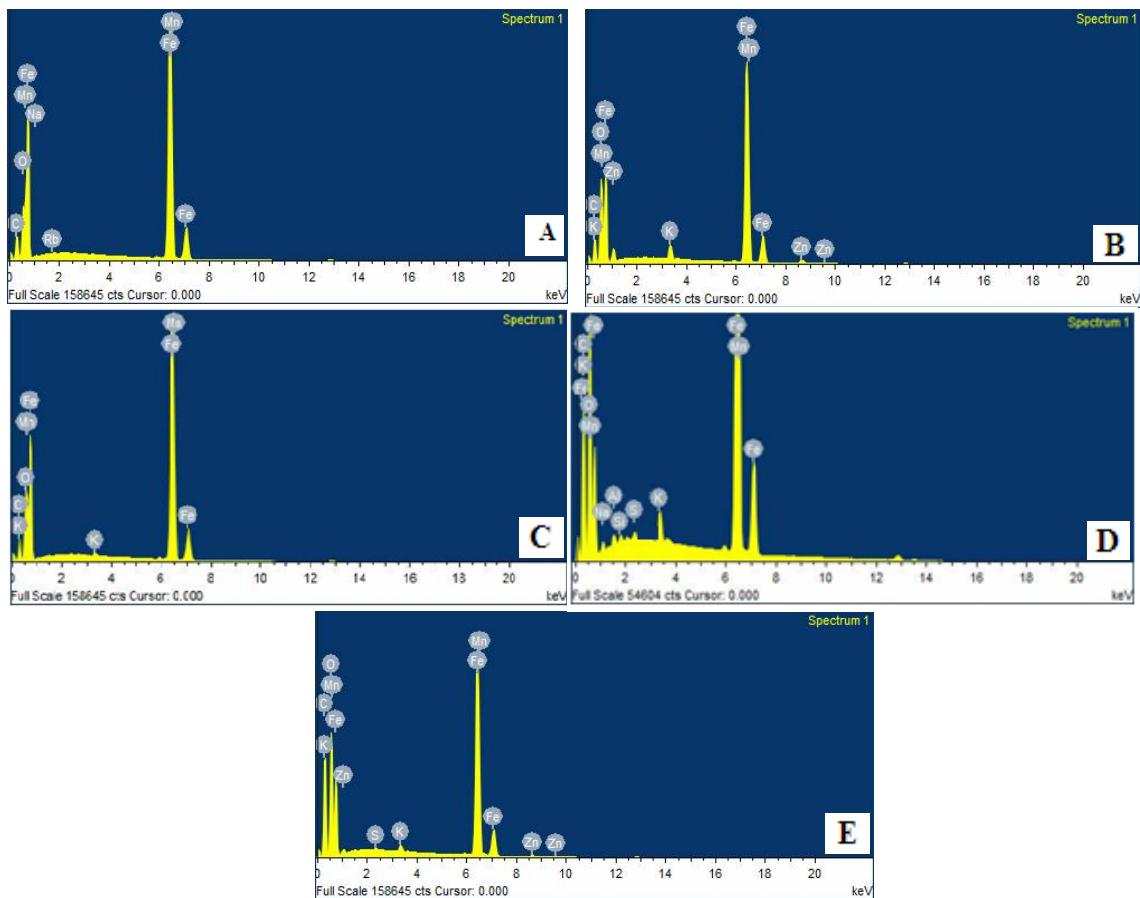


Figure 4.23 Elemental characterizations of the corroded mild steel samples from (a) apple medium; (b) grape medium; (c) mango medium; (d) orange medium and (e) mixture medium

The presence of Fe_2O_3 , MnO_2 and K_2CO_3 as the main oxide layers on the metal surface might be suspected. Similarly the major elemental content in Figure 4.23d comprises of Fe, O and C. The minor elemental characterization spotted on the corroded steel sample includes K, Na, Mn, S, Si, and Al. The deposition of the following oxide scales could be possible Na_2CO_3 , SiO_2 , Fe_2O_3 , MnO_2 , and Al_2O_3 . The result shown in Figure 4.23e reveals Fe, O and C as the major constituent elements on the corroded mild steel sample in the mixture medium. There were minor elements of Zn, K, Mn and S on the oxide layer with traces of Si and Ca (Table 4.1). Therefore ZnO , MnO_4 , Fe_2O_3 and K_2CO_3 might be the likely oxide scales found on the corroded metal specimen. The dominant oxide layer on the corroded mild

steel samples could depend on the percentage mass deposits of the metal constituents. Fe_2O_3 might be greater than other oxide scales and therefore the main corrosion product as supported by the corrosion mechanism.

CHAPTER 5

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Accelerated electrochemical corrosion behaviour of mild steel in apple, grape, mango, orange and the mixture of all the agro fluids was studied using weight loss measurement and open circuit potential electrochemical techniques. The following conclusions are drawn from the analyses of the results obtained:

- The analyses of the results obtained from the study showed that the amount of weight loss of the mild steel sample in the apple, grape, mango, orange and the mixture of the juices increased over the duration of immersion. The weight loss was highest in the grape medium losing 4.69g; followed by the steel specimen in the orange medium with 4.18 g loss. The weight loss in the mixture of these media was 4.15 g while that in the apple medium was 4.10 g. The mango juice showed lowest weight loss of the mild steel sample by just 2.25 g. These results were supported by the pH values of the weight loss analysis. Therefore the sequence of most to least weight loss was: Grape> Orange> Mixture>Apple>Mango.

- The corrosion rates of the mild steel sample decreased for all of the agro media tested by electrochemical analyses over the entire duration of the experiment. The mild steel sample corroded most in the orange medium at 1.530 mm/year, followed by grape medium (1.403 mm/year), mixture medium (0.672 mm/year), mango medium (0.339 mm/year) and apple medium (0.301 mm/year) respectively at the end of the study.

The summary of the electrochemical corrosion study is summarised in Figure 5.1(a)-(e) to depict the trends of individual corrosion rates in the agro media.

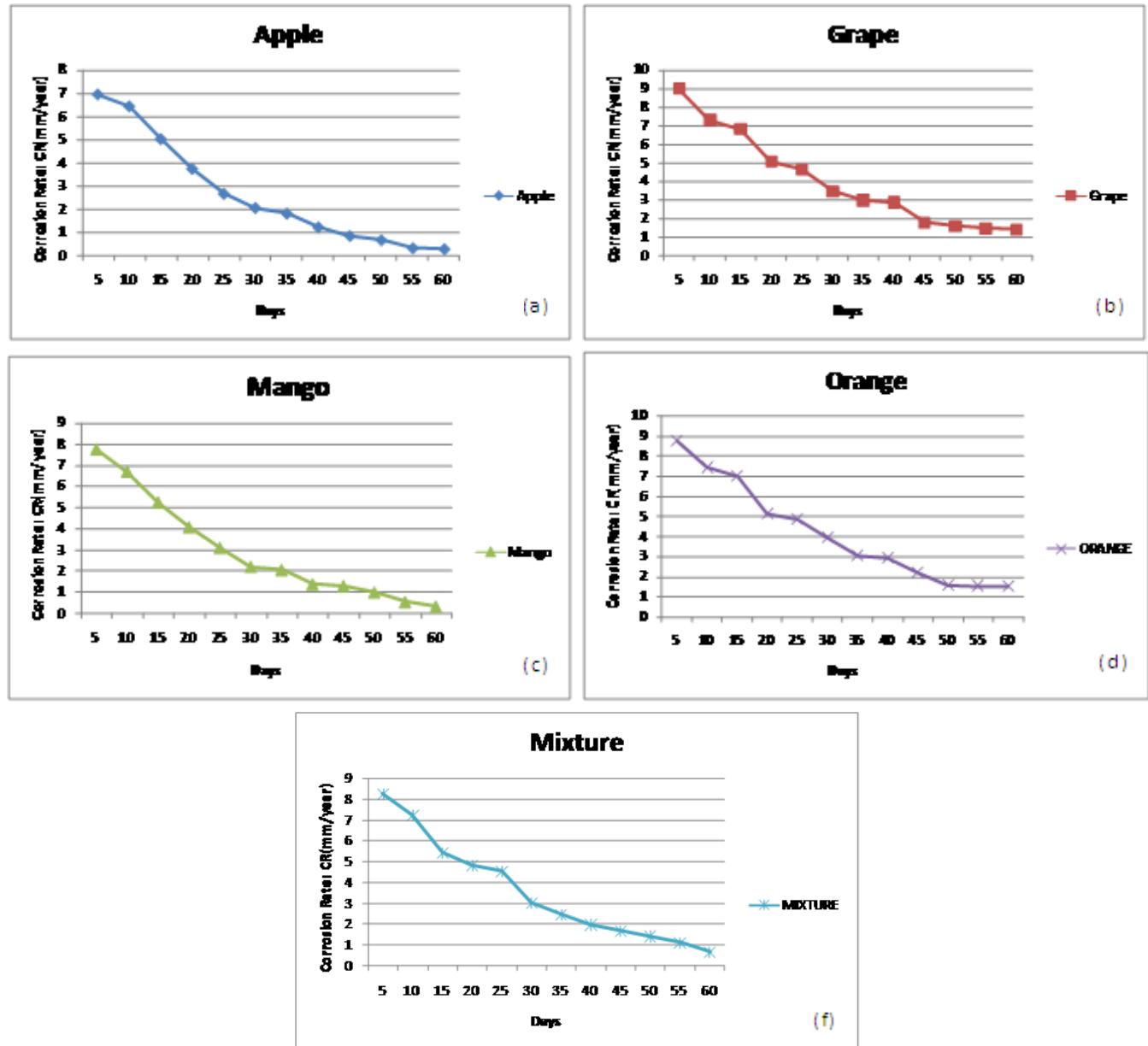


Figure 5.1 summary of the electrochemical corrosion study

The trend of decline in corrosion rates is illustrated as: Orange > Grape > Mixture > Mango > Apple.

➤ The electrochemical study showed significant increase in the pH values of the various agro media. This was a confirmation of reduction in the acidity of all the test environments due to near or complete evolution of dissociable hydrogen gas from the corrosion media. Orange medium contained the highest acidic level with the lowest pH values among the competing agro media and subsequently exhibited the highest corrosivity towards the mild steel samples; this is closely followed by grape medium, mixture medium, mango and apple media. The pH of the media increased as follows: Orange < Grape < Mixture < Mango < Apple.

➤ The corrosion mechanism of the mild steel sample in the apple, grape, mango, orange and mixture media showed that the rate of corrosion of the metal sample was proportional to the number of displaced hydrogen atoms per molecule of each acid medium. Citric acid contained more H⁺ per mole and subsequently had greater corrosive effect on the mild steel specimen than malic and tartaric acids respectively. Therefore, it can be concluded that the orange medium might have a more corrosive effect than other agro media on the mild steel sample as supported by the results of the electrochemical study because of more dissociable hydrogen ions.

➤ The microstructural analyses of the corroded mild steel samples revealed surface images of uniform and localised corrosion products across the oxide deposits with different sizes of surface fractures in the oxide. Based on the results of SEM/EDS analyses, it can be concluded that all agro media investigated showed almost similar corrosion products on the mild steel samples but differed completely in the composition of each surface element. Fe₂O_{3(s)} was spotted as the main corrosion product in all the agro media which was in conformity with the product of corrosion mechanism.

5.2 Recommendations

- Sequel to the successful study on the corrosion behaviour of the mild steel sample in the apple, grape, orange and mango juices, it is suggested to further evaluate the effects of these agro juices on other metallic alloys as the results obtained would have limited application to wider varieties of metals used in the agro allied industries.
- The relationship between metal thickness and corrosion rates in the agro media is important and should be investigated to determine the extent of corrosion effects on different sizes of the metal sample at the same physical condition.
- The study should be extended to include more varieties of agro juices so as to compare their chemical compositions and behaviours on the metallic specimen.
- Since most “organic acids” could be stored for longer period during industrial processes (Singh and Singh, 1995; Kangas, 1998), it may be feasible to investigate corrosion behaviour of the steel alloy in the agro media for duration of 120 days below ambient temperature.

REFERENCES

- Ababio, O. Y. ed, (2005) *New School Chemistry*. 3rd edn. Ibadan: Africana First Publishers.
- Abiola, O. K. Oforka, N. C. And Ebenso, E. E. (2004) The inhibition of mild steel corrosion in acidic medium by fruit juice of citrus paradisi. *Journal of Corrosion Science and Technology*. Vol. 1, No. 1, pp. 75-78.
- Adetunji, O. D. Aiyedun, O. J. Alamu, O. J. and Surakat, A. S. (2011) Electrochemical properties of metals in cassava fluid. *Journal of Engineering and Technology Research*. Vol. 3, No. 10, pp. 292-297.
- Afolabi, A. S. (2007) Corrosion and stress corrosion behaviours of low and medium carbon steels in agro-fluid media. *Leonardo Electronic Journal of practices and Technologies*. Vol. 10, pp. 55-66.
- Ahmad, N. Husain, M. I. Kumar, R. Mukherjee, S. and Dutta, R. (2012) Comparative kinetics of corrosion rates on mild steel in various citrus juices. *International Journal of Science and Advanced Technology*. Vol. 2 No 5, pp. 157-163.
- Ajila, C. M. Rao, L. J. Rao, U. J. and Rao, P. (2010) Characterization of bioactive compounds from raw and ripe magnifera indica L. peel extracts. *Journal of Food and Chemical Toxicology*. Vol. 48, pp. 3406-3411.
- Amin, M. A. Khaled, K. F. and Fadl-Allah, S. A. (2010) Testing validity of tafel extrapolation method for monitoring corrosion of cold rolled steel in HCl solutions-experimental and theoretical studies. *Journal of Corrosion Science*. Vol. 52, pp. 140-151.

Amin, M. A. Mersal, G. A. and Mohsen, Q. M. (2011) Monitoring corrosion and corrosion control of low alloy ASTM A213 grade T22 boiler steel in HCl solutions. *Arabian Journal of Chemistry*. Vol. 4, pp. 223-229.

Amri, J. Gulbrandsen, E. and Nogueira, R. (2011) Role of acetic acid in CO₂ top of the line corrosion of carbon steel. *CORROSION/II, Paper No. 11329 (Houston, TX: NACE)*.

Anthony, U. O. and Effiong, U. E. (1998) Nutritional quality of plant foods. *Post Harvest Research Report Unit. Department of Biochemistry, university of Benin, Benin, Nigeria.*

ASM International, (2000) Fundamentals of electrochemical corrosion (#06594G). Available: <http://www.asminternational.org> [10/05, 2013].

Awwiri, G. O. (2004) Corrosion resistance of copper and brass in various media. *Journal of Corrosion Science and Technology*. Vol. 1, No. 1, pp. 58-60.

Badmos, A. Y and Ajimotokan, H. A. (2009) The corrosion of mild steel in orange juice environment. *Technical Report, No: 2009-02, University of Ilorin, Ilorin, Nigeria.*

Bailey, P. S. and Bailey, C. A. (1995) *Organic Chemistry: A survey of Concepts and Applications*. Prentice Hall.

Bajah, E. T. and Godman, S. (1992) *Chemistry, IUPAC Edition*. Ibadan: Longman.

Bally, S. E. (2006) Species profiles for pacific island agroforestry. *Journal of Agro Food Technology*. Vol. 3.1, pp. 1-25.

Bastidas, J. M. De-Damborenea J. and Vazquez, A. J. (1997) Butyl substituents in nbutylamine and their influence on mild steel corrosion inhibition in hydrochloric acid, *Journal of Applied Electrochemistry*. Vol.27, pp.345-349.

Batchelor, A. W. Lam, L. N. and Chandrasekalan, M. (2002) *Material Degradation and its Control by Surface Engineering*. 2nd edn. London: Imperial College Press.

Bentiss, F. Traisnel, M. Gengembre, L. and Lagrenée, M. (1999) A new triazole derivative as inhibitor of acid corrosion of mild steel: electrochemical studies, weight loss determination, SEM and XPS. *Journal of Applied Science*. Vol. 152, pp. 237-249.

Bolton, W. ed, (1994) *Materials Technology*. 2nd edn. Oxford, London: B.H. Newness.

Calle, L. M. and Mac-Dowell, L. G. (2003) Electrochemical evaluation of stainless steel in acidified sodium chloride solution. *Paper Presented in Conference at Kennedy space Center, (KSC), Florida, USA*.

Callister, W.D. ed, (1997) *Material Science and Engineering: An Introduction*. 4th edn. New York: John Wiley and sons Inc.

Chao, C. Zhao, Z. Zhong-Ling, W. Jian-Feng, Y. and Jin-Feng, L. (2012) Electrochemical corrosion behaviour of pure Mg in neutral 1.0% NaCl solution. *Journal of Transitions of Nonferrous Metals Society of China*. Vol. 22, pp. 970-976.

Costescu, C. Parvu, D. and Rîvis, A. (2006) The determination of some physical-chemical characteristics for orange, grapefruit and tomato juices. *Journal of Agralimentary Process and Technologies*. Vol. XII, No. 2, pp. 429-432.

De-La Fuente, D. Diaz, J.S. Chico, B. and Morcillo, M. (2011) Long-term atmospheric corrosion of mild steel. *Journal of Corrosion Science*. Vol. 53, pp. 604-617.

De-Giorgi, V. G. (1992) Corrosion basics and computer modelling. *Naval Research Laboratory Report, Department of the Navy, Washington DC, 203755000 USA*.

Dougherty, J. A. (2004) A review of the effect of organic acids on CO₂ corrosion. *Corrosion/04 Paper No. 04376 (Houston, TX: NACE)*.

Ebenso, E. E. Okafor, P. C. Ibok, U. J. and Onuchukwu, A. I. (2004) The joint effects of halide ions and methylene blue on the corrosion inhibition of aluminium and mild steel in acid corrodent. *Journal of Chemical Society of Nigeria. Vol. 29, No. 1, pp.10-15.*

El-Masksoud, S. A. (2008) The effect of organic compounds on the electrochemical behaviour of steel in acidic media. A review. *International Journal of Electrochemical Science. Vol. 3, pp. 528-555.*

Evans, U. R. (1972) *An Introduction to Metallic Corrosion*. 2nd ed. London: Arnold.

Fekry, A. M. and Ameer, M. A. (2011) Electrochemical investigation of corrosion and hydrogen evolution rate of mild steel in sulphuric acid solution. *International Journal of Hydrogen Energy. Vol. 36, pp. 11207-11215.*

Frankel, G. S. (2008). Electrochemical techniques in corrosion: status, limitations and needs. *Journal of ASTM International. Vol. 5, No. 2, pp.101-127.*

Fonseca, M. P. Bastos, L. N. Caytlero, A. and Saitovitch, E. M. (2007). Rust formed on cannons of xviii century under two environment conditions. *Corrosion Science Journal. Vol. 49, pp. 1949-1962.*

Fontana, M. G. ed, (1992) *Corrosion Engineering*. 4th edn. New York: McGraw-Hill.

Fontana, M. G. ed, (1986) *Corrosion Engineering*. 3rd edn New York: McGraw-Hill.

Fontana, M. G. and Staehle, R. W. (1990) *Advances in Corrosion Science and Technology*. New York: Plenum Press.

Garsany, Y. Pletcher, D. and Hedges, B. (2002) The role of acetate in CO₂ corrosion of carbon steel: has the chemistry been forgotten? *Corrosion/02, Paper No. 2273 (Denver, CO: NACE International)*.

Genesca, J. Mendoza, J. Duran, R. and Garcia, E. (2002) Conventional DC electrochemical techniques in corrosion testing. *Technical Report on Corrosion, Department of Metallurgical Engineering, UNAN, City University.04510 Mexico D.F. and InstitutoMexicano delPetroleo, Eje Central Lazaro Cardenas, 152.07730 Mexico.*

George, K. (2003) Electrochemical investigation of carbon dioxide corrosion of mild steel in the presence of acetic acid. *MS Thesis, Department of Chemical Engineering, Ohio University, Athens, OH.*

Hsu, W. Yang, C. Huang, C. and Chen, Y. (2005) Electrochemical corrosion studies on Co-Cr-Mo implant alloy in biological solutions. *Journal of Material Chemistry and Physics. Vol. 93, pp. 531-538.*

Hussin, M. H. and Kassim, M. J. (2010) Electrochemical studies of mild steel corrosion inhibition in aqueous solution by uncaria gambir extract. *Journal of Physical Science. Vol. 21, No. 1, pp. 1-13.*

Ibrahim, T. and Habbab, M. (2011) Corrosion inhibition of mild steel in 2MHCl using aqueous extract of eggplant peel. *International Journal of Electrochemical Science. Vol. 6, pp. 5357-5371.*

Ita, B. I. and Eden, C. A. (2000) Inhibition of steel corrosion in hydrochloric acid solution by green S. erythrosine dyes. *Global Journal of Pure applied Sciences. Vol. 60, No.20, pp. 239-240.*

Ita, B. I. and Offiong O. E. (1997) Inhibition of steel corrosion in hydrochloric acid by pyridoxal (4-ethylsemicarbazide), pyridoxal (4-methylthiosemicarbazide) and its Zn (II) complex. *Journal of Materials Chemical and Physics*. Vol. 51, pp. 203-211.

Kadry, S. (2008) Corrosion analysis of stainless steel. *European Journal of Scientific Research*. Vol. 4, pp. 508-516.

Kangas, P. (1998) Anti-corrosion methods. *Journal of Corrosion Science, Mater.* Vol.45, pp.233-235

Karadenitz, F. and Eksi, A. (2002) Sugar composition of apple juices. *Journal of Science Food Agriculture, European Food Research Technology*. Vol. 215, pp. 146-149.

Kasai, N. Utatsu, K. Park, S. Kitsukawa, S. and Sekine, K. (2009) Correlation between corrosion rate and AE signal in acidic environment for mild steel. *Corrosion Science Journal*. Vol. 51, pp. 1679-1684.

Khaled, K. F. and Amin, M. A. (2009) Corrosion monitoring of mild steel in sulphuric acid solutions in the presence of some thiazole derivatives-molecular dynamics chemical and electrochemical studies. *Journal of Corrosion Science*. Vol. 51, pp. 1964-1975.

Kim, D. Muralidharan, S. Ha, T. Bae, J. Ha, Y. Lee, H. and Scantlebury, J. D. (2006) Electrochemical studies on the alternating current corrosion of mild steel under cathodic protection condition in marine environments. *Journal of Electrochimica Acta*. Vol. 51, pp. 5259-5267.

Li, X. Yu, B. Curran, P. and Liu, S. (2011) Chemical and volatile composition of mango wines fermented with different *saccharomyces cerevisiae* yeast strains. *S. Afr. J. Enol. Vitic.* Vol. 32, No. 1, pp.117-128.

Matos, M. Canhoto, C. Bento, M. and Gerando, M. (2010) Simultaneous evaluation of the dissociated and undissociated acid concentrations by square wave voltammetry using microelectrodes. *Journal of Electroanalytical Chemistry*. Vol. 647, pp. 144-149.

McCafferty, E. (2005) Validation of corrosion rates measured by tafel extrapolation method. *Journal of Corrosion Science*. Vol. 47, pp. 3202-3215.

Marcus, P. and Maurice, V. (2001) Fundamental aspects of corrosion of metallic materials. *Journal of Material Science and Engineering, Encyclopaedia of Life Support System*. Vol. II, pp. 2-7.

Martino, J. D. Rapin, C. Berthod, P. Podor, R. and Steinmetz, P. (2004) Corrosion of metals and alloys in molten glasses part 1: glass electrochemical properties and pure metals (Fe, Co, Ni, Cr) behaviours. *Journal of Corrosion Science*. Vol. 46, pp. 1849-1864.

McSwane, D. McSwane, D. Z. Rue, N. R. and Linton, R. (2003) *Essentials of Food Safety and Sanitation*. Prentice Hall.

MESSA PRODUCTS, 2000 - last update, Fundamental Corrosion Chemistry [Homepage of corrosion protection and corrosion prevention], *Messa Products Inc.*, Available: <http://www.messaproducts.com> [22/06, 2012].

Nagy, S. (1993) Fruit juice processing technology. *Journal of Agro Science*, Vol. 8 pp. 271-317.

Niu, L. Wu, J. Liao, X. Chen, F. Wang, Z. Zhao, G. And Hu, X. (2008) Physiochemical characteristics of orange juice samples from seven cultivars. *Journal of Agricultural Sciences in China*. Vol. 7, No.1, pp. 41-47.

Nour, V. Trandafir, I. and Ionica, M. (2010) HPLC organic acid analysis in different citrus juices under reversed phase conditions. *Nor. Bot. Hort. Agrobot. Cluj. Vol. 38, No.1, pp. 44-48.*

Ofoegbu, S. U. Ofoegbu, P. U. Neife, S. and Okorie, B. A. (2011). Corrosion behaviour of steels in Nigerian food processing environments. *Journal of applied Science and Environmental Management. Vol. 15, No.1, pp. 135-139.*

Ogundare, O. Momoh, I. M. Akinribide, O. J. Adetunji, A. R. Borode, J. O. Olusunle, S. O. and Adewoye, O. O. (2012) Comparative study of corrosion sensitivity of selected ferrous metals in crude oil. *Journal of Minerals and Characterisation and Engineering. Vol. 11, No.6, pp. 559-568.*

Ogunleye, I. O. Adeyemi, G. J. and Oyegoke, A. O. (2011) Effect of grape juice on the corrosion behaviour of mild steel in acidic medium. *American Journal of Scientific Industrial Research. Vol. 2, No. 4, pp. 611-615.*

Oguzie, E. E. Okolue, B.N. Ogukwu, C.E. and Unaegbu, C. (2006) Corrosion inhibition and adsorption on aluminium in sodium hydroxide solution. *Material Letters Journal. Vol. 60, No. 22, pp. 3376-3385.*

Oladele, S. K. and Okoro, H. K. (2011) Investigation of corrosion effect of mild steel on orange juice. *African Journal of Biotechnology. Vol. 10, No. 16, pp. 3152-3156.*

Oluwadare, G. O. and Agbaje, O. (2007) Corrosion of steels in steel reinforced concrete in cassava juice. *Journal of Applied Sciences Asian Network for Scientific Information. Vol. 7, No.17, pp. 2474-2479.*

Oluwole, O. O. Garus-Alaka, W. and Ajide, O. O. (2012) Comparative study of corrosion behaviour of nickel and gold plated carbon steels used as ornamentals in saline environment.

International Journal of Materials Engineering. Vol. 2, No.1, pp. 1-6.

Oluwole, O. and Olawale, O. (2010) Corrosion behaviour of nickel plated low carbon steel in tomato fluid. *Leonardo Electronic Journal of Practices and Technologies. pp. 33-42.*

Onen, A. I. (2004) Inhibition of acid corrosion of mild steel by OpuntaSpp (OSPP) cactus milk extract. *Journal of Applied Sciences. Vol. 22, pp. 147-175.*

Onen, A. I. (2000) Determination of amount of corrosion of iron using different concentrations of alkali halides with time. *Yedzaram Journal of Science and Technology, Vol. 1, No. 1, pp. 74-79.*

Poorsqasemi, E. Abootalebi, M. Peikari, M. and Haqdar, F. (2009) Investigating accuracy of the tafel extrapolation method in HCl solutions. *Journal of Corrosion Science. Vol. 51, pp. 1043-1054.*

Pud, A. A. Shapoval, G. S. Kamarachik, P. Ogurtsov, N. A. Gromovaya, V.F. Myronyuk, I. E. Kontsur, Y. V. (1999) Electrochemical behaviour of mild steel coated by polyaniline doped with organic sulfonic acids. *Synthetic metals. Vol. 107, pp. 111-115.*

RESTEK APPLICATIONS, (2003). Single-column method for HPLC analysis of organic acids in fruit juices, using an allure organic acids column. #59530, Available: <http://www.restek.com> [19/06, 2013].

Robin, A. (2004) Comparative study of Nb, Nb-10W and Nb-16 Ta-12W corrosion behaviour in sodium hydroxide solutions. *ElectrochimicaActica Vol. 49, pp. 1915-1923.*

Reger, D. L. Goode, S. R. and Ball, D. W. (2009) *Chemistry: Principles and Practice*. Thomson Brooks/Cole.

Saha, G. C. Kaha, G. C. Khan, T. I. and Zhang, G. A. (2011) Erosion-corrosion resistance of microcrystalline and near-nanocrystalline WC-17 Co high velocity oxy-fuel thermal spray coatings. *Corrosion Science Journal*. Vol. 53 pp. 2106-2114.

Sculling, J. C. ed, (1984) *Fundamentals of Corrosion*. 3rd edn. New York: Mc Graw Hill.

Sharma, K. K. and Sharma, L. K. ed, (1999) *Physical Chemistry*. 9th edn. New Delhi: Viska Publishers.

Shivakumar, S. S. and Mohana, K. N. (2012). Centella asiatica extract as green corrosion inhibitor for mild steel in 0.5 M sulphuric acid medium. *Advances in Applied Science Research*. Vol. 3, No. 5, pp. 3097-3106.

Shreir, L. L. (2000) Basic Concept of Corrosion. In: Corrosion, ed, *Great Britain: Butterworth Heinemann*, pp.74-95.

Shreir, L. L. Jarman, R. A. and Burstein, G. T. ed, (2000) *Metal/ Environment Reactions*. 3th edn. London: Heinemann.

Shreir, L. L. (2010) Basic concepts of corrosion. *Article on Corrosion Science*. Vol.1, pp.1:3-1:15.

Singh, M. M. and Gupta A. (1996) Corrosion behaviour of mild steel in formic acid solutions. *Journal of Material Chemistry and Physics*. Vol. 46 pp. 15-22.

Singh, S. K. Mukherjee, A. K. and Singh, M. M. (2011) Corrosion behaviour of mild steel in aqueous acetic acid solutions containing different amounts of formic acid. *Indian Journal of Chemical Technology*. Vol. 18, pp. 291-300.

Singh, M. M. and Singh, R. N. (1995) Corrosion behaviour of mild steel in organic acid solution. *Corrosion Science Journal*. Vol. 37, pp.1399-1402.

Smith, W. F. and Hashemi J. ed, (2006) *Foundation of Material Science and Engineering*. 4nd edn. New York: McGraw-Hill.

Talbot, D. and Talbot, J. (1998) *Corrosion Science and Technology*. New York: CRP Press.

Toaldo, I. M. Fogolari, O. Pimentel, G. C. Gois, J. S. Borges, D. L. Caliari, V. and Luiz, M. B. (2013) Effects of grape seeds on the polyphenol bioactive content and elemental composition by ICP-MS of grape juice from *vitis labrusca* L. *LWT-Food Science and Technology Journal*. Vol. 53, pp.1-8.

Tran, T. Brown, B. Nesic, S. and Tribollet, B. (2013) Investigation of the mechanism for acetic acid of mild steel. *NACE International Corrosion Conference and Expo. Paper No: 2487*.

Uhlig, H. H. (2000) *Corrosion Handbook*. Weinheim: Wiley-VCH [Classic textbook describing the basics and phenomenology of corrosion].

Uppal, M. M. and Bhatia, S. C. ed, (2001) *Engineering Chemistry*, 6th edn. Delhi: Khana Publishers.

USDA NUTRIENT DATABASE, (2011) Grape fruit for standard reference. *A journal onagro Science. Wikipedia Encyclopedia, Available: <http://www.nal.usda.gov/fnic/foodcomp> and <http://en.wikipedia.org/wiki/grapefruit> [15/06, 2012]*.

Vander Voort, G. F. (2002) Metallographic techniques in failure analysis. *Buehler Journal on Metallographic Techniques. 104738/6072, Vol. 3, pp.1-17*.

Vera, R. Rosales, B. M. and Tapia, C. (2003) Effect of exposure angle in the corrosion rate of plain carbon steel in a marine atmosphere. *Journal of Corrosion Science*. Vol. 45, pp. 321-337.

Vimala, J. R. Rose, A. L. and Raja, S. (2012) A study on the phytochemical analysis and corrosion inhibition on mild steel by ammonia muricata. L leaves in 1N hydrochloric acid. *Pelagia Research Library*. Vol. 3, No.3, pp. 582-588.

Walsh, F. (1991). Faraday and his laws of electrolysis. *Bulletin of Electrochem*. Vol. 7, No.11, pp.481-489

Wang, Y. M. Wang, F. H. Xu, M. J. Zhao, B. Guo, L. X. and Ouyang, J. H. (2009). Microstructure and corrosion behaviour of coated AZ91 alloy by microarc oxidation for biomedical application. *Applied Surface Science Journal*. Vol. 255, pp. 9124-9131.

Wang, W. Jenkins, P. E. and Ren, Z. (2012). Electrochemical corrosion of carbon steel exposed to biodiesel/simulated seawater mixture. *Journal of Corrosion Science*. Vol. 57, pp. 215-219.

Wu, J. Gao, H. Zhao, L. Liao, X. Chen, F. Wang, Z. and Hu, X. (2007). Chemical compositional characterization of some apple cultivars. *Journal of Food Chemistry*. Vol.103, pp. 88-93.

Yahaya, S. Othman, N. K. David, A. R. Jalar, A. (2013) Surface morphology studies of low carbon steel treated in aqueous lignin. *Journal of corrosion science, Malaysiana*. Vol. 42, No. 12, pp. 1793-1798.

Zhang, X. L. Jiang, Z. H. Yao, Z. P. Song, Y. and Wu, Z. D. (2009). Effect of scan rate on the potentiodynamic polarization curves obtained to determine the tafel slopes and corrosion current density. *Journal of Corrosion Science*. Vol. 51, pp. 581-58.

APPENDICES

APPENDIX A Summary of weight loss analysis of mild steel

Time/days	Apple/(g)	Grape/(g)	Mango/(g)	Orange/(g)	Mixture/(g)
5	0.84	1.47	0.33	1.32	1.15
10	1.00	2.20	0.64	1.77	1.30
15	1.33	2.67	0.96	2.15	1.63
20	1.65	2.82	1.21	2.19	1.95
25	2.04	3.01	1.49	2.53	2.17
30	2.26	3.18	1.58	2.75	2.56
35	2.63	3.40	1.75	3.08	2.70
40	3.01	3.63	1.77	3.43	2.80
45	3.30	3.79	1.81	3.70	3.21
50	3.60	4.04	1.95	3.95	3.53
55	4.00	4.40	2.14	4.10	3.80
60	4.10	4.69	2.25	4.18	4.15

APPENDIX B Summary of corrosion rates of mild steel by weight loss

Corrosion Rate: CR(mm/year)					
Time/days	Apple	Grape	Mango	Orange	Mixture
5	0.39	0.69	0.16	0.63	0.54
10	0.24	0.52	0.15	0.41	0.31
15	0.21	0.42	0.15	0.34	0.26
20	0.19	0.33	0.14	0.26	0.23
25	0.19	0.29	0.14	0.23	0.21
30	0.18	0.25	0.12	0.22	0.20
35	0.17	0.23	0.11	0.21	0.18
40	0.17	0.21	0.10	0.20	0.16

45	0.17	0.20	0.09	0.19	0.16
50	0.16	0.19	0.08	0.18	0.16
55	0.16	0.18	0.08	0.17	0.15
60	0.15	0.17	0.07	0.16	0.15

APPENDIX C Electrochemical corrosion rates of mild steel in the agro media

Corrosion Rate: CR(mm/year)					
Duration (days)	Apple	Grape	Mango	ORANGE	MIXTURE
D-5	6.946	8.984	7.759	8.756	8.224
D-10	6.435	7.278	6.705	7.435	7.231
D-15	5.031	6.809	5.250	7.014	5.430
D-20	3.747	5.068	4.080	5.154	4.796
D-25	2.675	4.632	3.106	4.862	4.545
D-30	2.069	3.469	2.215	3.972	3.031
D-35	1.825	2.975	2.063	3.052	2.444
D-40	1.240	2.853	1.387	2.947	1.978
D-45	0.867	1.752	1.305	2.200	1.690
D-50	0.683	1.560	1.006	1.593	1.422
D-55	0.344	1.451	0.552	1.558	1.099
D-60	0.301	1.403	0.339	1.530	0.672

APPENDIX D-1 Comparison of electrochemical corrosion parameters (5th day) calculated from Figure 4.7

Electrolyte	Parameter			
	ba (V dec ⁻¹)	bc (V dec ⁻¹)	I _{corr} (Acm ⁻²)	E _{corr} (mVolts)
Apple	0.150	0.065	2.102	-552
Grape	0.194	0.044	1.247	-578
Mango	0.127	0.09	6.621	-584
Orange	0.127	0.064	2.017	-763
Mixture	0.075	0.121	6.385	-573

APPENDIX D-2 Comparison of electrochemical corrosion parameters (10th day) calculated from Figure 4.8

Electrolyte	Parameter			
	ba (V dec ⁻¹)	bc (V dec ⁻¹)	I _{corr} (Acm ⁻²)	E _{corr} (mVolts)
Apple	0.179	0.092	1.165	-546
Grape	0.292	0.068	2.981	-559
Mango	0.119	0.100	2.051	-569
Orange	0.088	0.125	1.369	-694
Mixture	0.074	0.074	5.108	-568

APPENDIX D-3 Comparison of electrochemical corrosion parameters (15th day) calculated from Figure 4.9

Electrolyte	Parameter			
	ba (V dec ⁻¹)	bc (V dec ⁻¹)	I _{corr} (Acm ⁻²)	E _{corr} (mVolts)
Apple	0.338	0.900	4.671	-542
Grape	0.270	0.910	3.121	-556
Mango	0.113	0.067	1.151	-567
Orange	0.070	0.070	2.021	-680
Mixture	0.088	0.068	7.926	-565

APPENDIX D-4 Comparison of electrochemical corrosion parameters (20th day) calculated from Figure 4.10

Electrolyte	Parameter			
	ba (V dec ⁻¹)	bc (V dec ⁻¹)	I _{corr} (Acm ⁻²)	E _{corr} (mVolts)
Apple	0.114	0.106	2.691	-535
Grape	0.233	0.105	4.985	-548
Mango	0.103	0.06	1.121	-556
Orange	0.126	0.057	1.057	-617
Mixture	0.124	0.111	5.182	-564

APPENDIX D-5 Comparison of electrochemical corrosion parameters (25th day) calculated from Figure 4.11

Electrolyte	Parameter			
	ba ($V \text{ dec}^{-1}$)	bc ($V \text{ dec}^{-1}$)	I_{corr} ($A\text{cm}^{-2}$)	E_{corr} (mVolts)
Apple	0.195	0.091	3.745	-533
Grape	0.155	0.035	1.661	-532
Mango	0.087	0.063	4.903	-556
Orange	0.462	0.093	6.922	-574
Mixture	0.102	0.070	6.269	-560

APPENDIX D-6 Comparison of electrochemical corrosion parameters (30th day) calculated from Figure 4.12

Electrolyte	Parameter			
	ba ($V \text{ dec}^{-1}$)	bc ($V \text{ dec}^{-1}$)	I_{corr} ($A\text{cm}^{-2}$)	E_{corr} (mVolts)
Apple	0.181	0.084	1.496	-527
Grape	0.155	0.087	4.355	-531
Mango	0.091	0.067	5.800	-555
Orange	0.107	0.071	6.389	-565
Mixture	0.161	0.106	2.656	-552

APPENDIX D-7 Comparison of electrochemical corrosion parameters (35th day) calculated from Figure 4.13

Electrolyte	Parameter			
	ba ($V \text{ dec}^{-1}$)	bc ($V \text{ dec}^{-1}$)	I_{corr} ($A\text{cm}^{-2}$)	E_{corr} (mVolts)
Apple	0.083	0.062	1.778	-525
Grape	0.084	0.039	6.254	-527
Mango	0.096	0.070	5.224	-552
Orange	0.107	0.066	4.429	-559
Mixture	0.042	0.037	3.074	-546

APPENDIX D-8 Comparison of electrochemical corrosion parameters (40th day) calculated from Figure 4.14

Electrolyte	Parameter			
	ba ($V \text{ dec}^{-1}$)	bc ($V \text{ dec}^{-1}$)	I_{corr} ($A\text{cm}^{-2}$)	E_{corr} (mVolts)
Apple	0.135	0.067	1.346	-520
Grape	0.150	0.062	1.955	-522
Mango	0.147	0.086	1.437	-552
Orange	0.095	0.062	6.027	-550
Mixture	0.157	0.067	1.632	-538

APPENDIX D-9 Comparison of electrochemical corrosion parameters (45th day) calculated from Figure 4.15

Electrolyte	Parameter			
	ba (V dec ⁻¹)	bc (V dec ⁻¹)	I _{corr} (Acm ⁻²)	E _{corr} (mVolts)
Apple	0.170	0.060	1.155	-515
Grape	0.156	0.070	1.341	-520
Mango	0.168	0.093	1.980	-548
Orange	0.172	0.036	1.339	-543
Mixture	0.086	0.056	6.506	-537

APPENDIX D-10 Comparison of electrochemical corrosion parameters (day 50) calculated from Figure 4.16

Electrolyte	Parameter			
	ba (V dec ⁻¹)	bc (V dec ⁻¹)	I _{corr} (Acm ⁻²)	E _{corr} (mVolts)
Apple	0.132	0.059	1.188	-511
Grape	0.125	0.047	8.322	-518
Mango	0.070	0.059	3.622	-540
Orange	0.232	0.064	2.554	-541
Mixture	0.137	0.067	1.179	-523

APPENDIX D-11 Comparison of electrochemical corrosion parameters (55th day) calculated from Figure 4.17

Electrolyte	Parameter			
	ba ($V \text{ dec}^{-1}$)	bc ($V \text{ dec}^{-1}$)	I_{corr} ($A\text{cm}^{-2}$)	E_{corr} (mVolts)
Apple	0.122	0.032	1.568	-494
Grape	0.129	0.036	1.506	-517
Mango	0.245	0.088	2.632	-540
Orange	0.130	0.075	3.920	-536
Mixture	0.177	0.138	1.982	-518

APPENDIX D-12 Comparison of electrochemical corrosion parameters (60th day) calculated from Figure 4.18

Electrolyte	Parameter			
	ba ($V \text{ dec}^{-1}$)	bc ($V \text{ dec}^{-1}$)	I_{corr} ($A\text{cm}^{-2}$)	E_{corr} (mVolts)
Apple	0.169	0.153	5.969	-402
Grape	0.115	0.103	1.034	-499
Mango	0.123	0.065	6.667	-530
Orange	0.157	0.062	1.460	-515
Mixture	0.118	0.084	5.624	-490

APPENDIX E pH values of agro media from weight loss analysis

pH Values of agro media (weight loss)					
Duration(days)	Apple	Grape	Mango	Orange	Mixture
5	4.51	4.08	4.92	4.21	4.48
10	4.52	4.16	5.07	4.35	4.50
15	4.56	4.24	5.33	4.39	4.51
20	4.71	4.24	5.45	4.44	4.63
25	4.83	4.25	5.61	4.60	4.68
30	4.94	4.27	5.63	4.51	4.79
35	5.12	4.30	5.78	4.51	4.83
40	5.35	4.34	5.82	4.53	4.84
45	5.69	4.35	5.90	4.57	4.86
50	5.72	4.39	6.15	4.42	4.89
55	5.93	4.42	6.32	4.52	4.92
60	6.05	4.46	6.46	4.53	4.95

APPENDIX F pH values of agro media from electrochemical analysis

pH Values of agro media (electrochemical)					
Duration(days)	Apple	Grape	Mango	Orange	Mixture
5	4.28	3.98	4.20	4.10	4.09
10	4.41	4.26	4.25	4.15	4.15
15	4.60	4.32	4.30	4.23	4.30
20	4.75	4.39	4.56	4.28	4.41
25	4.92	4.41	4.77	4.31	4.55
30	5.26	4.45	5.00	4.37	4.76
35	5.28	4.47	5.21	4.42	4.84
40	5.63	4.50	5.42	4.48	4.93
45	5.81	4.56	5.58	4.48	5.10
50	5.82	4.58	5.61	4.52	5.26
55	5.87	4.62	5.75	4.53	5.32
60	5.91	4.63	5.77	4.55	5.48