INHIBITION EVALUATION OF CHEMICAL AND PLANT EXTRACTS ON THE CORROSION OF METALLIC ALLOYS IN ACIDIC ENVIRONMENT

BY

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A PH.D THESIS SUBMITTED TO THE SCHOOL OF POST GRADUATE STUDIES, COVENANT UNIVERSITY, OTA, NIGERIA IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF DOCTOR OF PHILOSOPHY IN MECHANICAL ENGINEERING

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CERTIFICATION

This thesis titled **Inhibition Evaluation of Chemical and Plant Extracts on the Corrosion of Metallic Alloys in Acidic Environment** carried out by **OMOTOSHO, Olugbenga Adeshola (CUGP070195)** under our supervision meets the regulation governing the award of the degree of Doctor of Philosophy, Ph.D, in Mechanical Engineering of the Covenant University, Ota, Ogun State, Nigeria. This is to certify that the thesis has not been submitted before now for the degree of Ph.D or any other degree in this or any other University, and that the thesis is approved for its contribution to knowledge and literary presentation.

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DEDICATION

First and foremost, this work is dedicated to God the Fathter, God the Son and God the Holy Spirit. Also, the work is dedicated to the memory of my late loving father, Johnson Badeji Omotosho for your undying love and provision of an enduring ethos for survival.

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ABSTRACT

Numerous failures and eventual losses in the chemical industry have been traced to corrosion processes. Failures resulting from the inability of metals to support designed load requirements because of losses imposed by corrosion effects can be combated economically through the use of chemical inhibitors. Despite the fact that synthetic inhibitors are effective, nonetheless they are associated with problems of toxicity, disposal, litigation and enormous costs. In order to protect the environment and reduce cost, the use of green inhibitors as substitutes and partial replacement of chemical inhibitors have become a method of choice. However, inhibitors are environment specific, therefore necessitating the need for deeper research into the metal-inhibitor-media combination that would produce the best results. In this study, stand-alone and synergistic inhibitor combinations were employed. In the synergistic combination a fractional substitution model was introduced to tailor the inhibitor to a desired performance. Mild steel and Aluminium samples sourced from the chemical industries were immersed in 0.5 M HCl and 0.5 M H_2SO_4 solution in the absence and presence of varying inhibitor concentrations of potassium chromate (PC) (K_2CrO_4), aniline (AN) $C_6H_5NH_2$, *Cassia fistula* (CF), *Terminalia catappa* (TC) and Synergistic Admixtures (SA). Weight Loss (WL) and Tafel Polarization (TP) techniques were adopted. WL data were recorded every 4 days for 60 days, while TP data were obtained instantaneously from the potentiostat after 90 minutes immersion period. Adsorption, Scanning Electron Microscopy (SEM) analysis and Artificial Neural Network (ANN) modelling of the ML data were also conducted. Precisely 1910 WL experiments were performed, out of which the best Inhibitor Efficiency (IE%) was by SA of 2PC+6CF (81.29) for steel in H_2SO_4 and 4PC+4CF (81.27) for Al in HCl media, while the stand-alone systems of CF (54.5) and TC (78.36) at 10 and 4 g/L concentration performed best for steel immersed in HCl and Al immersed in H_2SO_4 respectively. TP results showed the SA of 4PC+4AN, 2PC+6AN, 2PC+6TC and 6PC+2AN as having high IE% of 99.99 for steel in HCl, steel in H_2SO_4, Al in HCl and Al in H_2SO_4 respectively. Langmuir, Freundlich and Frumkin isotherms best described the 16 stand alone systems used based on R-value. Fourteen of the systems were best described by Langmuir while the remaining two were best explained by Freundlich and Frumkin isotherms respectively. SEM analysis indicated that the introduction of the inhibitors stifled the corrosion reactions for mild steel and aluminium in both acid media, as the micrograph displayed an almost smooth surface, while the frequency of pit occurrence was lowered when compared to the uninhibited samples. ANN model results showed that the trend depicted in the experimental data were captured almost perfectly by the neural network fitting tool. Thus, the control of corrosion induced wastage of infrastructure through novel inhibitor systems and the development of a modelling tool that could be used to mimic the exact corrosion process rather than costly experimentation are major contributions of the work. Fuzzy deduction systems and their composite forms are recommended for the development of predictive corrosion rate models.

CHAPTER ONE

1. INTRODUCTION

1.1 Background to the Study

Corrosion is often referred to as metallic deterioration by chemical attack or reaction of a metal with its environment (Popoola et al., 2013). It is an ever present and unceasing problem, often hard to eradicate totally. Deterrence would be more realistic and attainable rather than absolute elimination. Metallic deterioration progresses very fast after the destruction or penetration of the passive barrier which is followed by a number of reactions that alter the constituents and behaviour of both the superficial metal surface and the immediate environment. This is observed in, for example, oxides formation, metal cation diffusion into the coating matrix, local pH changes, and electrochemical potential. The investigation of metallic corrosion is a subject of immense conceptual and practical concern and has thus received a substantial amount of interest. In industrial acid cleaning, pickling, descaling and oil well acidizing operations, acid solutions are widely employed on metal substrates to achieve the intended purpose (Speller et al., 1927; Ajayi et al., 2011a and Omotosho et al., 2011). These processes however, require the use of corrosion inhibitors in order to reduce acid damage on metallic materials.

In the chemical, oil, gas, automobile and transportation industries metallic degradation is one of the main factors influencing the dependability of the systems (Koch et al., 2002). For instance in oil, gas and petrochemical concerns thousands of kilometres of pipeline, pumps, pressure and storage vessels are used to process, store and transport products. These infrastructures are not only critical to the survival of these industries but also indirectly to the economy of the nation. However, because a large majority of these installations with their components are made of carbon steel and aluminium alloys they are inevitably susceptible to corrosion or degradation. In most cases these failures may result in product spillage which is invariably harmful to society as it represents a risk on safety, hazard to the environment and substantial loss of production time and money. It is also bad publicity for such concerns as compensation and litigation may be involved. For these reasons a lot of attention is paid to monitoring and inspection of these facilities. However, the period or duration at which these components are inspected can be prolonged or eliminated by incorporating sound corrosion protection techniques. Moreover, these techniques will reduce corrosion rate and by extension prolong inspection or monitoring time thereby reducing cost of operation.

1.2 Statement of the Problem

Mild steel is the major item of construction of the cisterns in the petrochemical industrial processes involving storage of acids (often referred to as hold up tanks) before use. This is a major operation in all industries utilizing these acids. The mild steel option as a material of choice is because it is cheap and easily obtained when compared to stainless steel (six times as expensive). Also, in the transport of these acids from one point to another in the process plant, mild steel pipings are used because of the cost advantage. These pipings are also connected to fittings (valves, actuators and strainers) made of aluminium alloys and some other metallic alloys in some instances. However, they are prone to the damaging effects of the acid over time as they continuously interact with the acids. The damaging effects become obvious when the load carrying capacity of such facilities like shafts or shell thickness become compromised by reduction in the effective diameter or thickness as a result of metal loss from corrosive attack. The effective diameter or thickness is unable to support the tensile, compressive or radial load and so failure becomes imminent and sometimes catastrophic.

Over the years, reports of product spillage in industries have pervaded the tabloids. Many of such incidents are the direct effect of corrosion on facilities in service. In 2001, a United States (U.S) refinery experienced an incident in which one worker was killed, eight injured and significant offsite environmental impact on the surrounding water body which led to loss of marine life (CSB, 2002). Subsequent ultrasonic test report identified progressive corrosion of sulphuric acid steel storage tank as the major cause of the incidence. In specific terms it said approximately half of the corrosion allowance was used up in the large sections of the entire exposed area of the tank. These meant that the mechanical integrity of the tank was compromised which led to failure of the tank. A finite element analysis of the tank further revealed that the load carrying capacity of the tank had been reduced drastically. Additional challenges associated with these failures include:

- Economic losses such as loss of valuable man-hours,
- Facility replacement cost,

- Litigation for compensation by affected communities,
- Negative publicity,
- Inferred costs resulting from investigating/monitoring, overhaul and revamping and
- Untold hardship on the populace as a result of withdrawal of such facilities from use.

It is thus essential that these metallic structures are protected. Several means are available for preventing or protecting metallic structures in service. These techniques include: materials selection, coatings, cathodic/anodic protection and use of corrosion inhibitors. The use of inhibitors has grown in popularity over the years. There exist two major types of inhibitors. These are organic and inorganic/chemical inhibitors. The inorganic inhibitors contaminate the environment after use and cause a lot of problems like disposal and destruction of plant and animal life. Restrictions have been placed on the use of some of these chemical inhibitors because of their toxic nature (CSPC, 1977). The organic inhibitors are further sub-divided into synthetic or artificial organic inhibitors and the green organic inhibitors. Some of the artificial organic inhibitors are harmful to human existence. The focus of this study therefore, is on the utilization and partial substitution of chemical inhibitors with green inhibitors because it is a sustainable means of arresting corrosion problems. Moreover, it is cheap and easily available. It does not contaminate the environment therefore disposal is not an issue. For this reason litigations are not a common issue of concern. Also, the use of green inhibitors could prove to be an employer of labour. Once suitable plant extracts have been identified by appropriate testing in curtailing corrosion in particular environments by researchers in the field, the information could be communicated to growers who would in turn produce in commercial quantities based on agreements with investors.

Due to its economic and ecological implications and low level awareness, the problems of metallic degradation continue to reoccur worldwide. The world corrosion organization in April 24, 2009 started a campaign of creating awareness for corrosion and the problems associated with it. It was tagged international corrosion awareness day. The purpose was to stimulate education and best practices in corrosion control for socio-economic welfare of society, preservation of resources and protection of the environment.

A methodical scrutiny of numerous research efforts has also shown that gaps exist in the modelling of experimental corrosion data. Chief among such gaps is the fact that there appears to be no Artificial Neural Network (ANN) modelling of experimental data, thereby encouraging constant recourse to experimentation. The direct aim of this work will be to develop a tool that mimics the complex interrelationships of the corrosion process, thereby providing a means to artificially resolve corrosion problems.

1.3 Aims of the Research

The aim of the present research pertains to the generation of measurable and testable experimental data towards the control of corrosion induced wastage of infrastructure through the development of new inhibitor systems.

1.4 Specific Objectives of the Study

The objectives of the research are:

1. To evaluate the effects of potassium chromate, aniline and the extracts of *Cassia fistula* and *Terminalia catappa* on the corrosion of mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 through Weight loss and potentiodynamic polarization measurements;
2. To determine metal-inhibitor interaction mechanism using eight adsorption isotherms namely; Langmuir, Frumkin, Freundlich, Temkin, Flory-Huggins, Bockris-swinkel, El-awady and Dubinin-radushkevich adsorption isotherms;
3. To determine the inhibition mode of the inhibitors using the kinetic parameters;
4. To investigate the surface morphology of the metals in the presence and absence of the inhibitors and
5. To carry out ANN modelling of the corrosion test data emanating from the Weight loss experiments.

1.5 Justification for the Research

Corrosion is the degradation of the metallic properties of a metal. It progressively expends limited mineral resources and the energy utilized in the mining and processing of metals together with that employed in the production of machinery and infrastructures. Corrosion is known to affect practically all facet of contemporary development or advancement, therefore the deterrence of corrosion is of foremost commercial and ecological significance. The world corrosion organization has posited that the annual cost of corrosion globally is approximately 2.2 trillion US dollars. This represents more than 3 % of the World's Gross Domestic Product (GDP) (Koch et al., 2002). In Nigeria, the cost of corrosion has not yet being surveyed; however the Central Intelligence Agency (CIA) world fact book on Nigeria however puts it at an estimated 3.2 billion USD annually (CIA, 2006). This implies that further increases in corrosion control measures are required in every area of human life and industry. From the power sector where energy is generated and the wastewater treatment plants that purify our water to the pipelines and storage cisterns that transport our much needed petroleum products, corrosion control products are being used extensively.

The addition of an inhibitor to a system is one major technique of controlling corrosion. A study conducted by the National Association of Corrosion Engineers (NACE) in 2002, showed that the total expenditure on corrosion inhibitors in the United States increased by 83.3% from about $600 million in 1982 to almost $1.1 billion in 1998 (NACE, 2002). This shows a fast growing interest in the use of inhibitors as a corrosion protection technique. A passive protective film is formed on the metal when the inhibitor interacts with the metal. Inhibitors that work this way are normally the types added to vehicle cooling units and corrosion retarding extracts in protective coatings for metals. Conversely most of the inhibitors employed presently are harmful with attendant undesirable effect on plant and animal life. At the moment in the industrialized countries like the U.S, there is mounting demands by lawmakers for the eradication of heavy metal mixtures and noxious inorganic and organic corrosion inhibitors, thus making research efforts geared towards the enhancement and development of efficient and eco-friendly inhibitors crucial. A look at literature shows that there has been some progress made in the emergence of new and efficient inhibitors currently, meanwhile there is an inclination by lawmakers to abolish several of the inhibitors utilized presently.

Consequently heavy metal based inhibitors like potassium, magnesium, lead, chromates and also those comprising of a mixture of lethal anions (molybdates, benzoates, nitrites, phosphates and fluorides) are to any further extent adequate or suitable. Accordingly, a greater part of inhibitors presently utilized in the metal surface engineering and finishing, chemical, coatings and automobile industry need substitution by eco-friendly materials. Unfortunately too, there are insufficient facts on eco-friendly corrosion inhibitors. Therefore, it is an objective of this work to come up with corrosion inhibitor compositions appropriate for use with hydrochloric and sulphuric acid solutions on steel and aluminium alloys.

1.6 Scope of the Study

The scope of this study includes the following:

i. Laboratory designed experimentation for weight loss study of mild steel and aluminium alloy specimens in hydrochloric and sulphuric acid media in the presence of varying concentrations of inorganic (potassium chromate), organic (aniline) and green inhibitors (extracts of *Cassia fistula* and *Terminalia catappa*);

ii. Potentiodynamic polarization study of mild steel and aluminium alloys in hydrochloric and sulphuric acid media in the presence of varying concentration of inorganic (potassium chromate), organic (aniline) and green inhibitors (extracts of *Cassia fistula* and *Terminalia cattapa*); and

iii. ANN simulation of the corrosion rate data obtained from weight loss experiment.

1.7 Limitation and Delimitation of the Study

Besides the necessity to determine the effects of the inhibitors on the corrosion rate through weight loss measurements, any other measurements and analysis will be restricted to the electrochemical method with particular focus on Tafel polarization method. For this reason this study is not preoccupied with bioaccumulation study, storage stability, durability of the extracts/chemical inhibitors and other non-electrochemical methods. Of course other non-electrochemical methods like chemical analysis and X-ray fluorescence for determining corrosion products in process liquor; acoustic emission with application in the aviation industry; ultrasonic techniques for thickness measurements to detect metal losses caused by corrosion and hydrogen probes for obtaining corrosion rate data have proved very useful in corrosion monitoring. However, electrochemical method of polarization resistance measurements together with weight or Weight loss measurements are adequate enough to carry out the analytical work in this research and results are valid with enough merit. This work is delimited to the use of the linear sweep voltammetry, since the other electrochemical techniques that is available on the DY2312 potentiostat that was utilized in this study, produce same data output which is to evaluate the performance of the inhibitors on the candidate metals. Also, the work is delimited to the use of 8 g/L baseline for the synergy experiments. The combination of the inorganic inhibitor with the organic and the green inhibitors will not exceed 8 g/L. This is the assumed criterion for the synergy (partial replacement model) experiment of this study.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Introduction

This section focuses on literature survey relevant to the corrosion of steel and aluminium alloys in different environments with varying concentration in the presence of a variety of inorganic/organic/green inhibitors. Several environmental conditions exist in industry and most metals are exposed to such conditions. Therefore, an appraisal and review of issues regarding the evaluation of chemical and plant extracts on the corrosion of metallic alloys in acidic environments is presented under the following topics:

- Inhibitor and inhibitor types
- Economic effects and cost implication of corrosion
- Green inhibitor as stand alone
- Multiple green inhibitors
- Steel versatility
- Aluminium versatility
- Significance of hydrochloric acid
- Significance of sulphuric acid
- Artifical neural network application to corrosion inhibition studies

2.2 Inhibitor and Inhibitor Types

The use of corrosion retardants or inhibitors amongst many other techniques offers a versatile means of preventing or controlling corrosion. Several texts and articles have extensively discussed issues relating to corrosion control and protection (Fontana, 1987 and Al-Turkustani, et al., 2012). These techniques include the use of appropriate metals and alloys, metal purification, use of non-metals, altering the environment, design techniques, cathodic and anodic protection, metallic coatings, organic coatings and use of inhibitors. The use of inhibitors primarily involves the introduction of a retarding catalyst into a corrosive media with the sole aim of reducing or eliminating corrosion or degradation. These can be done by using different inhibitor types which have been developed by empirical experimentation with many of such inhibitors being proprietary in nature so that their constituents are not readily available. However, it is possible to classify inhibitors according to their mechanism and composition. Inhibitor types include; adsorption-type inhibitors, hydrogen evolution poisons; scavengers; oxidizers and vapour-phase inhibitors (Fontana, 1987).

Adsorption type inhibitors like organic amines represent the general group of inhibiting substances and are organic compounds which adsorb on the metal surface to stifle metal dissolution and reduction reactions. In most cases, it appears that adsorption inhibitors affect both anodic and cathodic processes, although in many instances the effect is unequal. Arsenic and antimony ions which are hydrogen evolution poisons retard the hydrogen evolution reaction (Fontana, 1987). Thus, they are very effective in acid solutions but are relatively ineffective in media where other reduction processes such as oxygen reduction are the governing reactions. Inhibitors that act by removing corrosive reagents from solutions are scavengers. Such inhibitors include sodium sulphite and hydrazine which remove dissolved oxygen from aqueous solutions and have the ability to work very effectively in solutions where oxygen reduction is the controlling corrosion cathodic reaction but may not be effective in strong acid solutions.

Substances like chromate, nitrate and ferric salts that act as inhibitors in many systems are called oxidizers (Fontana, 1987). They largely retard the corrosion of metals and alloys which demonstrate active-passive transitions, such as iron and its alloys and stainless steels. Vapour-phase inhibitors are very similar to adsorption inhibitors and possess a very high partial vapour pressure. As a result these substances can be used to retard atmospheric corrosion of metals without being placed in direct contact with the metal surface. When in use they are placed in the vicinity of the metal to be protected, and they are transferred by sublimation and condensation to the metal surface. Vapour-phase inhibitors are usually only effective if used in closed spaces such as inside packages or in the interior of machinery during shipment (Fontana, 1987).

Most inhibitors are substances (or a combination of substances) that function, when added in a very low concentration to a corroding system where a metal that is exposed to corrosive environment by diminishing the corrosion rate of the metal. They are also known as site blocking elements, blocking species or adsorption site blockers, due to their adsorptive properties (Jerkiewicz et al., 1995; Koch et al., 2002; Devarayan et al., 2012). The term green inhibitor or eco-friendly inhibitor refers to substances that are biocompatible with nature. Inhibitors like plant extracts presumably possess biocompatibility property due to their biological origin. Similar to the general classification of "inhibitors", "green inhibitors" can also be grouped into two categories, namely organic green inhibitors and inorganic green inhibitors (Devarayan et al., 2012).

Inhibitors are specific in terms of metal, environment, temperature and concentration range. It is important to use enough inhibitor, since many inhibiting agents accelerate corrosion, particularly localized attack such as pitting, when present in small concentrations. Thus, too little inhibitor is less desirable than none at all. To avoid this possibility, inhibitors should be added in excess and their concentration checked periodically. The inhibiting effect that is achieved when two or more inhibiting substances are added to a corrosive system is sometimes greater than that which would be achieved by either of the two (or more) substances separately. This is called a synergistic effect (Fontana, 1987). Even though inhibitors can be used to great advantage to suppress the corrosion of metals in many environments, there are certain limitations of this type of corrosion prevention which should be recognised. The reasons may be that, it is not possible to add inhibitors to all corrosive systems because they contaminate the environment and also that many inhibitors are toxic and their application is limited to those media which will not be used directly or indirectly in the preparation of products which will come in contact with humanbeings. Inhibitors are primarily used in closed systems where corrosive environment is either contained for long periods or re-circulated.

2.3 Economic Effects and Cost Implication of Corrosion

Currently, it is essential to pay a keen interest to corrosion because of several reasons ranging from; increased world population that puts pressure on resources including metal/mineral resources, the utilization of certain metals with protection requiring specific safeguards, utilization of high strength alloys that are more prone to particular kinds of corrosive attack, rising contamination of air and water resources in corrosive environments, burden of disposal and litigation arising from product spillage in corrosion related damage.

Researchers are of the opinion that corrosion is inescapable. Damages due to corrosion can be reduced significantly through a deeper application of the key principles of corrosion. Rather than applying control or preventive measures to corrosion issues the attention in the industry has been disproportionately placed on maintenance. A deliberate focus on corrosion prevention not maintenance or overhaul should therefore be encouraged.

The enormous resources expended on the corrosion challenge (about $6 bn dollars annually in the US alone) is an issue of global concern, though the degree of anxiety may differ from advanced to developing countries but the effort of reducing or preventing the corrosion menace is a key and critical issue the world over. Therefore, several means of adequately combating these challenges must be deployed with extreme determination. The over dependence on the utilization of chemical or harmful organic inhibitors must be dissuaded all over the globe, also, the huge energy investment in producing these toxic chemicals and inconsistency, shortage and dwindling manner of these sources have made them inappropriate and unjustifiable. Consequently, the solution is for researchers to study ways of making appropriate inhibitors massively obtainable. It therefore means that such methods must be inexpensive, easily accessible, widely available and eco-friendly. A source of inhibitor that complies with this description is the GREEN INHIBITOR. It is non-diminishing, readily available, non-hazardous source of valuable protection.

The use of inhibitors has been a technique of choice for controlling corrosion in acidic and alkaline environments (I-Sayed et al., 2001; Loto, 2003; Bouyanzer et al., 2006; Ayeni et al., 2007; Okafor et al., 2008; Norr 2009; Satapathy et al., 2009; Sivaraju and Arulanantham, 2010 and Rmila et al., 2010) as exemplified by the growing number of publications on corrosion inhibition. However, a review by Kesevan et al., (2012) showed that though publications on corrosion inhibition has doubled in the last decade from 4819 between 1991-2000 to 9873 between 2001-2010, only 5% amongst the publication is related to green inhibitors. The increase in research publications shows the current interest in studying novel new inhibitors for varied corrosive environments to reduce the deterioration of different metals. The fact that only 5% amongst the literature on corrosion inhibition is related to green corrosion inhibition shows paucity in available materials and therefore a limitation on the use of green inhibitors. This obviously suggests the need for more research efforts in this area.

2.4 Green Inhibitors as Stand Alone

The subject of toxicity of most synthetic inhibitors is an issue of concern and presently research efforts are geared towards replacing these hazardous substances partly or wholly with natural or green inhibitors. The reason being that, they are proven to be cheap, easily obtained, available and applicable. Moreover, strict environmental legislation has made the focus and emphasis on the utilization of green inhibitors more relevant. The term “green inhibitor” or “eco-friendly inhibitor” refers to the substances that are biocompatible with nature. The inhibitors like plant extracts apparently possess biocompatibility properties due to their biological origin (Koch et al., 2002). Tannins, saponins, flavonoids, alkaloids and other natural products are the organic green inhibitors obtained from natural sources like plants (Jerkiewicz et al., 1995; Koch et al., 2002; Devarayan et al., 2012). Moreover, it also includes synthetic compounds with negligible toxicity.

Overall, green inhibitors are not harmful to human beings and therefore friendly to the environment. These positive attributes and the need to prolong the lifespan of engineering infrastructure by using natural inhibitors have encouraged interest as well as research into these naturally occurring substances as inhibitors. Most of the works done in this research area have focused on solitary (single) use of inhibitors (Ekpe et al.,1994; Ebenso and Ekpe, 1996; Khamis and Alandis, 2002; Rajenderan et al., 2005; Abiola et al., 2007; Rajalakshmi et al., 2008; Abdel Gaber et al., 2008; Umoren et al., 2008; Njoku and Oguzie, 2009; Okafor et al., 2009; De-Souza and Spinelli, 2009; Noor, 2009; Saratha et al., 2009; Eddy and Odoemelam, 2009; Chauhan, 2009; Shyamala and Arulanantham, 2009; Rajenderan et al., 2009; Oguzie et al., 2010; Okafor et al., 2010; Obot and Obi-Egbedi, 2010; Quraishi et al., 2010; Abiola and James, 2010; Ajayi et al., 2011b; Rocha et al., 2012) while few others used multiple inhibitors (Tantawi and Sehim, 1996; Loto, 2001; Quraishi, 2004; Arab et al., 2008;

Dakmouche et al., 2009; Anca et al., 2009; Raja et al., 2010; Al-Turkustani, 2010; Saratha and Vasudha, 2010; Ating et al., 2010; Uwah et al., 2010; Lebrini et al., 2010; Sivaraju and Kannan, 2010; Kasthuri and Arulanantham, 2010; Al-Turkustani et al., 2010; Eddy and Odiongenyi, 2010; Obot et al., 2010 and Omotosho et al., 2010).

For instance Ajayi et al. (2011a) sought to determine the effect of *Vernonia amygdalina* (single inhibitor) plant extract on the failure of mild steel in 2 M sulphuric acid (H_2SO_4) using the gasometric technique. Their result showed that while extract quantity was increasing, hydrogen gas evolution and inhibitor efficiency (IE) was also increasing. In addition, the phytoconstituent-metal interaction mechanism was best explained by Freundlich isotherm, with the 4 minutes curve being the best contact time for extract phytochemicals to properly adsorb to metal surface across all quantities used. The microstructural studies also revealed that increasing the extract quantity led to considerable reduction in the dominant coarsening of the oxide of iron phase, while the pearlite and ferrite phases were highly dispersed.

Recently, Omotosho and Ajayi (2012) used the gasometric method to investigate the acid failure of aluminium alloy in 2 M hydrochloric (HCl) acid solution in the presence of *Vernonia amygdalina* extract. Metal coupons were immersed in test solutions of free acid and those containing extract volumes of 2, 3, 4 and 5 cm^3 at ambient temperature for 30 minutes. The analysis of the result revealed that maximum IE was obtained when inhibitor quantity was 5 cm^3. The reduction in corrosion rate was observed to follow in order of increasing extract volumes. The adsorption study showed that the Temkin isotherm best described the metal surface interaction mechanism, while the 12 minutes curve became the best exposure time for phytochemicals to adsorb to alloy surface. Microstructural studies, showed an indirect relationship between crack growth rates and extract volumes, while consistency of the irregular intermetallic phases increased with increasing extract volumes.

Other recent example from literature shows that the use of single inhibitors is quite popular. Abiola and James (2010) studied the effect of *Aloe vera* extract on the kinetics and corrosion process of zinc in 2 M HCl solution. They found out that a first order kinetic relationship existed between inhibitor phytochemicals and zinc metal surface. The results also revealed that Langmuir adsorption best described the metal-extract interaction mechanism. On the other hand, Eddy and Odoemelam (2009) investigated the inhibition of corrosion of mild steel in sulphuric acid using ethanol extract of *Aloe vera*. Their study was conducted at 303 and 333K using the gasometric technique and it showed the existence of a chemical adsorption isotherm. Mild steel coupons in 1 M HCl in the presence of *Menta pulegium* extract were studied by Bouyanzer et al. (2006). The studies were conducted using weight loss measurements, electrochemical polarization and electrochemical impedance spectroscopy methods. Their findings revealed *Menta pulegium* as a cathodic inhibitor.

De Souza and Spinelli (2009) immersed mild steel samples in 0.1M H_2SO_4 acid solution in the presence of caffeic acid using weight loss, potentiodynamic polarization, electrochemical impedance and raman spectroscopy. The results of their study showed that caffeic acid controlled the anodic reaction during the experiment.

Also, Okafor et al. (2008) immersed mild steel samples in 1 M HCl and H_2SO_4 solution in the presence of a combination of leave and seed extracts of *Phylanthus amarus* using weight loss and gasometric techniques. They discovered that the extracts adsorption to the metal was best explained by Temkin isotherm. Another single inhibitor use was conducted by Noor (2009) in which *Hibiscus sabdarifa* leave extract were used as corrosion inhibitor in 0.5 M sodium hydroxide (NaOH) solution. Aluminium alloy was immersed in the solution and its corrosion was monitored by electrochemical impedance spectroscopy, potentio-dynamic polarization and weight loss measurements. Results show that Langmuir adsorption isotherm best explained metal-extract interaction mechanism. The inhibitor also showed mixed-type inhibition behaviour.

Weight loss and thermodynamic studies at temperatures of 30, 50 and 70^0C were conducted on Al-Zn-Mg chilled cast alloy immersed in 0.5 M NaOH solution in the presence of *Hibiscus teterifa* by Ayeni et al. (2007). It was discovered that corrosion inhibition was achieved by adsorption of molecules of hibiscus teterifa extracts on the alloy surface having the resultant effect of blocking active corrosion sites. The adsorption mechanism was best explained by Langmuir adsorption isotherm. Another study of mild steel in 1 M HCl and 0.5 M H_2SO_4 in the presence of *Murraya koenigii* was conducted by Quraishi et al. (2010). The techniques used include weight loss, electrochemical impedance spectroscopy, linear polarization and potentio-dynamic polarization. It was discovered that the interaction between metal surface and extract phytochemicals was best explained by Langmuir adsorption isotherm.

Furthermore, mild steel was immersed in 1 M HCl solution in the presence of *Murraya koenigii* using weight loss, gasometric, electrochemical polarization, impedance measurements and scanning electron microscope (SEM) at a temperature range of 30-80^{0}C by Rmila et al. (2010). The results of the study showed that the protective film was deposited on the metal surface and inhibitor efficiency (IE) decreased as temperature increased.

Also, corrosion inhibition of mild steel in 2 M sulphuric acid by aqueous extract of *Ajowan* (carom) seeds was studied using hydrogen evolution, Weight loss and impedance measurements at 30^{0}C by Al-Turkustani (2010). The results revealed that *Ajowan* extract inhibited the corrosion process in 2 M H_2SO_4 and the IE increased as concentration increased. The impedance studies further revealed that charge transfer influenced the degradation process of mild steel across the phase boundary with and without the inhibitor. The potentiodyanamic polarization results indicated that *ajowan* seeds extract acted as mixed type inhibitor. The IE obtained from all methods utilized was in good agreement. Adsorption mechanism of ajowan extract molecules on steel surface is impulsive and it is attributed to the Freundlich adsorption isotherm. Lebrini et al. (2011) examined the effects of steel immersed in 1 M HCl acid in the presence of *Oxandra asbeckii* plant extract using the electrochemical techniques of potentiodynamic polarization and electrochemical impedance spectroscopy at a temperature range of 25 - 55^{0}C. Experimental results from the study revealed mixed type inhibition behaviour and Langmuir adsorption isotherm best explained the metal-extract interaction mechanism.

Lebrini et al. (2010) used potentio-dynamic polarization and electrochemical impedance methods to investigate the effect of alkaloid extract of *Annona squamosa* on corrosion inhibition of steel in 1 M HCl acid solution. The results of the study showed the inhibition mechanism as mixed and the adsorption behaviour was best explained by Langmuir adsorption isotherm. The effect of *Chromolaena odorata* extract on the corrosion of aluminium alloy in 2 M HCl acid solution at a temperature range of 30-60^{0}C was investigated by Obot and Obi-Egbedi (2010) using gasometric and thermometric techniques. Results obtained showed that the Leaf Extracts of *Chromolaena odorata* (LECO) functioned as an excellent corrosion inhibitor for aluminium in acidic environment. IE increased with extract concentration but decreased with temperature. The adsorption mechanism of LECO on Al surface was in accord with Langmuir adsorption isotherm. It was deduced from the experimental results obtained, that LECO have the potential to be a cost effective alternative to synthetic corrosion inhibitors. Furthermore, asides from providing new information on the inhibiting characteristics of LECO extract under stated conditions, it was also discovered that the inhibitor could find suitable use in metal surface anodizing and surface coating industries.

Another single inhibitor investigation by Eddy and Odiongenyi (2010) was conducted on mild steel immersed in sulphuric acid solution in the presence of ethanol extract of *Heinsia crinatia*. The techniques adopted in the study were weight loss, thermometric, hydrogen evolution and infrared spectroscopy for surface analysis. The IE of the extract varied with concentration of the extract, period of immersion and temperature. The extract is adsorbed impulsively on the surface of mild steel sample in accordance with Temkin and Frumkin adsorption isotherms. The mechanism of physical adsorption was proposed from the trend in the values of IE with temperature as well as the values of some kinetic and thermodynamic parameters calculated in the study.

In another study on green inhibitor, the immersion of mild steel in 1 M HCl and 0.5 M sulphuric acid solutions in the presence of *Dacryodis eduli* at room temperature was investigated for corrosion inhibition by Oguzie et al. (2010). The techniques adopted were gasometric and electrochemical techniques. The plant extract was found to inhibit the uniform and localized corrosion of steel in the acidic media. Studies on aluminium alloy coupon immersed in HCl solution in the presence of ethanolic extract of *Ananas sativum* were conducted using the weight loss and hydrogen evolution method. The study was carried out by Ating et al. (2010) and results of the investigation revealed very high activation enthalpy, entropy and high activation energies. Langmuir isotherm best described the metal-extract interaction mechanism. Raja et al. (2010) investigated corrosion inhibition behaviour of mild steel in 1 M HCl and H_2SO_4 solution in the presence of *Kopsia singapurensis* using electrochemical techniques such as potentiodynamic polarization and AC impedance. Investigations revealed the inhibitor as anodic and mixed type inhibitor in HCl and H_2SO_4 respectively.

Further single green inhibitor investigation was conducted by Obot et al. (2010). The candidate metal employed was aluminium alloy and it was immersed in 1 M HCl solution in the presence of *Ipomoea invulcrata*. Weight loss, kinetic and thermodynamic techniques were employed for the study which was conducted at a temperature range of 30-60^{o}C. Langmuir adsorption isotherm best described the metal-extract interaction mechanism.

A recent investigation by Saratha and Vasudha (2010) indicated that *Emblica officinalis* leaves extract acted as a mixed type inhibitor for mild steel in 1 M HCl medium. The study which utilized a single inhibitor was conducted using weight loss, potentio-dynamic polarization and impedance techniques. The result showed the inhibitor as having efficiency of 87.9% at 2% v/v inhibitor concentration. It was also revealed that corrosion inhibition may be due to the impulsive physical adsorption of the phytochemicals on the mild steel surface and exothermic adsorption process as shown by the negative enthalpy value. Experimental data fitted the Freundlich, Langmuir, Temkin and Flory- Huggins adsorption isotherms. Sivaraju and Kannan (2010) conducted another study on the use of single inhibitor, alcoholic extract of *Tributes terrestris* was employed as corrosion inhibitors for mild steel in 1 M phosphoric acid solution. The techniques adopted were the Weight loss and polarization methods to obtain corrosion data, while Scanning Electron Microscopy was used for surface analysis. Results from the study showed Temkin adsorption isotherm as having the best fit with experimental data. The inhibitor also showed mixed-type inhibition behaviour. The extracts of *euphorbia hirta* as corrosion inhibitor on mild steel in sulphuric acid medium was investigated by Kasthuri and Arulanantham (2010) using weight loss measurements. The results showed the Temkin isotherm as the best adsorption isotherm that best fits the experimental data.

The inhibition effect of the alcoholic extract of *Acalypha indica* on mild steel corrosion in 1M phosphoric acid was conducted by Sivaraju and Arulanantham (2010) using Weight loss and polarization techniques at a temperature of 303 and 333 K. Results showed that inhibition efficiency increased with increase in concentration of plant extract. The corrosion rate increased with increase in temperature and decreased with increase in concentration of inhibitor compared to blank. The adsorption of inhibitor on mild steel surface was found to obey Temkin's adsorption isotherm. It is found that *acalypha indica* acted as a mixed-type inhibitor. Fourier Transform–Infrared (FT-IR) and SEM analysis showed the presence of compounds in the plant extract that reacted with metal ion to form a thin film on the metal surface. Another single inhibitor study by Al-Turkustani et al. (2010) investigated the use of *Ruta chalepensias* as a corrosion inhibitor for steel in 2 M sulphuric acid solution. The methods adopted include hydrogen evolution, Weight loss, potentiodynamic polarization and impedance techniques. Surface analysis was conducted using SEM. The results of the study revealed that *Ruta chalepensias* is a mixed-type inhibitor and its adsorption mechanism is best explained by the Langmuir adsorption isotherm.

The corrosion inhibition of mild steel in 1 M hydrochloric acid solution by *Justicia gendarussa* plant extract (JGPE) was conducted by Satapathy et al. (2009) at 25^0C using weight loss and electrochemical techniques. Surface analysis was conducted using (Atomic Force Microscopy) AFM and Electron Spectroscopy for Chemical Analysis (ESCA). The result showed that inhibition efficiency of 93% was achieved with 150 ppm JGPE at 25 °C. Also, the polarization studies showed that JGPE has mixed-type inhibitor behaviour. The Nyquist plots revealed that increased JGPE concentration led to corresponding increases in charge transfer resistance and decreased double layer capacitance. Furthermore, JGPE obeys the Langmuir adsorption isotherm. The adsorption of JGPE on mild steel surface was established by AFM and ESCA.

Another study on the inhibition of secnidazole (SEC) on the corrosion of mild steel in 0.01-0.04 M H_2SO_4 at 303-323 K was conducted using gravimetric method by Ebenso and Obot (2010). Results obtained revealed that SEC inhibits mild steel corrosion in H_2SO_4 solution. The IE had a direct relationship with SEC concentration, while it had an indirect relationship with acid concentration and temperature. This implied the existence of a physical adsorption mechanism although chemisorption may be the cause. Langmuir adsorption isotherm best explained the adsorption of SEC onto the mild steel surface. Furthermore, the kinetic parameters (activation energy, pre-exponential factor, enthalpy of activation and entropy of activation) and thermodynamics of adsorption (enthalpy of adsorption, entropy of adsorption and Gibbs free energy) were calculated. Quantum chemical calculations using Density Functional Theory (DFT) was further used to calculate the electronic properties of the molecule in order to determine any correlation between the inhibitive effect and molecular structure of SEC. The calculations using DFT showed that the adsorption of SEC on mild steel was initiated through the imidazole heterocyclic ring, the nitro and hydroxyl functional groups which forced the inhibitor molecule to have a plane orientation at the metal surface. The use of SEC led to a passive film formation on the mild steel surface, perhaps containing the complex of SEC-Fe^{2+}, and having the potential of protecting the steel from corrosion.

Saratha and Vasudha (2009) investigated mild steel corrosion in 1 M sulphuric acid medium using acid extracts of *Nycanthes arbortristis* leaves. The study was carried out by weight loss and polarization techniques. The results of the study showed that the inhibitor was a mixed-type inhibitor and an efficiency of 90% was attained. Okafor et al. (2009) also conducted another single inhibitor investigation using extracts of *Combretum bracteosum* leaves in 1 M sulphuric acid solution with mild steel. The techniques adopted were the gravimetric and gasometric methods at a temperature range of 30 to 60^0C. The results of the study proved the suitability of the inhibitor as a useful agent in chemical cleaning and pickling processes. It also showed that the Frumkin isotherm best explained the interaction mechanism between metal and plant phytochemicals.

Shyamala and Arulanantham (2009) worked on extracts of *Eclipta alba* as pickling inhibitor for mild steel in 1 M HCl solution using gravimetric, polarization and impedance techniques. The results of the study showed that the inhibitor acted as a mixed type inhibitor and metal extract interaction was best fitted to the Langmuir adsorption isotherm.

Saratha et al. (2009) used weight loss measurements and electrochemical techniques to study the effect of *Citrus aurantiifolia* leaves extracts on mild steel immersed in 1 M HCl solution. The study was able to establish that *Citrus aurantiifolia* exhibited a mixed-type inhibition behavior with IE of 97.51%. Experimental data were also well fitted to the Langmuir, Temkin, Freundlich, Frumkin and Flory-Huggins adsorption isotherms.

Rajendran et al. (2009) conducted a study on the corrosion behavior of aluminium in the presence of an aqueous extract of *Hibiscus rosasinensis* at a pH of 12 with the inclusion of zinc ion additive in the media. The methods adopted included gravimetric and (alternating current) AC impedance. The surface analysis technique used was Fourier Transform Infra Red (FTIR). The results of the study showed that the inhibitor was a cathodic inhibitor.

Another single inhibitor study of the ethanol extract of *Aloe vera* on the corrosion of mild steel in sulphuric acid solution at temperatures of 303 and 333K was conducted by Eddy and Odoemelam (2009) using gasometric and thermometric methods. The concentrations of inhibitor used were 0.1, 0.2, 0.3 and 0.4g/L. The result showed the suitability of ethanol extract of *Aloe vera* as a good inhibitor for mild steel corrosion at 303 and 333K. The inhibition mechanism is by chemical adsorption isotherm. Also, the functional groups identified in the extract may have played dominant roles in the adsorptive and inhibitive potentials of this extract. The values of IE obtained from gasometric and thermometric analysis were discovered to be analogous.

Raja and Sethuraman (2009) worked on the use of *Solanum tuberosum* as an inhibitor of mild steel corrosion in acid media of HCl and sulphuric acid using weight loss and electrochemical techniques at temperatures of 303, 313 and 323 K. The surface analysis technique employed was the SEM. Result revealed mixed type inhibitor behavior and the interaction mechanism between metal and extract was best fitted to the Temkin isotherm.

The anticorrosion behaviour of *Zenthoxylum alatum* extract in 0.1 M HCl media was investigated by Chauhan (2009). The methods used were the weight loss and electrochemical techniques and the experiment was conducted at room temperature. The results of the study showed that the experimental data fitted Langmuir adsorption isotherm the most. Another instance of single inhibitor use was by Oguzie (2008) in which he conducted a study on corrosion inhibitive effect and adsorption behaviour of *Hibiscus sabdariffa* on mild steel in acidic media containing 2 M HCl and 1 M H_2SO_4 using the gasometric technique. The results showed the inhibitor behavior as a mixed type and interaction mechanism between metal and extract was best fitted to Langmuir adsorption isotherm.

The observation from all this previous studies is that all the experiments employed the traditional weight loss method which involved weighing before immersion of the candidate metal and re-weighing after removal from the media when the experimental time is reached. The same metal was subsequently re-immersed to carry out the experiment for the next interval. Adoption of this technique did not allow the completion of all chemical reactions taking place. The removal and subsequent immersion deprived the metal from achieving maximum surface coverage that might better explain the behaviour of the inhibitor upon completion of the experiment.

A scrutiny of the previous studies also revealed that none of the studies used artificial intelligence tool to systematically model inhibitor behaviour. Artificial intelligence tool are rapidly gaining popularity in corrosion studies but has not been used for corrosion inhibition studies based on available literature. They can assist engineers in solving some fundamental corrosion engineering problems, such as corrosion rate prediction from inhibitor responses with accuracy comparable to actual analysis. The tool is also capable of addressing case specific problems that may be encountered in the field. This work also will apply artificial intelligence to achieve this objective.

Furthermore, another study by Rajalakshmi et al. (2008) studied the efficacy of sprouted seed extracts of *Phaseolus aureus* on the corrosion inhibition of mild steel in 1 M HCl solution using the gravimetric and electrochemical techniques at room temperature of 25^0C. The result indicated IE of 93% and a mixed type inhibition behavior was exhibited by the inhibitor employed for the study.

The inhibition of aluminium corrosion in alkaline solutions using natural compound was investigated by Abdel-Gaber et al. (2008) and conducted by gasometric and electrochemical techniques. The study was conducted at a room temperature of 25^oC. The result of the study revealed a mixed type inhibitor behavior. Umoren et al. (2008) worked on the adsorption and corrosive inhibitive properties of *Vigna unguiculata* in alkaline and acidic media using weight loss and electrochemical studies at temperature of 30 and 60^0C on aluminium substrate. The result of the study indicated anodic inhibitor behavior, while the experimental data of the metal-extract interaction mechanism best fitted the Freundlich and Temkin adsorption isotherm. Premkumar et al. (2008) investigated the extract of *Thymus vulgar L.* as volatile corrosion inhibitor for mild steel in sodium chloride environment using weight loss and electrochemical techniques at a temperature of 25^0C. Results of the study showed that the Temkin isotherm best explained the metal-extract interaction mechanism.

Studies on the inhibitive effect of *Datura stramonium* extract on the acid corrosion of mild steel was conducted by Raja and Sethuraman (2007) using weight loss and electrochemical techniques. Surface analysis was carried out using the SEM apparatus. Results from the study indicated a mixed-type inhibition and metal-extract interaction mechanism is best explained by the Temkin isotherm.

Ayeni et al. (2007) conducted a study on the non-toxic plant extract of *Hibiscus teterifa* as corrosion inhibitor for chill cast Al-Zn-Mg alloy in caustic soda solution using weight loss and thermometric studies at temperatures of 30, 50 and 70^0C. The outcome of the study revealed that the adsorption mechanism between metal and extract was best fitted to the Langmuir adsorption isotherm.

El-Etre (2007) worked on the corrosion inhibition of carbon steel in 2 M HCl solution using aqueous extract of olive (*Olea europaea L.*) leaves using weight loss measurements, tafel polarization and cyclic voltammetry at room temperature of 30^0C. The Langmuir adsorption isotherm best explained the interaction mechanism.

A study by Gunasekaran and Chauhan (2004) which employed *Zenthoxylum alatum* inhibitor for corrosion inhibition of mild steel in aqueous orthophosphoric acid medium at a temperature range of $50\text{-}80^0$C using the weight loss and electrochemical techniques. Surface analysis procedure was done using X-ray photoelectron spectroscopy (XPS) and FT-IR. Results showed that the extract is effective in 88% phosphoric acid medium at a temperature of 70^0C.

Chauhan and Gunasekaran (2007) conducted a study on the corrosion inhibition of mild steel by *Zenthoxylum alatum* extract in dilute HCl medium using the weight loss and electrochemical impedance techniques at a temperature range of 50-80^{0}C. Surface analysis was carried out through the use of the SEM, XPS and FT-IR. Results showed the Langmuir adsorption isotherm as the best isotherm that explained the interaction between the metal and the extract.

A study on the adsorption and corrosion inhibitive properties of *Azadirachta indica* in acid solutions of HCl and H_2SO_4 on mild steel was conducted by Oguzie (2006) at ambient temperature of 30^{0}C using the gasometric technique. Results of the study indicated the inhibitor as having a mixed-type inhibition behavior and the metal-extract interaction mechanism was best explained by the Langmuir isotherm.

Abdel-Graber et al. (2006) studied the effect of temperature on inhibitive action of *Ambrosia maritime L.* extract on the corrosion of steel in acidic media at a temperature of 25-40^{0}C using the weight loss measurement and electrochemical techniques. Results showed mixed type inhibition behavior and the experimental data were well fitted to the Langmuir, Frumkin and Flory- Huggins adsorption isotherms. Another single inhibitor work by Sethuram and Raja (2005) carried out studies of the corrosion inhibition of mild steel by *Datura metel* in 1 M H_2SO_4 medium using electrochemical and weight loss methods. The study showed the viability of the plant extract as a suitable inhibitor of corrosion in the industry and the experimental data were well fitted to the Temkin and Langmuir adsorption isotherm. The inhibition of mild steel corrosion in H_2SO_4 medium by *Allium sativum* extracts was investigated by

Okafor et al. (2005) using weight loss and gasometric techniques. Results show that experimental data was well fitted to the Langmuir adsorption isotherm. Sathiyanathan et al. (2005) tested the ethanolic extract of *Ricinus communis* leaves for corrosion inhibitory effects towards mild steel in 100ppm sodium chloride solution. The study was carried out using weight loss, electrochemical polarization and impedance measurements. Results showed weight loss measurements to have inhibition efficiency of 84 % in 300 ppm of plant extract. Polarization measurement indicated that the plant extract acted as an anodic inhibitor while impedance result show that plant extracts increased corrosion resistance and the formation of iron-organic complex reduced corrosion resistance of mild steel in neutral solution.

El-Etre et al. (2005) investigated the aqueous extract of the leaves of *Henna* (*Lawsonia*) as corrosion inhibitor of carbon steel, nickel and zinc in acidic, neutral and alkaline solutions, using the polarization technique. It was found that the extract acted as a good corrosion inhibitor for the three tested electrodes in both media. The inhibition efficiency increases as the extract concentration increased. The degree of inhibition depends on the nature of metal and the type of the medium. For carbon steel and nickel, the inhibition efficiency increases in the order: alkaline < neutral < acid, while in the case of zinc it increases in the order: acid < alkaline < neutral. The extract acted as a mixed type inhibitor. It was found that the adsorption followed Langmuir adsorption isotherm in all tested systems. The formation of a complex between metal cations and lawsonia was also proposed as additional inhibition mechanism of carbon steel and nickel corrosion.

Another study on the corrosion inhibition of aluminum in hydrochloric acid solutions by peepal (*Ficus religeosa*) extracts by Weight loss and thermometric methods was conducted by Jain et al., (2005). It was discovered that the corrosion inhibition efficiency was dependent on the concentrations of the inhibitor and the acid media.

Soror, (2004) carried out a study on *Medicago polymorpha roxb*. Medipolymorphol, a new sterol isolated from the whole plant of *Medicago polymorpha roxb* was used as corrosion inhibitor for stainless steel (316) in 5% HCl at room temperature. Electrochemical techniques have been established to be reliable in evaluating system corrosion characteristics, thus several of such techniques were employed. These include; tafel, linear polarization, potentio-dynamic polarization, and open circuit potential (OCP) studies. The result indicated that the additives slowed down the anodic process, intensified the cathodic process and provided a stable passive state, giving good inhibition efficiencies to stainless steel electrodes. Furthermore, adsorption isotherm was fitted for the inhibitor under investigation and Langmuir adsorption suitably fits the experimental data.

Another single inhibitor work by El-Etre (2003) studied the inhibition of aluminium corrosion using *Opuntia* extract in 2 M HCl media by the weight loss, thermometric, hydrogen evolution and polarization techniques. The results of the study showed that Langmuir adsorption isotherm best explained the metal-extract interaction mechanism.

Loto and Mohammed (2003) worked on the inhibition evaluation of mango juice extracts on the corrosion of mild steel in 0.1M HCl solution using weight loss and potential measurement techniques at ambient temperature. The results of the study showed that 5ml/100ml juices of bark and leaves gave high inhibition efficiency. Loto (2003) carried out another study on the effect of bitter leaf extract on the inhibition of mild steel in HCl and H_2SO_4 at temperature of 28 and 80^0C using weight loss and polarization techniques. The result showed the inhibitor to be effective at 28^0C in the 0.5 M HCl solution.

Another study on the extract of *Andrographis paniculata* as corrosion inhibitor of mild steel in acid medium was conducted by Ramesh et al. (2001). The study was performed using the following techniques; Weight loss, tafel polarization and impedance techniques. The study revealed the plant extract as having the potential of serving as an excellent inhibitor. Loto and Mohammed (2000) carried out a study on the effect of cashew (*Anacardium occidentale*) juice extract on corrosion inhibition of mild steel in 0.1M HCl solution at ambient temperature using weight loss and potential measurements. The outcome of the study showed that 2ml/100ml HCl gives good inhibition efficiency.

Nigam and Srivastava (1998) studied the role of amaranthus on the dissolution of mild steel in sulphuric acid medium using weight loss techniques at ambient temperature. Results of the study showed that metal-extract interaction mechanism was best explained by Langmuir adsorption isotherm thus the chemisorptions mode was proposed. El-Etre (2007) investigated the inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves using weight loss, tafel polarization and cyclic voltammetry techniques. The result of the study showed that olive extract decreased the charge density in the transpassive region and the metal-extract interaction mechanism was best explained by Langmuir adsorption isotherm.

Fekry and Mohamed (2010) studied the effect of acetyl *Thiourea chitosan* (ATUCS) as an eco-friendly inhibitor for mild steel in sulphuric acid medium using potentiodynamic polarization and electrochemical impedance spectroscopy. The surface analysis was carried out using SEM. The ATUCS showed very good inhibition efficiency of 94.5% in 0.5 M sulphuric acid. This efficiency was obtained at a concentration of 0.76 M.

The effect of *Zenthoxylum alatum* plant extract on the corrosion inhibition of mild steel in varying phosphoric acid medium was investigated by Gunasekaran and Chauhan (2004) using weight loss measurements and electrochemical impedance spectroscopy at 50 and 80^0C. Surface analysis was done with XPS and FT-IR. The inhibitor was found to be effective up to 70^0C in 88% phosphoric acid medium.

Weight loss, electrochemical impedance spectroscopy and linear polarization were the techniques adopted by Quraishi et al. (2010) to study the effect of extracts of *Murraya koenigii* leaves on mild steel corrosion in hydrochloric and sulphuric acid solutions. The study showed the experimental data to be best fitted to Langmuir adsorption isotherm.

Subhashini et al. (2010) used the weight loss and potentiodynamic polarization technique to investigate the effect of *Cyamopsis tetragonaloba* seed extract on mild steel in 1 M HCl solution at ambient temperature. The IE was found to be 92% while metal-extract interaction mechanism was best explained by the Temkin and Langmuir adsorption isotherm.

Rajalakshmi et al. (2009) studied the inhibiting effect of seed extracts of *Abrus precatorius* on corrosion of aluminium in sodium hydroxide at ambient temperature using weight loss and polarization techniques. Several adsorption isotherms were tested and the Langmuir adsorption best explained the adsorption mechanism.

Buchweishaija and Mhinzi (2008) used the gum exudates from *Acacia seyal var.seyal* as a corrosion inhibitor for mild steel in drinking water at ambient temperature of 30^0C. The study was conducted by the potentiodynamic polarization and electrochemical impedance spectroscopy techniques. It was revealed from the study that when gum concentration was 400ppm the IE was 95% and efficiency decreased with temperature, while its inhibitive effect was anodic.

Okafor, et al., (2009) performed an experimental study on the effect of *Combretum bracteosum* extracts as eco-friendly corrosion inhibitor for mild steel in sulphuric acid medium using the gravimetric and hydrogen evolution technique at a temperature range of $30\text{-}60^0$C. The study showed that the metal extract interaction mechanism was best explained by the Frumkin isotherm.

A study on the effectiveness of ginseng root extract on the corrosion inhibition of aluminium alloy of type AA 1060 in hydrochloric acid solution was carried out by Obot and Obi-Egbedi (2009) at a temperature range of $30\text{-}60^0$C. The result of the study showed IE of 93.1% at 30^0C at 50% v/v concentration of ginseng. The adsorption isotherm that best explained metal-extract interaction mechanism is the Freundlich adsorption isotherm.

Another single inhibitor study on the adsorption and corrosion inhibitive properties of *Vigna unguiculata* in 0.5 M NaOH and sulphuric acid solution was conducted using weight loss and electrochemical methods by Umoren et al. (2008). The study was carried out at temperatures of 30 and 60^0C. The study result showed that the experimental data were best fitted to Freundlich and Temkin adsorption isotherm. Bouyanzer and Hammouti (2004) carried out a study on naturally occurring ginger as corrosion inhibitor for mild steel in hydrochloric acid at 353 K using weight loss measurements. The study showed that IE increased as temperature increased.

A critical look at previous literatures shows that none is yet to model the interactions across the corrosion inhibition system. Modelling of the corrosion inhibition system allows detailed analysis of individual parameters such as time, temperature and inhibitor concentration as well as the quantification of the interactions that occur throughout the entire inhibition process. Thus, the key benefit will be to use the number of experimental runs to rapidly screen and rank options, thereby accelerating deployment. Moreover, ANN modelling of corrosion inhibition process will take into account a set of inter-related parameters as a whole system that interacts in many different ways. Also, artificial intelligence is known to benefit from large experimental runs, thus, all the previous studies may not find adaptability to artificial intelligence modelling. However, it is the focus of this research to increase the experimental runs so as to increase the possibility of its applicability to artificial intelligence modelling.

2.5 Multiple Green Inhibitors

Many other researchers carried out studies on the effect of green inhibitors on the degradation of metals using more than one inhibitor (multiple inhibitors). Okafor et al. (2010) investigated the effect of leaves (LV), root (RT) and seeds (SD) extracts of *Azadirachta indica* on the corrosion behavior of mild steel in sulphuric acid solution using weight loss and gasometric techniques. The results obtained indicate that the extracts functioned as good inhibitors in acid solutions. Inhibition efficiency was found to increase with extracts concentration and followed the trend: SD > RT > LV. Based on the trend of inhibition efficiency with temperature and from the obtained values of activation energy and heat of adsorption, the corrosion inhibition was attributed to chemical adsorption of the phytochemical components of the plant on the surface of the mild steel. A mechanism of chemical adsorption of the phytochemical components of the plant extracts on the surface of the metal was proposed for the inhibition behaviour. The Freundlich adsorption isotherm best describes the adsorption mechanism.

Studies on leaf, bark and root extract of *Nauclea latifolia* were also conducted by Uwah et al. (2010). Mild steel samples were immersed in sulphuric acid solution in the presence of *Nauclea latifolia* extract at a temperature range of 30-60^{0}C. Weight loss and gasometric techniques were used to carry out the experiment. The extracts were discovered to retard corrosion of mild steel in sulphuric acid solution and the efficiencies of the inhibitor follow the order: root > leaf > bark. IE increased as the concentration of extract was increasing, while it reduced when temperature increased. Adsorption of the phytochemical components of the plant on the metal surface was proposed as a physical adsorption mechanism.

Loto (2001b) did another work on the effect of mango bark and leaf extract solution additives on the corrosion inhibition of mild steel in dilute sulphuric acid at ambient temperature using weight loss and potential measurement techniques. It was however revealed from the study that 1ml of the combined extracts/100ml of sulphuric acid shows efficiency of 70.15% and 0.5 ml/100ml is also effective but the extent of IE was below average. Furthermore, at 1.0ml/100ml of 0.2M dilute sulphuric acid concentration gave good IE. Rajenderan et al. (2005) investigated the inhibition efficiency of an aqueous extract of rhizome (*Curcuma longa L.*) powder, in controlling corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of Chloride ion, in the absence and presence of Zn^{2+}, using a mass-loss method. The study also examined the influence of pH on the inhibition efficiency of the plant extract and analyzed the protective film by Fourier transform infrared (FTIR) spectroscopy and fluorescence. The outcome of the study showed a synergistic effect between rhizome powder and Zn^{2+}, with the protective film consisting of Fe^{2+} , curcuma complex and zinc hydroxide.

The inhibition efficiency of an aqueous extract of garlic in controlling corrosion of aluminium immersed in sodium hydroxide solution at a pH of 11 and 12, in the absence and presence of Zn^{2+}, was evaluated using the weight loss method by Priya et al. (2005). The influences of N-cetyl-N, N,N-trimethylammonium bromide (CATB) (a biocide and a cationic surfactant) and immersion period on the inhibition efficiency were investigated.

The protective film was analysed with the use of Fourier transform infrared spectra. The outcome of the study showed that at pH 11, the extract accelerated corrosion of aluminium in the absence and presence of Zn^{2+}. The influence of sodium sulphite, an oxygen scavenger, on the inhibition efficiency of the inhibitor system revealed that transport of inhibitor towards the metal surface plays a greater role than the removal of oxygen from the aqueous solution in determining the inhibition efficiency of the system. FTIR analysis of the passive film showed the formation of a complex compound consisting of all the participating ions. Table 2.1 (pages 42-60) shows a list of investigation conducted by researchers on multiple (synergy) inhibitor use.

All of the findings point to the fact that the inhibitors (*Cassia fistula* and *Terminalia catappa*) being utilized in this study may not yet have been utilized in the manner used in this work. Other studies that were examined utilized the conventional weight loss method in which metal samples are initially weighed, then immersed in the test solution for weight loss experiment for the specific duration. The same sample is then re-immersed for the next interval duration of experiments. This method may be fraught with errors because removing and re-immersing the metals samples makes it impossible to capture in accurate terms the metal surface interactions with the inhibitors. Thus, an inconsistency may be introduced into the formation and breakdown of corrosion products on the metal surface which may interfere with accuracy of the measurements. In this work weight loss measurements were carried out by setting up experiments for each interval of observation. Thus, eliminating re-immersion after the interval has been completed. In other words, each metal sample

Table 2.1: Summary of multiple inhibitor corrosion experiments.

S.No.	Substrate	Media	Green Inhibitor	Technique/ Surface Analysis	Result	Conventional Weight loss
1.	Steel	1 M HCl	Extracts of orange, mango, passion fruit and cashew peels	Electrochemical impedance spectroscopy, potentiodynamic polarization, weight loss and surface analysis techniques	The IE increased as extract concentration increased but decreases with temperature. Langmuir adsorption isotherm best fitted the experimental data (Rocha et al., 2010).	Yes / not used

S.No.	**Substrate**	**Media**	**Green Inhibitor**	**Technique/ Surface Analysis**	**Result**	**Conventional Weight loss**
2.	Mild steel		*Azadirachta indica*, *Agaricus*, *cordia*, *Latifolia*,*curcumin*, *Eucalyptus*, *hibiscus*, *jasminum*, *Momordica*, *charantia* and *Punica granatum*	Weight loss polarization and impedance	*Azadirachta*, *cordia*, *eucalyptus*, *hibiscus* and *punica* were predominantly under cathodic control, whereas inhibition by *momordica* and *jasminum* were under anodic control (Quraishi, 2004).	Yes / not used

S.No.	**Substrate**	**Media**	**Green Inhibitor**	**Technique/ Surface Analysis**	**Result**	**Conventional Weight loss**
3.	Mild steel	Sulphuric acid	*Thyme, coriander*, *hibiscus, anis, black cumin,* and garden cress	a.c, d.c electrochemical techniques and potentiodynamic polarization	It was established that the inhibitors were mixed type inhibitors. Order of increasing IE was correlated with the change of the constituent active materials of the compounds. The powerful antiseptic thymol in thyme is the active ingredient that offers exceptional protection for steel surface (Khamis and Alandis, 2002).	NA/ not used

S.No.	Substrate	Media	Green Inhibitor	Technique/ Surface Analysis	Result	Conventional Weight loss
4.	Mild steel		*Eucalyptus* leaves, *hibiscus* flower and *agaricus*	Weight loss (under static and dynamic conditions) and polarization methods	Langmuir and Freundlich isotherms best fitted the experimental data. The agaricus extract was predominantly cathodic, while the extract of *eucalyptus* and *hibiscus* were found to be mixed inhibitors (Minhaj et al., 1999).	Yes / not used

S.No.	**Substrate**	**Media**	**Green Inhibitor**	**Technique/ Surface Analysis**	**Result**	**Conventional Weight loss**
5.	Mild steel	Industrial water	Raddish leaves and black *cumin*	EIS, potentiodynamic polarization and weight loss measurements at a temperature range of 30 to 60^0C and velocity range of 1.44 to 2.02 ms^{-1}.	Black *cumin* provided better inhibition than radish leaves. The inhibitors showed anodic behavior and the flory-huggins isotherm model best explained the interaction mechanism (Badiea and Mohana, 2009).	Yes / not used

S.No.	Substrate	Media	Green Inhibitor	Technique/ Surface Analysis	Result	Conventional Weight loss
6.	Mild steel	Sulphuric acid	*Allii cepae bulbus, agrimonia, eupatoria-herba, fagus silvatica, juglans regia*	potentiodynamic polarization	Mixed type inhibitor behavior (Lingvay et al., 2009).	NA / not used
7.	Mild steel	1 M Sulphuric acid	*Allium sativum, Juglans regia* and *Pogostemon cablin*	potentiodynamic polarization and EIS	Mixed type inhibitor behavior, *allium sativum* could serve as an effective inhibitor (Anca et al., 2009).	NA /not used

S.No.	Substrate	Media	Green Inhibitor	Technique/ Surface Analysis	Result	Conventional Weight loss
8.	X52 mild steel	2.3 M sulphuric acid	*Cotula cinerae*, *Retama retam* and *Artemisia herba alba* plants	Weight loss measurements and electrochemical measurements	Mixed type inhibitor behavior (Dakmouche et al., 2009).	Yes / not used
9.	Mild steel	1 M Sulphuric acid	Acid extract of dry *Nyctanthes arbortristis* (night *Jasmine, coral jasmine*) leaves	Weight loss and polarization measurements	IE of 90% and mixed type inhibitor behavior (Saratha and Vasudha, 2009).	Yes / not used

S.No.	Substrate	Media	Green Inhibitor	Technique/ Surface Analysis	Result	Conventional Weight loss
10.	Mild steel	HCl	*Jasminum grandflorum, Jasminum auriculatum, Oleum palmaroasae, Ocimum basilicum* and *Vetiveria zizaniodes* oils	Stevenson chamber tests	Inhibition efficiency up to 50% (Poongothai et al., 2009).	NA / not used
11.	Mild steel	Basic solution	Leaves, latex and fruit from the *Calotropis procera* and *Calotropis gigantea*	Mass los method and thermometric method	IE up to 80.89 % (Kumar et al., 2009).	NA / not used

S.No.	Substrate	Media	Green Inhibitor	Technique/ Surface Analysis	Result	Conventional Weight loss
12.	Mild steel	Sulphuric acid	*ITCalotropis procera*/ IT	Weight loss, electrochemical, SEM and UV methods	Temkin adsorption isotherm (Raja and Sethuraman, 2009).	NA / not used
13.	Duplex stainless steel	HCl and Sulphuric acid	Honey, Mugwort oil eucalyptus oil	Electrochemical technique	For 2507 stainlesss steel the eucalyptus oil is anodic (Potgieler et al., 2008).	NA / not used

S.No.	Substrate	Media	Green Inhibitor	Technique/ Surface Analysis	Result	Conventional Weight loss
14.	Mild steel	2 M HCl and 1 M sulphuric acid	*Occimum viridis, Telferia occidentalis, Azaridachia indica, Hibiscus sabdariffa, Garcinia kola* seeds	Electrochemical and thermometric techniques	Protonated and molecular species were responsible for the inhibiting action of the extracts (Oguzie, 2008).	NA / not used
15.	Al	0.5 M HCl	*Azaridachia indica* Plant, iodide ion	Potentiodynamic and impedance techniques	Freundlich adsorption isotherm (Arab, 2008).	NA / not used

S.No.	Substrate	Media	Green Inhibitor	Technique/ Surface Analysis	Result	Conventional Weight loss
16.	Mild steel	Sulphuric acid	*Carica papaya* leaves and seed, heartwood and bark	Gravimetric and gasometric techniques at temperature of 30 and 60^0C.	Suitable for application in chemical cleaning and pickling. Data was best fitted to Langmuir and Temkin (Okafor and Ebenso, 2007).	Yes / not used
17.	Copper	3.4% NaCl	*Medicago sativa*, *Withania somnifera*, *Atropa belladonna* and *Medicago polymorpha*	EIS potentiodynamic and polarization method	Complex formation of extract inhibitor molecules with copper causes a blocking barrier to copper corrosion (El-Dahan, 2006).	NA /not used

S.No.	Substrate	Media	Green Inhibitor	Technique/ Surface Analysis	Result	Conventional Weight loss
18.	Mild steel	1 M sulphuric acid	*Chamomile*, *halfabar*, black *cumin* and kidney bean	EIS and potentiodynamic polarization techniques	Mixed-type inhibitor, Langmuir, flory-huggins and kinetic thermodynamic model (Abdel-Graber, 2006).	NA /not used
19.	N80 steel	15% HCl	alcoholic extract of plant leaves and formaldehyde	Potentiostatic polarization and weight loss measurements at a temperature of 90^{0}C	Anodic inhibitor due synergetic effects, frumkin and Langmuir adsorption isotherm (Emranuzzaman et al., 2004).	Yes /not used

S.No.	Substrate	Media	Green Inhibitor	Technique/ Surface Analysis	Result	Conventional Weight loss
20.	Al	HCl	*Carica papaya* and *azadirachta indica*	Thermometric weight loss and hydrogen evolution techniques at temperature of 30-40^{0}C	Freundlich, temkin and flory-huggins adsorption isotherm (Ebenso et al., 2004).	Yes / not used
21.	Mild steel	1 M HCl, 1 M Sulphuric and 1 M Nitric acid	Acid extracts of seed leaves and bark of *Prosopis juliflora*	Weight loss method at 26-28^{0}C	Inhibition increased with the increase in concentration of the additives of seed, leaves and bark in 1 M HCl, 1 M Sulphuric and 1 M Nitric acid (Chowdhary et al., 2004).	Yes / not used

S.No.	Substrate	Media	Green Inhibitor	Technique/ Surface Analysis	Result	Conventional Weight loss
22.	Mild steel	0.1 MHCl	TL and BR inhibitors from green tea and rice bran	Polarization and weight loss techniques	Cathodic inhibitor (Liu and Xiong, 2003).	Yes / not used
23.	Al, Cu and brass	Acid chloride and sodium hydroxide	date palm leaves, *Phoenix, dactylifera*, *Henna*, *lawsonia inermis* and corn	Weight loss and potential measurments	Date palm and henna extracts were found highly effective in reducing corrosion rate of steel in acid chloride solutions and Aluminium in sodium chloride solutions (Rehan, 2003).	Yes / not used

S.No.	**Substrate**	**Media**	**Green Inhibitor**	**Technique/ Surface Analysis**	**Result**	**Conventional Weight loss**
24.	Mild steel	0.2 M sulphuric acid	Leaf and bark solution extracts of *Magnifera indica*	Weight loss and potential measurement technique	1 ml of combined extracts/ 100 ml of sulphuric acid show inhibition efficiency (I.E) of 70.15%, while 0.5 ml/100 ml is also found effective but the magnitude of I.E was below average (Loto, 2001a).	Yes/ not used

S.No.	**Substrate**	**Media**	**Green Inhibitor**	**Technique/ Surface Analysis**	**Result**	**Conventional Weight loss**
25.	Mild steel	aqueous medium	*Eucalyptus*, *hibiscus* and *agaricus*	Weight loss polarization methods	I.E of *Eucalyptus*, *hibiscus* and *agaricus* are 74, 79 and 85% respectively. Eucalyptus and hibiscus are mixed-type inhibitors while *agaricus* extracts are cathodic inhibitors (Minhaj et al., 1999).	Yes / not used

S.No.	Substrate	Media	Green Inhibitor	Technique/ Surface Analysis	Result	Conventional Weight loss
26.	Mild steel	1200 and 600 mg hydrogen sulphide/ L in 3% NaCl aqueous solution and pH of 3	*Coumarines* plant: *Nigellia saliva,Coriandrum sativum, Ricinus cummunis*	Galvanostatic anodic and cathodic polarization measurements at a temperature of 25^0C	All three plant extracts showed good inhibition efficiency (Barakat et al., 1998).	NA / not used

S.No.	Substrate	Media	Green Inhibitor	Technique/ Surface Analysis	Result	Conventional Weight loss
27.	Mild steel	0.5 M sulphuric acid	*Carica papaya* and *Azadirachta indica* leaves	Weight loss techniques at a temperature of 30 and 40^0C	At 30^0C I.E of *Carica papaya* is 87.5% at 1.25e-5 g/dm^3 conc which is better than azadirachta indica with 75.95% at 1.25e-5 g/dm^{3}conc (Ebenso et al., 1998).	Yes/ not used
28.	Mild steel	0.1 M HCl	*Calotropis procera* (CP) and *Diospyros mesipiliformis* (DM) plant extracts	Polarization and weight loss measurements	Both extracts provide adequate inhibition of corrosion of mild steel but DM is more efficient than CP (Awad, 1985).	Yes / not used

S.No.	Substrate	Media	Green Inhibitor	Technique/ Surface Analysis	Result	Conventional Weight loss
29.	Mild steel	HCl	*Papaya, poinciana pulcherrima, cassia occidentalis,Datura stramonium seeds, Calotropis proceraB, Azydracta indica* and *Auforpio turkiale*	Weight loss and electrochemical measurements	All extracts except *auforpio turkiale* and *azydrachta indica* shows IE of 88-96% in 1M HCl. Both cathodic evolution and of hydrogen and anodic dissolution of steel are inhibited (Zuchhi and Omar, 1985).	Yes / not used

S.No.	Substrate	Media	Green Inhibitor	Technique/ Surface Analysis	Result	Conventional Weight loss
31.	Tin	Nitric acid	(1) *Ammi mijus L*; (2) *amii visnaga L;* (3) *ficus carica L;* and (4) *glycyrrhiza glabra*	Thermometric method	The degree of inhibition of these extracts increases in the order 1 approximately equals 2 greater than 3greater than 4 (Ibrahim et al., 1981).	NA / not used

remains in the media until the duration is reached before final weight are taken to obtain weight loss. By adopting this technique the metal surface interaction with the inhibitor and the media will not experience any distortion, thereby making the measurements more accurate.

This work introduced the partial substitution model in the synergistic study. This is a systematic replacement of the inorganic with organic or green inhibitors in parts by keeping a baseline figure which the combination will not surpass. This could create an important basis for comparison amongst the synergistic combinations utilized in the study. Furthermore, none of the works considered so far has employed an artificial intelligence tool in the form of artificial neural network (ANN) to model inhibitor behaviour. All of the findings points to the fact that there is need to create a representative model for predicting corrosion rate, that can be used to predict and evaluate at any time the amount of metal wastage. Most researchers on corrosion focus on direct evaluation through experimental observations. This is mostly time consuming, at times expensive and may give results that are specific to the research objective. One major way by which versatility can be introduced to corrosion study is to employ the modelling technique for analysis and evaluation of corrosion behaviour of metals. Modelling has been reported to be a cheap means of carrying out robust studies (Achenbach, 1995; Li and Chyu, 2003; Damm and Fedorov, 2005; Wang et al., 2006; Lu, et al., 2006; Ali et al., 2009).

Only recently has artificial intelligence tool been employed for corrosion studies and most of such works did not implement their analysis on corrosion inhibition studies

(Malinov et al., 2000; Yecas et al., 2001; Metzbower et al., 2001; Gundersen et al., 2001; McShane et al., 2001; Malinov et al., 2001; Malinov and Sha, 2004; Kiselev et al., 2006; Aprael, 2008; Ramana et al., 2009; Oluwole and Idusuyi, 2012;). Artificial intelligence tool in the form of Artificial Neural Network (ANN) are used for modelling complex relationships between inputs and outputs. The process of corrosion inhibition can be likened to a complex one since several chemical substances are involved in the inhibition process.

ANN performance is also known to benefit from large sample size, thus by employing more experimental variations, the results will become more meaningful and acceptable to researchers. This research is therefore an effort to address this caveat as it attempts to conduct a study into quaternary (four inhibitors separately and in synergy) use of inhibitors on mild steel and aluminium in hydrochloric (HCl) and sulphuric acid (H_2SO_4) media.

2.6 Steel Versatility

The versatility of mild steel as an item of construction is unsurpassed by other alloys. It is the most extensively used construction material with more than 1.4 billion tons manufactured annually (World Steel Association, 2013). It is a crucial aspect of everyday existence because it links every sector such as housing, energy, agriculture and water supply. Structures, chemical plants, equipment, machines, tools, transport pipelines, pressure vessels and storage tanks are just a fraction of its applications and utilization in our daily existence. Steel is therefore a major driver of the world's economy (World Steel Association, 2013). A continuous growth in steel production will be experienced principally in developing areas like Africa, Asia and Latin America where the production of steel will be essential in improving the standard of living. It is estimated that in these regions sixty percent of the steel utilized will be for fresh infrastructure. This sustained but continuous growth will not allow producers to meet demand by the reprocessing of end-of-life steel products and the conversion of new ore to steel, hence making it necessary to protect and prolong the life of steel that is already in service condition by appropriate corrosion protection and control techniques.

Mild steel is an alloy made of iron and other elements such as carbon and traces of silicon, manganese, sulphur, phosphorous and aluminium. Steel quality, strength, ductility and hardness differ with the quantity of the alloying element. As steels deteriorate in numerous environments, their resistances to corrosion in the very common and frequently used reagents like sulphuric (H_2SO_4) and hydrochloric (HCl) acid is a vital and important economic consideration for many industries. Acids, especially phosphoric, nitric, sulphuric and hydrochloric acids are utilized in virtually every manufacturing process. They are used in the manufacture of metals, food, explosives, paper, dyes, leather and fertilizers. Fortifying steel against corrosion as they function as pressure, reaction, transport and storage devices in the service environment where they come in contact with these ubiquitous and hostile acids is a major consideration for all concerned industries.

The significance of the use of inhibitors as an appropriate corrosion protection technique in the industry is growing (Sangeetha et al., 2011). Corrosion inhibition using green inhibitors offer some advantages over chemical or organic inhibitors like chromates, nitrides and nitrates in that it is easily obtained, inexpensive, eco-friendly, easily disposed, non-contaminating and litigation free. With the drift towards environmentally friendly substances, green inhibitors has established itself as a corrosion protection technique of choice. Green inhibitors also hold immense promise as an application pigment in coating systems.

2.7 Aluminium Alloy Versatility

Aluminium is also another important metal with great potential. The beneficial properties of aluminium and its alloys are clear determining features for metallurgists, engineers, producers and designers to apply them in various environments. These experts are continuously on the watch for superior materials and state-of-the-art processes. Aluminium has a density of 2700 kg/m^3 and the least weight amongst all ordinary metals. It is estimated to be nearly three times as light as steel (steel density is about 8700 kg/m^3) (Ungureanu et al., 2007). The reduction of weight is a valuable answer to issues of enhanced energy productivity, reduced carbon footprint and business profitability on account of reduced overheads on materials handling in the workshop. Other advantages attributed to aluminium and its alloys are excellent thermal and electrical conductivity; superior corrosion resistance in atmospheric/ industrial/marine environments; applicability for surface treatments and ease of recyclability without any adverse effect on its basic and essential features and the added advantage of reduced energy cost in the processing.

The numerous qualities of aluminium and its alloys also explain the reason for its increasing utilization in automated applications. Manufacturers of equipment with rotating or moving components, like robots, are making use of a growing amount of aluminium components to decrease inertia or sluggishness. The thermal conductivity of aluminium is a significant factor in heat exchange considerations in electronics, seawater desalination, hydraulic ventilation and air conditioning (HVAC) exchangers and plastics industry where the utilization of aluminium alloy moulds with distinct mechanical properties can reduce fabrication cycles by about one-third (Hartley, 1996; Bruna and Sladek, 2011). The increasing applications to which aluminium and its alloy can be put have put pressure on meeting demands. Demands for aluminium products have been increasing over the years (there is a doubling in the demand since 1990 according to Nappi, 2013). Worldwide energy cost has been on the increase, this has negatively affected the processing of aluminium. Even though it is easily recycled with attendant energy cost reduction during processing, it is essential that critical steps are taken to protect and control the corrosion of aluminium alloys in hostile industrial service environments. The use of green inhibitors offers a versatile means of controlling the corrosion of aluminium and its alloys. These steps will prolong the time for replacement of parts and reduce the pressure on demand. These will also have the added advantage of reducing power needs thereby decreasing the carbon footprints.

2.8 Significance of Hydrochloric Acid

Hydrocchloric acid is used widely for steel pickling, oil well acidizing, food manufacturing, production of calcium chloride and ore processing. In steel pickling operations, hydrochloric acid is used in treating carbon, alloy and stainless steels. Pickling is the method by which iron oxides and scales are removed from the surface of steel by transforming the oxides to soluble compounds. Pickling is a necessary step for steel products that undergo additional processing such as wire production, coating of sheet and strip, and tin mill products. Hydrochloric acid is essential in continuous pickling operations in which hot-rolled strip steel is passed through an opposing current flow of acid solution (Robson, 1993). Aluminium etching, metal surface preparation for galvanizing and soldering as well as metal cleaning is usually done with hydrochloric acid.

Also, oil well acidizing operation is used to improve oil yield (Rajeev et al., 2012). HCl is thus used in this operation to remove tarnishing, scale and undesirable carbonate deposits in oil well tubings. This is to enhance oil or gas flow to the well and this activity is referred to as "stimulation" which is usually done in carbonate or limestone configurations. An acid solution is introduced into the configuration to dissolve part of the rock in order to initiate a sizable hole or pore structure in the formation. Though this will eventually increase its valuable porousity and increase oil flow, the production casing, float collar and casing shoe become dangerously exposed to the acid. Corrosion is thus, in most instances initiated.

Even though chemical inhibitors have been introduced in such instances to forestall metallic deterioration, the problem of toxicity to plant and animal life as well as litigation that may arise from pollution of the environment are issues of immense concern. In the food industry, hydrochloric acid is used in handling a variety of food items. A key application of HCl by the food industry is in the manufacture of syrups from corn in the form of high-fructose corn syrup (HFCS) (Parker et al., 2010). Ion exchange resin regeneration which is used to eradicate impurities in the HFCS industry is achieved using hydrochloric acid. It is also used to acid-transform cornstarch and to control the pH of intermediates, final product and litter-water.

2.9 Significance of Sulphuric Acid

Sulphuric acid (H_2SO_4) often referred to as the “king of chemicals” is utilized virtually everywhere. Over the last 100 years a nation’s industrialization is measured by the quantity of sulphuric acid it can produce and it is an indicator of its industrial strength. It is used as a catalytic agent in refinery alkylation process. This process involves the formation of compounds called alkylates through the combination of small molecules (isobutane and butylenes) in the presence of H_2SO_4 (Cheung and Gates, 1997). The alkylates are high-octane constituents of gasoline. After utilization in the alkylation process, the sulphuric acid which is now designated as spent acid characteristically comprises 87 to 94 percent H_2SO_4, up to 5 percent water and the rest is hydrocarbons, together with some weightless hydrocarbons that can evaporate (Akpabio and Neeka, 2013). In order to reutilize the acid, it is sent through a redevelopment process or step. This involves boiling and breakdown into sulfur dioxide (SO_2) and water vapour. The SO_2 invariably combines with air and is transformed into sulfur trioxide (SO_3). This then undergoes another oxidation reaction and is successively converted to H_2SO_4 (99 percent acid) in an absorber through contact with water. Sulphuric acid also has applications in the production of several varieties of food products. It is utilized in the hydrolysis or conversion of corn starch to corn syrup.

As these acids come in contact with facilities, mechanical components, reaction vessels, storage facilities and pressure vessels which are made with mild steel and aluminium alloys, deterioration sets in overtime with attendant cost implications especially if steps are not put in place to prevent or reduce the corrosion taking place.

2.10 Artificial Neural Network (ANN) Application to Corrosion Inhibition Studies

The corrosion of metals in service is classified as a natural process that will definitely occur. The general perception unfortunately is that nothing can be done to prevent it. In collecting corrosion data during corrosion experiments variations and fluctuations are frequently noticed and the causes of such variations are basically as a result of the complex reaction processes involved in corrosion. A variety of chemical substances are involved in the process: the metal alloy is composed of several elements; the aggressive media is composed of ionic and anionic compounds; and the green inhibitor is made up of many organic compounds which have polar atoms like oxygen, nitrogen, phosphorous and sulphur (Sangeetha et al., 2011). All these constitute complexities that tend to impact on the data output of corrosion monitoring processes. Therefore, it is imperative to design a system that is based on neural network to predict the corrosion rate. The process parameters to be employed will include temperature, metal alloy composition, inhibitor concentration, media concentration and initial weight. Neural network will be used to understand the dynamics of the process due to their memorization ability such that corrosion rate values might be predicted accurately. It is expected that the results will show that the designed network performs creditably the prediction tasks.

Different methodologies are available for obtaining corrosion test data. These include amongst many, weight loss, gasometric, potentio-dynamic polarization, galvanostatic, potentiostatic and electrochemical impedance which have been used extensively. Significant considerations include the concentration of the media, temperature, inhibitor concentration, cathodic, anodic parameters, current density and charge transfer. Despite the fact that various literatures exists on the corrosion inhibition studies of metal alloys in acidic media in the presence of green inhibitors, very few studies validate or establish the reliability and quality of data from such experiments through stochastic characterization. This essentially removes the uncertainties associated with some of the test data since corrosion is a very complex process involving several reacting species at the same time. However, ANN is a category of statistical learning models stimulated by biological neural networks which will deal with the uncertainties in the test data.

CHAPTER THREE

3. METHODOLOGY

3.1 Experimental Materials and Techniques

3.1.1 Metallic materials

The metals used for the study are mild steel and aluminium alloy. Mild steel was used because of its versatility as material of construction. It is used wildely in the construction industry because of its availability and strength. It finds wide spread application in the utilities, food, chemical and petrochemical industries even though it is easily affected by the aggressive environment. Because of its strength it is used for load bearing applications like the shell of a pressure vessel or the rotating shaft of a machine. The replacement of mild steel parts is six times cheaper when compared to stainless steel.

In the case of aluminium and its alloys they are utilized principally in light weight applications. They also offer some form of corrosion resistance because of their affinity for oxygen to form a passive oxide layer. They are used mostly as component parts in valves, pumps, actuators. However, when these metals are exposed to some aggressive media they become vulnerable as they experience metal losses which ultimately lead to reduction in their effective sizes, thickness or diameter. This means the machine part will be unable to support tensile, compressive, torsion or axial loads as the case may be and failure might ensue. However, the option of prolonging the life of the metal before eventually replacing it offers a cost effective solution by putting more money in the hand of a manufacturer. The use of inhibitors is a viable option which was investigated in this study.

3.1.2 Chemical composition of the metals

The metals were sourced from Granges Nigeria Limited, an indegenious storage tank fabrication and rehabilitation company involved in the revamping of crude oil tank 301-TK at the Warri Refining and Petrochemical Company. It was subsequently subjected to chemical composition test at the University of Lagos Metallurgy and Materials Engineering Department by making use of an optical electron spectroscopy (OES). Tables 3.1 and 3.2 are presentations of the chemical composition of the mild steel and aluminium alloy samples.

3.1.3 Metal preparation for the experiment

In order to conduct the weight loss experiment the metals were cut into 2 cm by 2 cm sizes or dimension using the guillotine. They were then subjected to chemical treatments. The mild steel sample was degreased by immersion in benzene and then dried. It was then immersed in a solution of HCl with acid to water ratio of 1 to 4 for 30 minutes at room temperature. They were then dried with clean cloth and stored in a desiccator. On the other hand, the aluminium samples were degreased with benzene and then dried before being immersed in nitric acid for 3 minutes at room temperature. After they were removed from the acid, they were rinsed with distilled water twice. Finally they were stored in desiccators prior to the commencement of the

Table 3.1: Elemental composition of mild steel employed for the study

S.No.	Metal	% Elemental Composition
1	Fe	98.89
2	C	0.1203
3	Si	0.0547
4	Mn	0.2654
5	P	<0.008
6	S	0.034
7	Cr	0.0528
8	Ni	0.2212
9	Mo	0.0361
10	Cu	0.0492
11	Al	0.0227
12	Ti	<0.000
13	V	0.011
14	Co	0.0313
15	Nb	0.0553
16	W	<0.042
17	Sn	<0.003

Table 3.2: Chemical composition of aluminium alloy employed for the study

S.No.	metal	% Elemental Composition
1	Al	98.88
2	Si	0.1487
3	Fe	0.3972
4	Cu	<0.007
5	Mn	0.0618
6	Mg	0.0462
7	Zn	<0.000
8	Cr	0.178
9	Ni	<0.000
10	Ti	0.0115
11	Sr	<0.000
12	Zr	<0.000
13	V	0.0195
14	Ca	<0.000
15	Be	<0.000

experiment.

3.1.4 Commercial chemicals utilized for the study

All chemicals utilized in this research were of commercially pure and analytical grade quality. The chemicals utilized include:

i. Inorganic inhibitor - Potassium chromate (PC) with chemical formula K_2CrO_4 is a lemon-yellow and strong oxidizing agent. It was purchased from Burgoyne Burbidges and Co (India) with 99% purity. It is a toxic substance with a density of 1.00g/ml, water solubility of 640g/l and vapour density of 6.7(vs air) (Dixit and Shrivastava, 2011). It was used as an inorganic inhibitor in this study.

ii. Organic inhibitor – Aniline (AN) with chemical formula $C_6H_5.NH_2$ is a colourless oily liquid with a musty fishy odour. It was obtained from J.T. Baker ® and it has purity of 99.5%. It has a melting and boiling point of -6 and 184^oC respectively. It is heat sensitive and classified as very toxic (EPA, 1994). It was used in this study as an organic inhibitor.

iii. Chemicals used for the treatment of metals:

a. Benzene is an aromatic organic compound with molecular formula of C_6H_6 and density of 0.879 g/mL. It is a clear, colorless, highly flammable liquid with a pronounced characteristic odour and a boiling point of 80^oC. It has a purity of 99% and was obtained from Qualikems® and used for degreasing the mild steel and aluminium alloy samples.

b. Nitric acid (HNO_3) is an oxidizing agent and it was obtained from Scharlau®. It is a clear colourless liquid with a boiling point of 120.5^oC and purity of 65%. It has a density of 1.41 g/mL and it was used for treating aluminium alloy sample.

c. Isopropyl alcohol has a molecular formula of $(CH_3)_2$ CHOH with boiling point and density of 82^oC and 0.785 g/mL respectively. It is a colourless liquid with slight alcohol odour. It was obtained from Kermel® and used for treating mild steel and aluminium samples.

d. Hydrochloric acid (HCl) fumes strongly in moist air and is soluble in water with resultant heat evolution. It has a density and boiling point of 1.2 g/mL and 57^oC respectively. It is air and light sensitive and it was obtained from Sigma Aldrich® and used for treating the mild steel sample to completely remove the rust.

e. Silica gel (blue) used as an active drying and absorption agent for moisture during the storage of the samples in the desiccators. Its high specific surface area (800m^2/g) makes swift moisture adsorption possible (Christy, 2012). It was obtained from Burgoyne Burbidges and Co (India) and placed in the desiccators. It has a bulk density, melting and boiling point of 570-700 g/L, 1610 and 2230^oC respectively.

iv. Media or Environment: The environments utilized in this study were HCl and Sulphuric acid. HCl has been described earlier under the metals treatment section. The concentration of the HCl used in this study was 0.5 M. Sulphuric acid (H_2SO_4) is a colourless, odourless and viscous oily liquid with a melting and boiling point of 10.5

and 290°C respectively (Zeleznik, 1991). It is hygroscopic and corrosive in nature and was obtained from Sigma Aldrich and used as the environment for the experimental study at a concentration of 0.5 M.

3.1.5 Green inhibitors utilized for the study

Extracts of two plants were employed for the study. These are:

a. *Cassia fistula* (CF), Plate I (a), which is widely known as golden shower tree or Indian laburnum (Bahorun et al., 2005; Sartorelli et al., 2009). It was obtained from within the Covenant University Campus in Ota (Lat. 6.672^0N, Long. 3.160^0 E), South-West Nigeria because of its abundance. The major plant phytochemicals have been identified as phenolics, flavonoids and proanthocyanidins with the –OH and =O functional group (Bahorun et al., 2005). This functional group have corrosion inhibiting properties.

b. *Terminalia catappa* (TC), Plate I (b), is popularly known as ‘fruit’ in South west Nigeria or ‘mbansan mbakara’ in Efik, South-South Nigeria. It was obtained from Ota, Ogun State (Lat. 6.672^0N, Long. 3.160^0 E) in South-West Nigeria. The major phytochemicals in TC have been established as alkaloids, resins, steroids, tannins, saponins and phenols. The functional groups of -NH and -OH are present in the identified phytochemicals (Neelavathi et al., 2013).

PLATE I: Plant used for preparing *Cassia fistula* leave extract.

PLATE II: Plant used for preparing leave extract of *Terminalia catappa*.

In order to prepare the extract, leaves from CF and TC were obtained in their fresh forms and subjected to drying under aerated or ventilated cover. This was done to make sure that the natural constituent of the leaves were not denatured. The dried leaves still maintained their "greenness" after drying. The leaves were pulverized using a grinding machine to obtain a very fine powder. This was then placed in a filter paper thimble and put into a compartment of the Soxhlet extractor, furnished with a condenser that was stationed on a distillation flask containing methanol as extraction solvent (Hameurlaine et al., 2010). The deluge into the compartment housing the thimble of plant leaf, of the reflux of the methanol heating from the distillation flask enables the methanol solvent to simmer down and trickle back into the Soxhlet chamber. As a result of this, the extract from the plant in the thimble dissolves into the warm reflux of methanol solvent and then the stable or non-volatile extracts dissolved in the solvent was concentrated through the use of a rotary evaporator.

3.1.6 Preparation of individual inhibitor concentrations

The preparation of the inorganic inhibitor (potassium chromate) was performed by weighing the required quantities on a weighing balance (i.e. 2, 4, 6, 8 and 10g). These were then dissolved in the appropriate quantities of distilled water and acid mixture. The breakdown was as follows: 2g of the potassium chromate inhibitor was weighed in the weighing balance and dissolved in 200 cm^3 of distilled water. Afterwards, 500 cm^3 of distilled water was put in a 1 litre flat bottomed flask and 42 cm^3 of HCl acid was added in a fume chamber. The solution of the 2g potassium chromate (a little bit above 200 cm^3) was then introduced into the acid solution (about 542 cm^3). This added up to a little bit above 742 cm^3. This mixture was made up to 1 litre with distilled water. This technique was adopted to prepare all the inhibitor concentrations employed in this study.

3.1.7 Preparation of synergetic inhibitor concentrations

The synergetic admixture (SA) concentrations were prepared by a novel fractional substitution method. A total concentration of 8g was maintained and the component parts making up the synergetic admixtures were split as either; 2 to 6g/L, 4 to 4g/L or 6 to 2g/L. These were made up of the inorganic inhibitor on one part and the organic or natural inhibitor on the other part. This design was employed to introduce a fractional replacement of the inorganic inhibitor with organic and green inhibitor. The method creates a pragmatic way of tailoring the inhibitor to produce better inhibitor efficiency.

3.1.8 Acid preparation and calculations

This was done by using the following equation:

$$Stock\ concentration\ (C_1) = \frac{\%\ purity\ of\ acid\ x\ density\ x\ 10}{molar\ mass\ of\ acid} \tag{3.1}$$

Where:

% purity of HCl acid = 37%,

Density of HCl = 1.19 g/cm^3 and

Molar mass of acid = 36.46 g/mol

Thus, the concentration of stock from which the 0.5 M hydrochloric acid solution was prepared from is 12.08M.

The quantity (volume) of the stock needed is then estimated by using the relation:

$$C_1V_1 = C_2V_2 \tag{3.2}$$

Where:

C_1 = Concentration of the stock,

C_2 = the required molarity of the acid (0.5 M),

V_1 = Volume of stock solution needed to prepare the 0.5 M acid and

V_2 = Volume of acid required (1000 cm^3)

$$V_1 = \frac{C_2V_2}{C_1} \tag{3.3}$$

Therefore, approximately 41.5 cm^3 of the stock was made up to 1000cm^3 in a 1Litre standard flask to obtain the 0.5 M concentration of hydrochloric acid solution.

It is also possible to obtain the stock concentration and volume of H_2SO_4 required to produce 0.5 M H_2SO_4. The following parameters are for H_2SO_4.

% Purity of H_2SO_4 acid = 94%,

Density of H_2SO_4 = 1.840g/cm^3 and

Molar mass of H_2SO_4acid = 98 g/mol

By using Equation (3.1) above, we obtain our stock concentration as 18.1 M and the volume of acid as 28 cm^3.

Also, approximately 28 cm^3 of the stock was made up to 1000cm^3 with distilled water in a 1Litre standard flask to obtain the 0.5 M concentration of H_2SO_4 solution.

3.2 Set up for Weight loss Experiment

The conventional weight loss method involves the weighing of the sample before immersion and then re-weighing after duration of pre-determined period. Afterwards same sample is re-immersed for the next duration. For example if the experiment is to run at 2 day interval for 10 days, it means every two days sample is removed, re-weighed and re-immersed until the 10th day period. The removal and re-immersion disrupts the metal-inhibitor interaction and may make the capture of the corrosion indices impossible. However, in this study we introduced an innovation by setting up Weight loss experiment for each interval. Metals were only removed for final re-weighing at the end of the experimental period. This way it was possible to capture the exact metal-inhibitor interaction. Pretreated metal coupons measuring 2cm by 2cm were weighed and subsequently immersed in the test media consisting of varying concentrations of the inorganic, organic, green inhibitors and control solutions (0.5 M HCl and 0.5 M H_2SO_4 minus inhibitor). After the duration, the samples were removed from the test media and reweighed and subsequently returned into the dessicator. The Weight loss experiment was conducted in accordance to ASTM G 1-03 standard procedure. Tables 3.3 and 3.4 show the various metal-inhibitor-acid combinations with the experimental duration.

To obtain the Weight loss, the mass obtained after the experiment was subtracted from the mass before the experiment. After obtaining the Weight loss data, it was possible to determine the corrosion rate, inhibitor efficiency and surface coverage. Corrosion rate is evaluated by Equation 3.4 as stated below (ASTM G 1-03):

$$Corrosion\ rate\ (mmpy) = \frac{87.6\ W}{A\ X\ T\ X\ D} \tag{3.4}$$

Where:

T = immersion time in hours

W = Weight loss in grams

A = Area of sample in square cm (cm^2)

Table 3.3 Metal-inhibitor-acid combinations

Inhibitor Concentration (PC, AN, TC, CF)	Media	Metal	Duration
0 g (control)	HCl or H_2SO_4	Mild steel or Al	Mass readings were taken every four days for 60days for each combination.
2 g	HCl or H_2SO_4	Mild steel or Al	
4 g	HCl or H_2SO_4	Mild steel or Al	
6 g	HCl or H_2SO_4	Mild steel or Al	
8 g	HCl or H_2SO_4	Mild steel or Al	
10 g	HCl or H_2SO_4	Mild steel or Al	

Table 3.4 Metal-synergetic inhibitor- acid combinations

S.No.	Inhibitor concentration (g/L)	Media	Metal	Immersion time(60 days)
1	2PC + 6AN	0.5 M HCl or H_2SO_4	MS or Al	Mass data was taken every 4 days for 60 days
2	4PC+ 4AN	0.5 M HCl or H_2SO_4	MS or Al	Mass data was taken every 4 days for 60 days
3	6PC + 2AN	0.5 M HCl or H_2SO_4	MS or Al	Mass data was taken every 4 days for 60 days
4	2PC + 6TC	0.5 M HCl or H_2SO_4	MS or Al	Mass data was taken every 4 days for 60 days
5	4PC + 4TC	0.5 M HCl or H_2SO_4	MS or Al	Mass data was taken every 4 days for 60 days
6	6PC + 2TC	0.5 M HCl or H_2SO_4	MS or Al	Mass data was taken every 4 days for 60 days
7	2PC + 6CF	0.5 M HCl or H_2SO_4	MS or Al	Mass data was taken every 4 days for 60 days
8	4PC + 4CF	0.5 M HCl or H_2SO_4	MS or Al	Mass data was taken every 4 days for 60 days
9	6PC + 2CF	0.5 M HCl or H_2SO_4	MS or Al	Mass data was taken every 4 days for 60 days

D = density of metal in g per cm^3.

The inhibitor efficiency based on mass data (IE%) was obtained from the relationship in Equation 3.5 and as described by (Ebenso et al., 2004; Omotosho et al., 2012a; Omotosho et al., 2012b and Omotosho et al., 2012c):

$$Mass\ based\ Inhibitor\ Efficiency\ (IE_M\%) = \frac{CR_{cont} - CR_{inh}}{CR_{cont}}(100) \tag{3.5}$$

Where:

CR_{cont} = Corrosion rate of sample in acid media (HCl and H_2SO_4) and

CR_{inh} = Corrosion rate of metal sample in the presence of the inhibitor and the acid

The surface coverage was determined from the expression in Equation 3.6 (Obot et al., 2009):

$$Surface\ coverage\ (\theta\ ) = \frac{W_c - W}{W_c} \tag{3.6}$$

Where:

W_c = Weight loss of metal sample in the control solution (solution without inhibitor) and

W = Weight loss of metal sample in solution with acid and inhibitor.

3.3 Electrochemical Measurements

A model DY2312 potentiostat manufactured by Digi- Ivy in the USA was used for the test. For the Linear Sweep Voltammetry (LSV) measurement, the potential of the working electrode changed linearly with time from Initial E (V_o) to the End E (V_i). The measured current was displayed as a function of time. The DY 2300 series software was used for the measurements. From the experimental measurements the values of corrosion potential (E_{corr}), corrosion current density (I_{corr}) anodic and cathodic Tafel slope constants (b_a and b_c) can be evaluated from the anodic and cathodic regions of Tafel plots. However, the extrapolation of the linear Tafel portion of the anodic and cathodic plot to corrosion potential was done to obtain corrosion current densities (I_{corr}). The Tafel inhibition efficiency ($IE_T\%$) was obtained from the Tafel polarization method, by using the I_{corr} values obtained from equipment readout but can also be calculated using the formula in Equation 3.7 as described by Abdel-Rehim et al. (2011) and Fouda et al. (2013).

$$Tafel\ Inhibitor\ efficiency\ (IE_T\%) = \left(\frac{I_{corr(cont)} - I_{corr(inh)}}{I_{corr(cont)}}\right) 100 \qquad (3.7)$$

Where:

$I_{corr(cont)}$= uninhibited solution corrosion current density and

$I_{corr(inh)}$ = inhibited corrosion current densities.

3.4 Adsorption Studies

Inhibitor molecules retard the corrosion process by instituting an interaction with the metal surface. Thus inhibition is said to take place when the molecules are adsorbed on the metal surface. In theory, the process of adsorption can be considered as a single substitutional process in which an inhibitor molecule, N, in the aqueous phase substitutes a "J" adsorbed on the surface of the metal. This is given by (Riggs et al., 1967; Stupnisek-Lisac et al., 1992; Singh and Quraishi, 2010; Tan et al., 2011; Fouda et al., 2013):

$$N_{(aq)} + JH_2O_{(surf)} \rightarrow N_{(surf)} + JH_2O_{(aq)}$$

Where J is identified as the size ratio and absolutely corresponds to the number of adsorbed water molecules exchanged by a lone inhibitor molecule. Therefore the adsorption is contingent on inhibitor configuration, metal type and the features of its surface, nature of corrosion medium and measure of its pH, the temperature and the corrosion potential of the media-metal interface. Adsorption further offers data about the relations amongst the absorbed molecules specifically and in addition to their metal surface interaction. This means that the adsorption isotherm can be said to be an expedient approach that promotes the interpretation of the process of corrosion or electrochemical reactions in the adsorption process (Singh and Quraishi, 2010). An adsorption isotherm offers explanation for the relation between the metal exposed surface to the coverage of an interface with adsorbed species.

There is a usual assumption that inhibitors in acid corrosion act through a process of adsorption on a metal substrate. Inhibitor adsorption may influence the physical change of the coating thus decreasing the degree or rate of electrochemical partial reaction. The degree of surface coverage, θ, for varying inhibitor concentration at room temperature was used to elucidate the adsorption isotherm in order to establish the adsorption processes involved. To achieve these, several adsorption isotherms were fitted to the experimental data to determine which one will best explain the metal surface-inhibitor interaction through the R^2 value of the various graphical plots. These include Frumkin (El-Sayed et al., 2010; Ajayi et al., 2011a), Freundlich (Ajayi et al., 2011b; Ajayi et al., 2011c), Temkin (Omotosho et al., 2012; Omotosho and Ajayi, 2012), Langmuir (Foo and Hameed, 2010), Florry-huggins (Foo and Hameed, 2010), Dubinin-Radushkevick (Foo and Hameed, 2010), Bockris-swinkel (James et al., 2009) and El- Awady kinetic thermodynamic model (Adejo et al., 2013). Surface Morphological Studies

The study of the superficial effects of the acids on the mild steel and aluminium samples were conducted using the following techniques:

- Optical Emission Spectrometer (OES) and
- Scanning Electron Microscopic (SEM)

The metal samples were washed methodically with de-ionized water prior to placing them on the slide. The snapshots of the specimen were taken from the section of the sample where superior details could be obtained. In order to have detailed insight of the morphology of the mild steel and aluminium surface in the absence and presence of inhibitors the metallurgically clean mild steel and aluminium sample were investigated, Mild steel and aluminium sample immersed in 0.5 M HCl and 0.5 M

H_2SO_4 acid solution were investigated and Mild steel and aluminium sample immersed in 0.5 M HCl and 0.5 M H_2SO_4 acid solutions incorporated with PC/AN/CF/TC extracts and synergetic admixtures were also investigated.

3.4.1 Optical Emission Spectrometer (OES)

The OES was used to analyze the surface morphology of the plain (unimmersed) sample and the blank sample (sample immersed in acid) for mild steel and aluminium. The operation of OES requires the utilization of electrical energy in the pattern of a spark generated between an electrode and a metal sample, such that the vaporized atoms experiences a high energy state that is within a so-called “discharge plasma”. In the discharge plasma, excited atoms and ions create a distinctive emission range or spectrum well defined to each element. Therefore, a single element produces a multitude of characteristic emission spectral lines.

3.4.2 Scanning Electron Microscope (SEM)

SEM was used to assess the change in the surface morphology caused by interaction with the test solutions, and to monitor the effect of adding of the inhibitor. It was deployed to examine surface profile of the mild steel and aluminium metal after corrosion in the presence of the inhibitor. The superficial effects on the surface of mild steel and aluminium samples after contact with 0.5 M HCl and 0.5 M H_2SO_4 solution in the presence of PC/AN/CF/TC extracts and synergetic admixtures for 60 days at room temperature of 30^0C were examined by PHENOM PRO X SEM (PW-200-017).

3.5 Artificial Neural Network (ANN) Modelling of Test Data

In a bid to carry out ANN modelling of the test data, the MATLAB® neural network toolbox was employed. ANN was used to evaluate the effect of inhibitors on the behaviour of metals in the corrosion systems and to predict corrosion rate. In this neural network, two hidden layers were employed. The number of neurons was obtained by trial and error and so the number was selected after several trials. For the corrosion rate prediction the input layer admitted the variables of: exposure time, temperature, inhibitor concentration, media concentration, initial weight and metal composition. The output layer gave the corrosion rate as network result. In the first hidden and second layer the tan-sigmoid transformation function was employed. The neural network training algorithm deployed was the Levenberg Marquadt feed forward algorithm and it was used with 100 experimental measurements taken every four days for 60 days for the Weight loss experiment.

CHAPTER FOUR

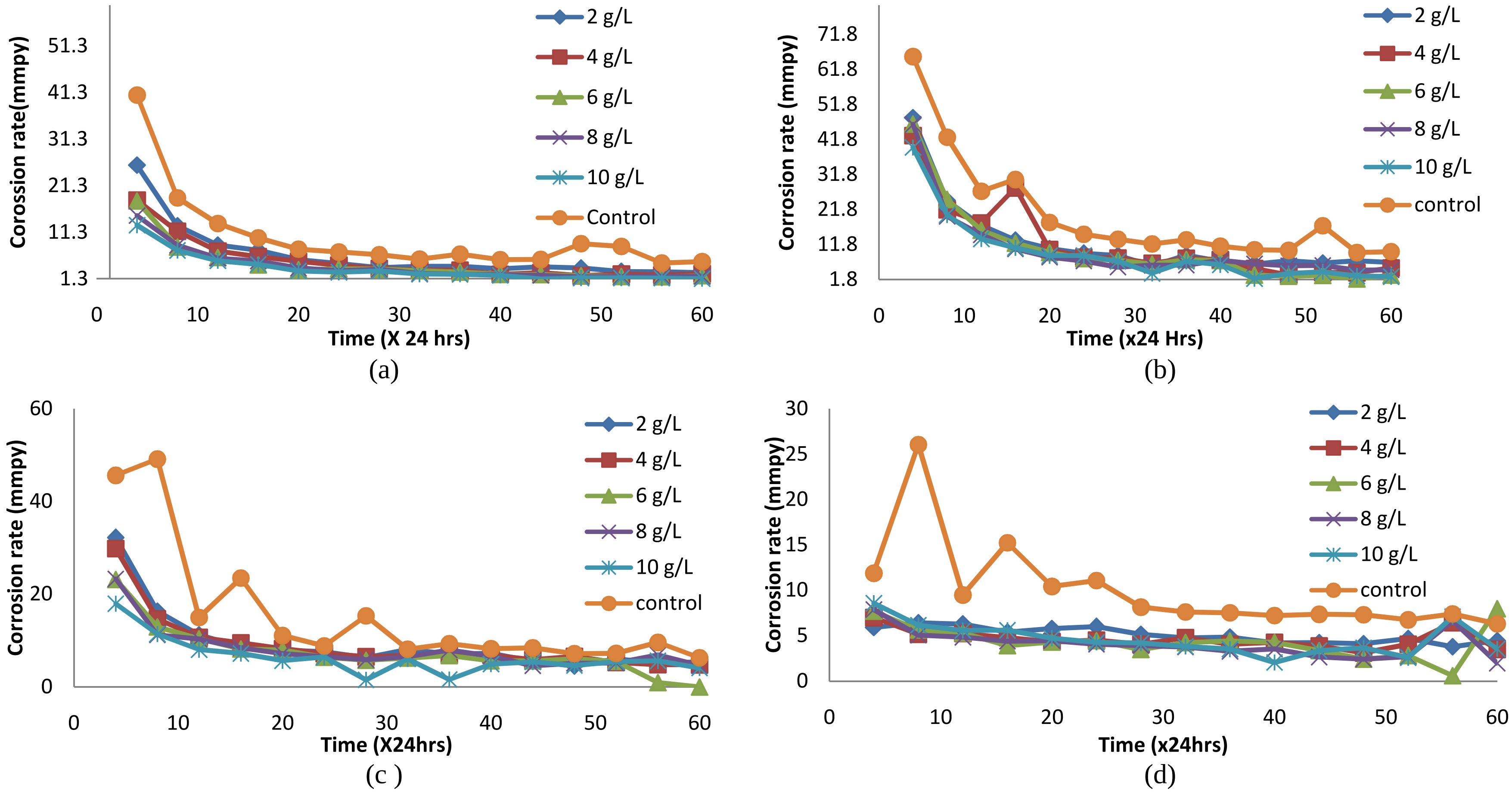
4. RESULTS AND DISCUSSIONS

4.1 Introduction

This section presents the results and discussion concerning the weight/Weight loss measurements, Tafel polarization plots, adsorption isotherms, dynamic surface coverage, metal surface morphology and ANN modelling of corrosion data obtained from Weight loss experiments in a concise and precise manner.

4.2 Corrosion Rate and Inhibitor Efficiency

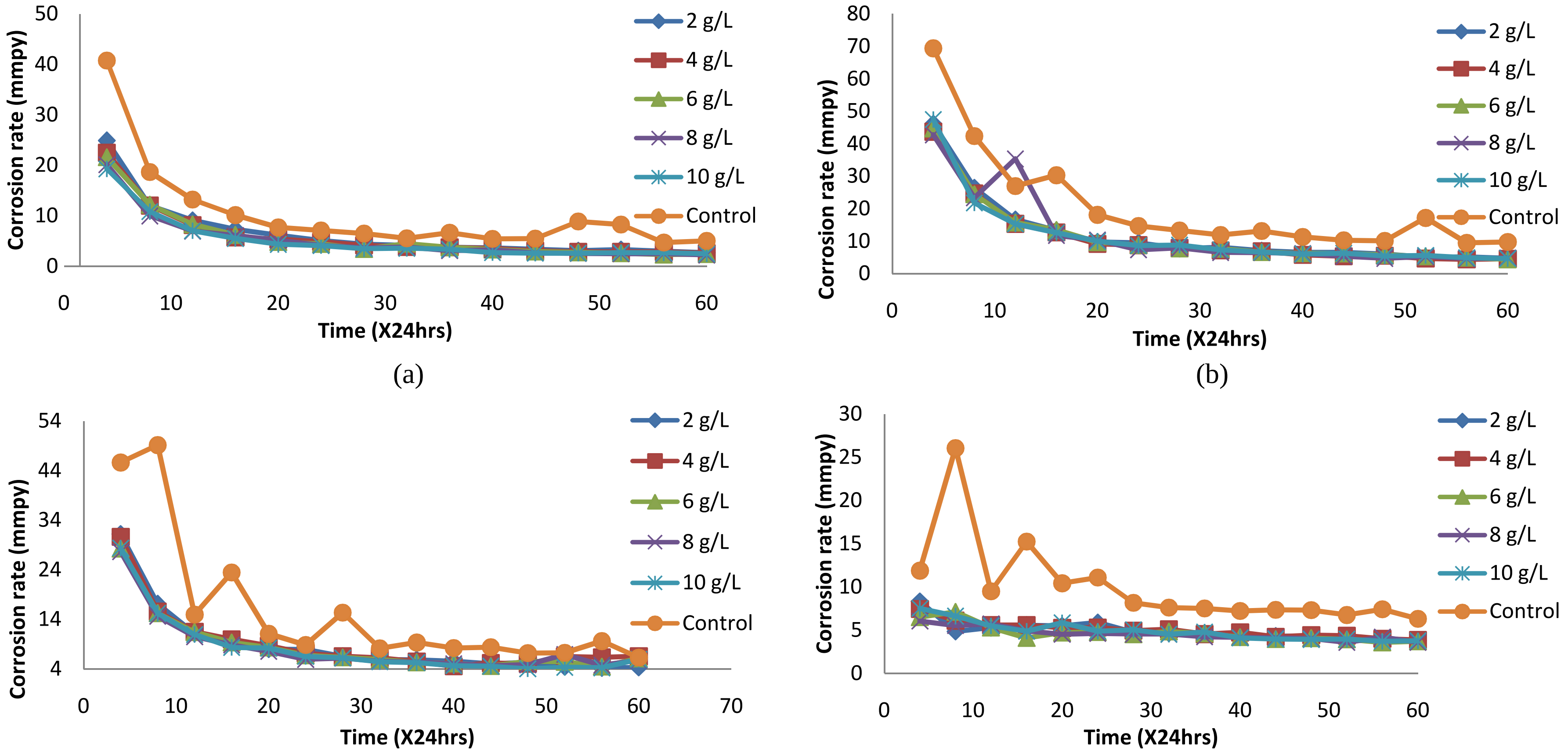
In order to properly situate the interpretation for corrosion rate vs time graph considering that the curves on the graphs (Figures 4.1 - 4.5) are not so distinctly separated to delineate performance (see Appendix B for re-scaled plot of corrosion rate against time) it was necessary to develop an inequality Table. This was done by averaging the corrosion rate values for each of the inhibitor concentration over the 60 day period. These values were then compared to the control experiment to rank inhibitor performance. Based on this criterion it was possible to compare corrosion rate data with IE values (Figures 4.6 - 4.10) since an indirect relationship exists between them. Table 4.1 shows the ranking of the performance of the inhibitor concentration in inhibiting corrosion. By comparing the information in the Table 4.1 to the IE graph (Figures 4.6 - 4.10) we see that an indirect relationship exists. The inhibitor concentration with the highest corrosion rate had the lowest IE, while the inhibitor concentration with lowest corrosion rate had the highest IE.



(a) (b) (c) (d)

Fig. 4.1: Corrosion rate (mmpy) against time (hours) of mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the presence of PC

(a) mild steel in HCl, (b) mild steel in H_2SO_4, (c) aluminium in HCl, and (d) aluminium in H_2SO_4.



(a)

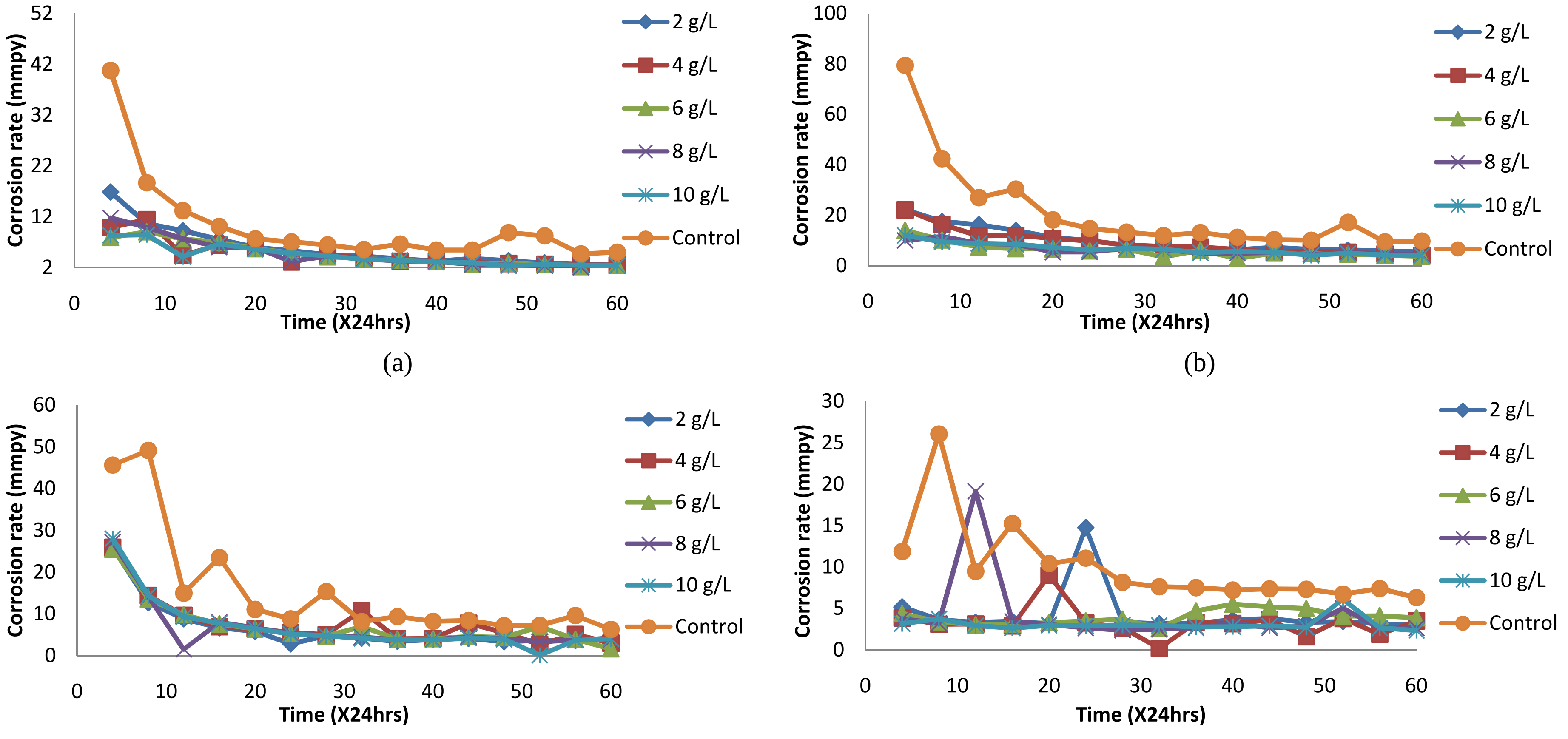
(b)

(c)

(d)

Fig. 4.2: Corrosion rate (mmpy) against time (hours) of mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the presence of AN

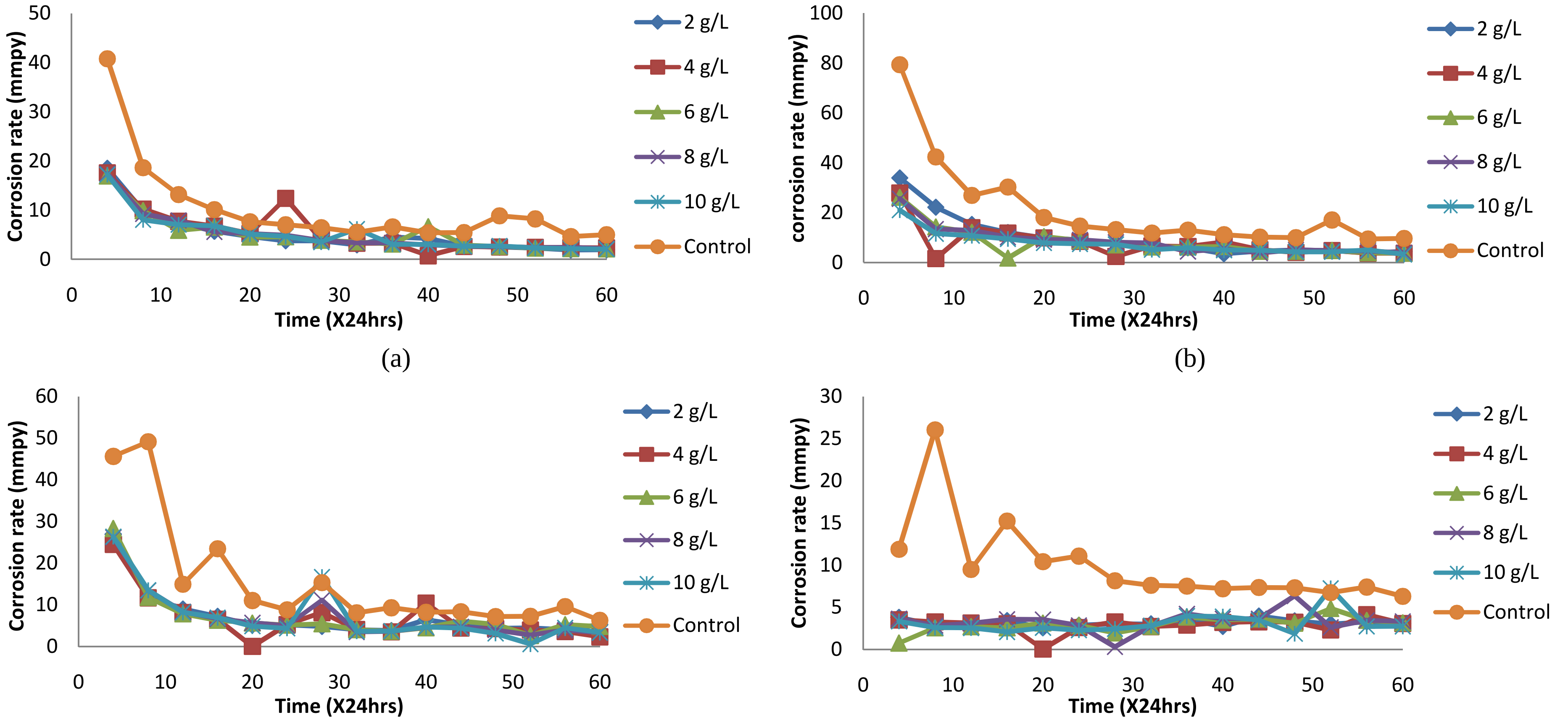
(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) aluminium in HCl (d) aluminium in H_2SO_4



(a) (b) (c) (d)

Fig. 4.3: Corrosion rate (mmpy) against time (hours) of mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the presence of CF

(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) aluminium in HCl (d) aluminium in H_2SO_4.

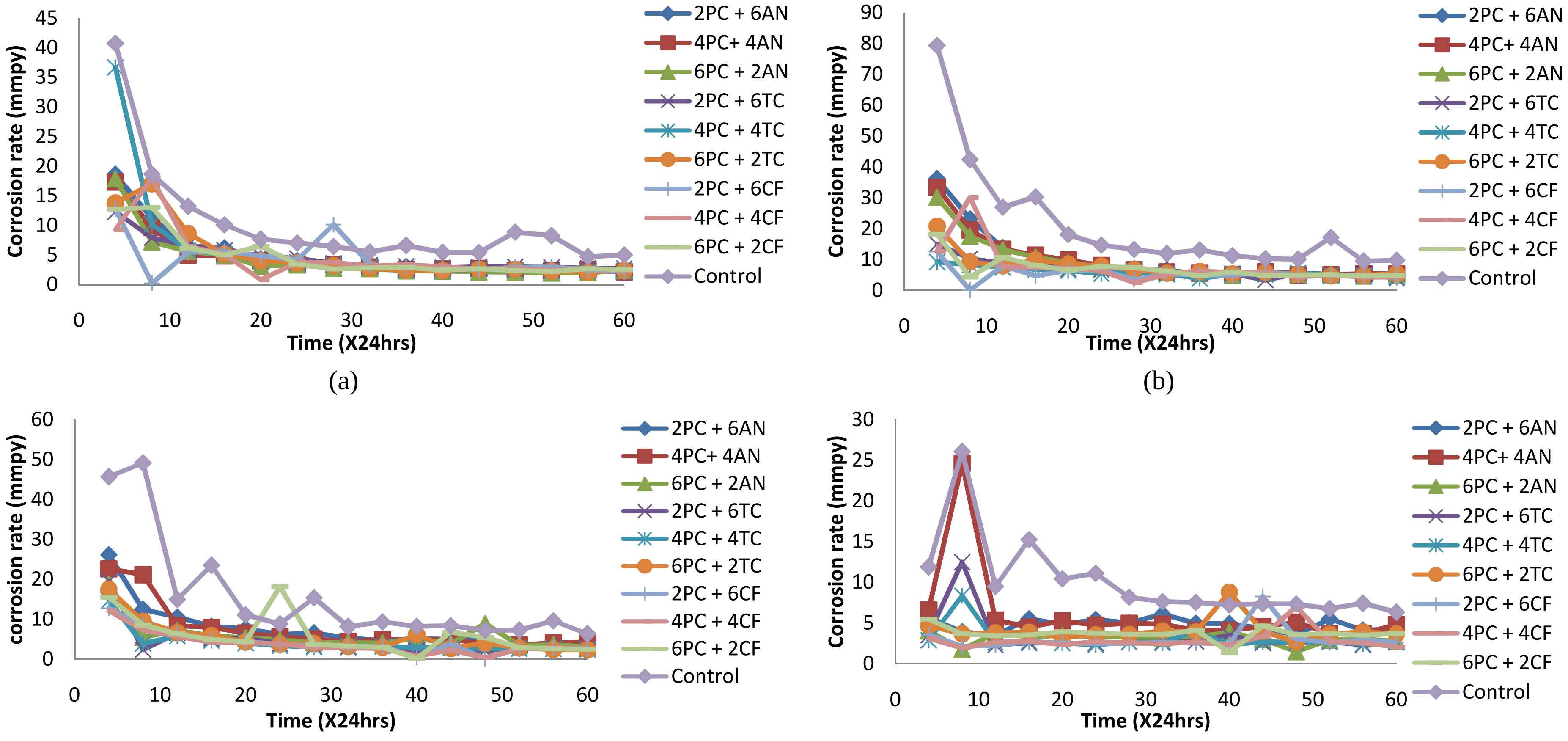


(a) (b)

(c) (d)

Fig. 4.4: Corrosion rate (mmpy) against time (hours) of mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the presence of TC

(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) aluminium in HCl and (d) aluminium in H_2SO_4.



(a)

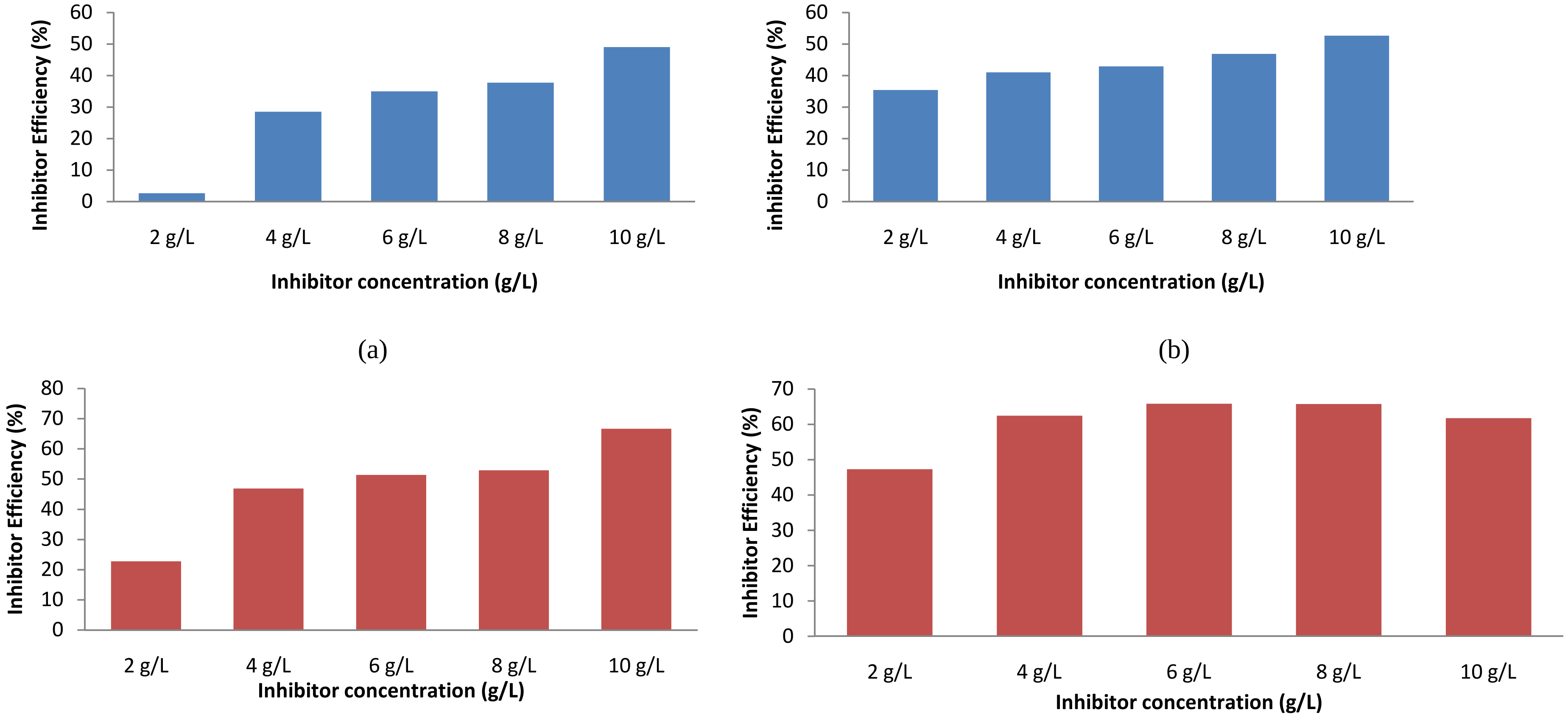
(b)

(c)

(d)

Fig. 4.5: Corrosion rate (mmpy) against time (hours) of mild steel and aluminium in 0.5 M HCl and 0.5 M H2SO4 in the presence of SA

(a) mild steel in HCl (b) mild steel in H2SO4 (c) aluminium in HCl and (d) aluminium in H_2SO_4.

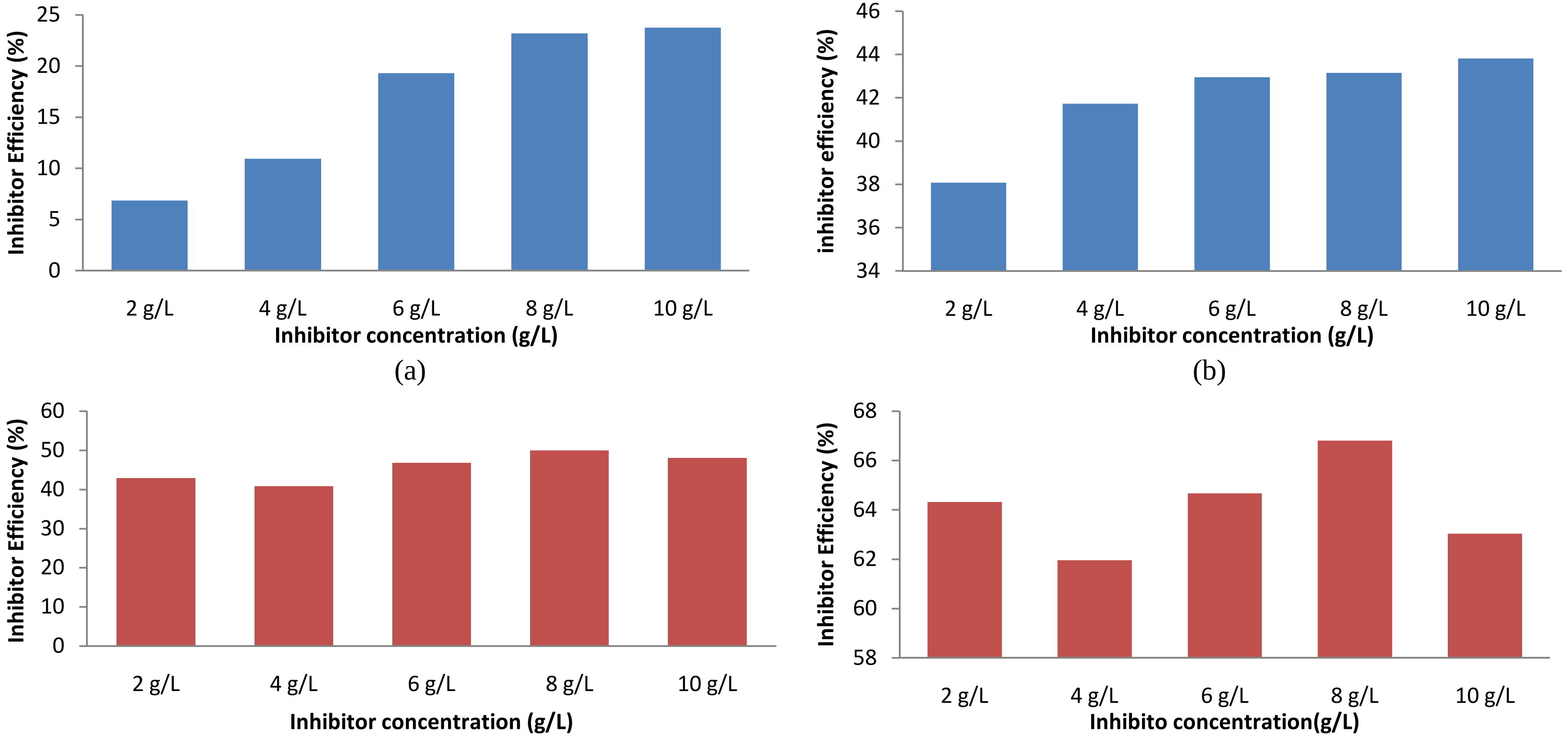


(a) (b)

(c) (d)

Fig. 4.6: Inhibition efficiency of PC on the corrosion of mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 solutions

(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) aluminium in HCl and (d) aluminium in H_2SO_4.

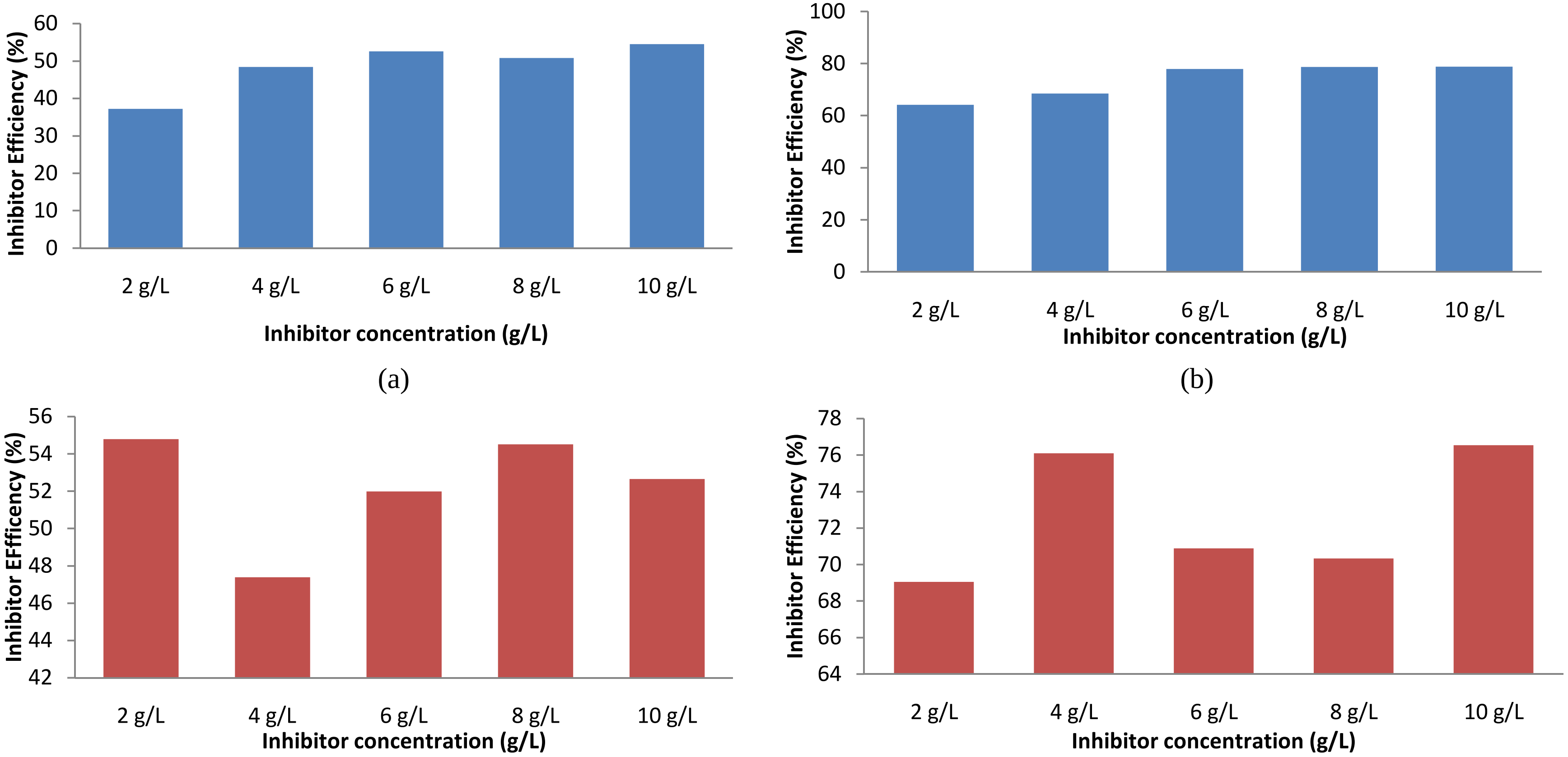


(a) (b)

(c) (d)

Fig. 4.7: Inhibition efficiency of AN on the corrosion of mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 solutions

(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Aluminium in HCl and (d) Aluminium in H_2SO_4.

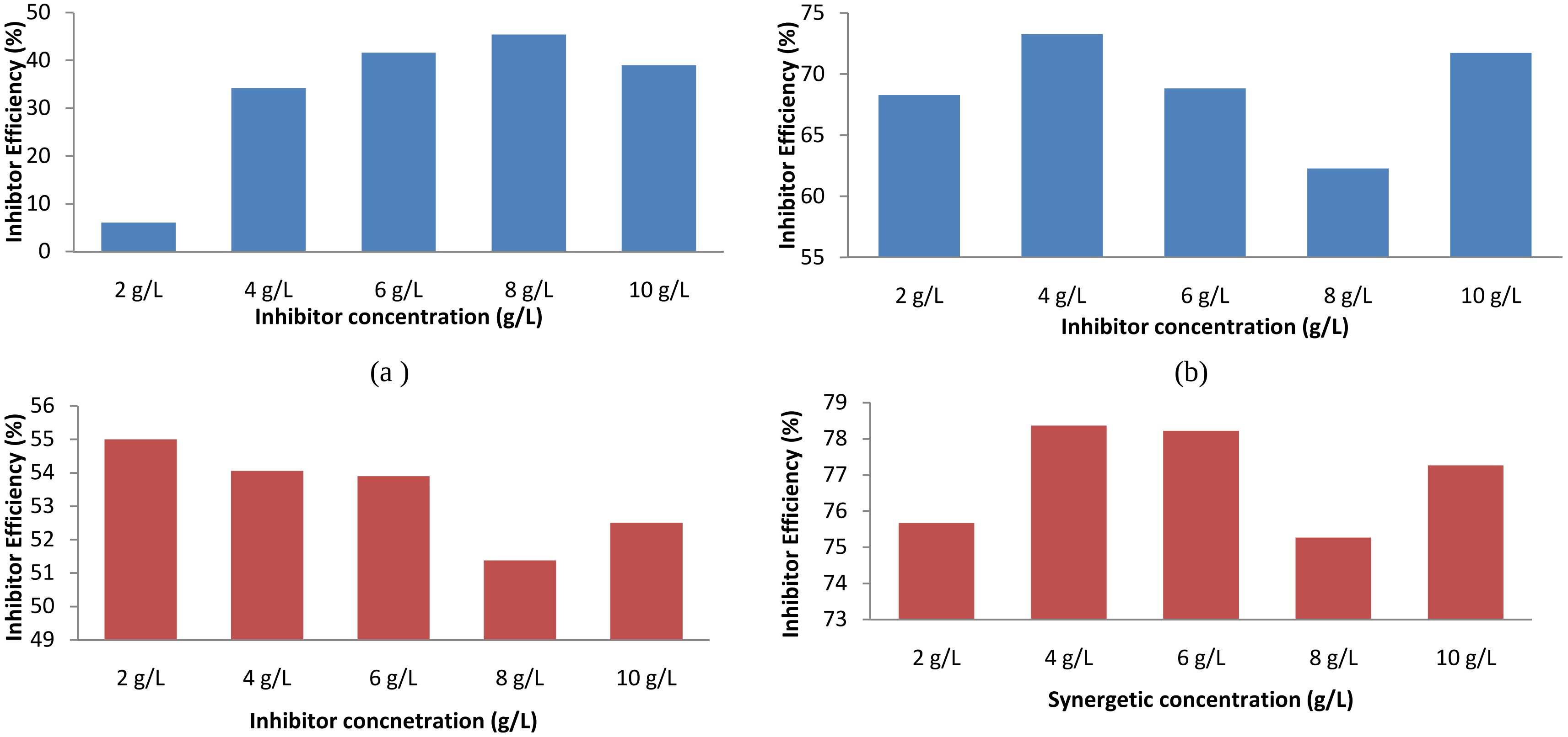


(a) (b)

(c) (d)

Fig. 4.8: Inhibition efficiency of CF on the corrosion for mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 solutions

(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Aluminium in HCl and (d) Aluminium in H_2SO_4.



(a)

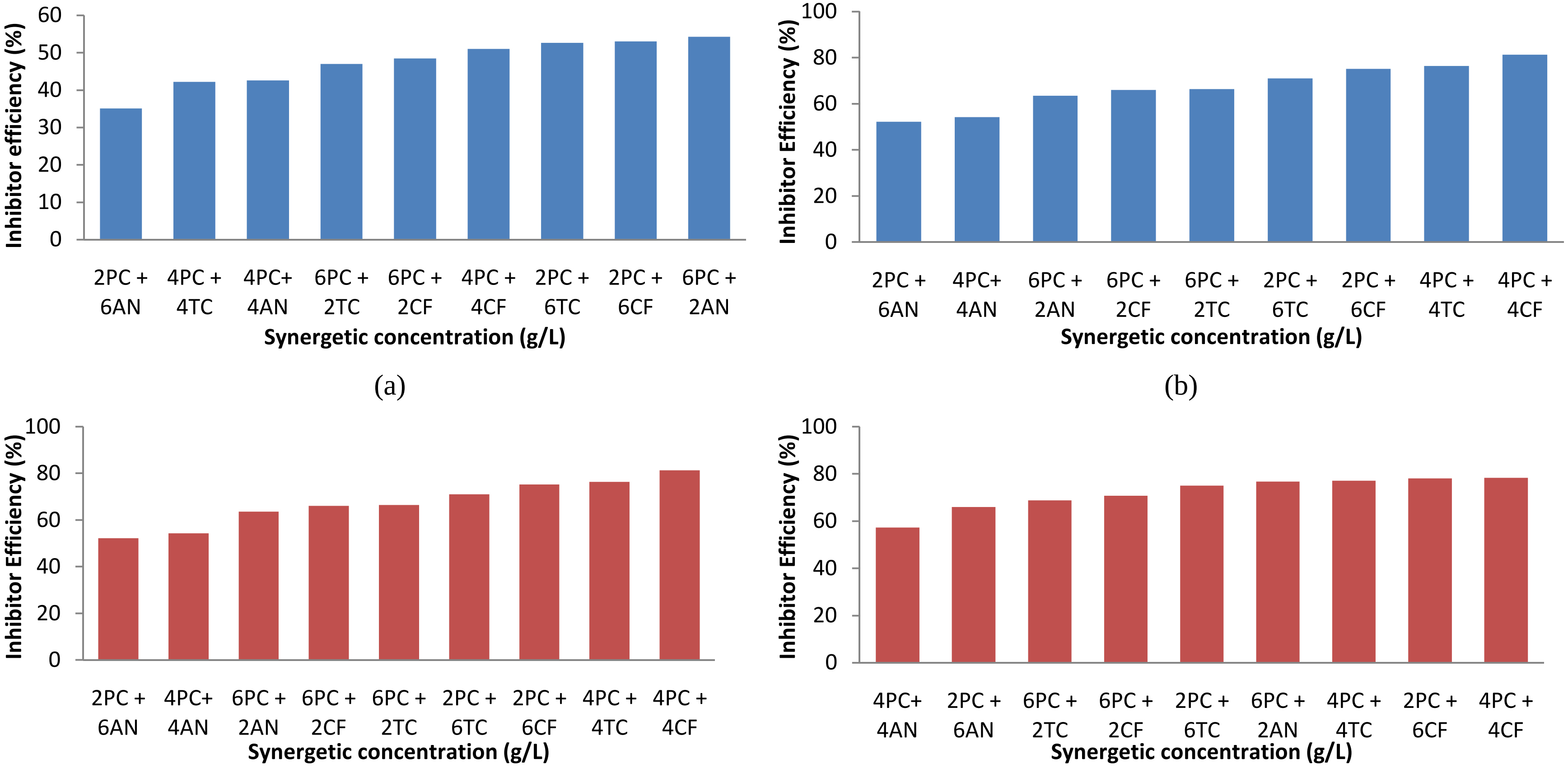
(b)

(c)

(d)

Fig. 4.9: Inhibition efficiency of TC on the corrosion for mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 solutions

(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Aluminium in HCl and (d) Aluminium in H_2SO_4.



(a) (b)

(c) (d)

Fig. 4.10: Inhibition efficiency of SA on the corrosion for mild steel and aluminium immersed in 0.5 M HCl and 0.5 M H_2SO_4

(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Aluminium in HCl and (d) Aluminium in H_2SO_4.

Table 4.1 Trend of inhibitor concentration performance in corrosion rate terms

S.No.	Description	Trend	Best Performing	Least Effective
1	Ms_HCl_PC	Control > 2g/L > 4g/L > 6g/L> 8g/L > 10g/L	10 g/L	2 g/L
2	Ms_H_2SO_4_PC	Control > 2g/L > 4g/L > 6g/L> 8g/L > 10g/L	10 g/L	2 g/L
3	Al_HCl_PC	Control > 2g/L > 4g/L > 6g/L> 8g/L > 10g/L	10 g/L	2 g/L
4	Al_H_2SO_4_PC	Control > 2g/L > 10g/L > 4g/L> 8g/L > 6g/L	6 g/L	2 g/L
5	Ms_HCl_AN	Control > 2g/L > 4g/L > 6g/L> 8g/L > 10g/L	10 g/L	2 g/L
6	Ms_H_2SO_4_AN	Control > 2g/L > 4g/L > 6g/L> 8g/L > 10g/L	10 g/L	2 g/L
7	Al_HCl_AN	Control > 4g/L > 2g/L > 6g/L> 10g/L > 8g/L	8 g/L	4 g/L
8	Al_H_2SO_4_AN	Control > 4g/L > 10g/L > 2g/L> 6g/L > 8g/L	8 g/L	4 g/L
9	Ms_HCl_CF	Control > 2g/L > 4g/L > 8g/L> 6g/L > 10g/L	10 g/L	2 g/L
10	Ms_H_2SO_4_CF	Control > 2g/L > 4g/L > 6g/L> 8g/L > 10g/L	10 g/L	2 g/L
11	Al_HCl_CF	Control > 4g/L > 6g/L > 10g/L> 8g/L > 2g/L	2 g/L	4 g/L
12	Al_H_2SO_4_CF	Control > 2g/L > 8g/L > 6g/L> 4g/L > 10g/L	10 g/L	2 g/L
13	Ms_HCl_TC	Control > 2g/L > 4g/L > 10g/L> 6g/L > 8g/L	8 g/L	2 g/L
14	Ms_H_2SO_4_TC	Control > 8g/L > 2g/L > 6g/L> 10g/L > 4g/L	4 g/L	8 g/L
15	Al_HCl_TC	Control > 8g/L > 10g/L > 6g/L> 4g/L > 2g/L	2 g/L	8 g/L
16	Al_H_2SO_4_TC	Control > 8g/L > 2g/L > 10g/L> 6g/L > 4g/L	4 g/L	8 g/L
17	Ms_HCl_SA	2PC+6AN>4PC+4TC>4PC+4AN>6PC+2TC>6PC+2CF>4PC+4CF>2PC+6TC>2PC+6CF>6PC+2AN	6PC+2AN	2PC+6AN
18	Ms_H_2SO_4_SA	2PC+6AN>4PC+4AN>6PC+2AN>6PC+2TC>6PC+2CF>4PC+4CF>2PC+6TC>4PC+4TC>2PC+6CF	2PC+6CF	2PC+6AN
19	Al_HCl_SA	2PC+6AN>4PC+4AN>6PC+2AN>6PC+2CF>6PC+2TC>2PC+6TC>2PC+6CF>4PC+4TC>4PC+4CF	4PC + 4CF	2PC+6AN
20	Al_H_2SO_4_SA	4PC+4AN>2PC+6AN>6PC+2TC>6PC+2CF>2PC+6TC>6PC+2AN>4PC+4TC>2PC+6CF>4PC+4CF	4PC + 4CF	4PC+4AN

Table 4.2: Performance ranking of all inhibitor concentrations utilized for mild steel in 0.5 M HCl and 0.5 M H_2SO_4 system

S.No.	Description	IE%	S.No.	Description	IE%
	A			B	
1	Ms_HCl_CF_10 g/L	54.50	1	Ms_H_2SO_4_2PC + 6CF	81.29
2	Ms_HCl_6PC + 2AN	54.26	2	Ms_ H_2SO_4_4PC + 4TC	80.90
3	Ms_HCl_2PC + 6CF	53.05	3	Ms_ H_2SO_4_CF_10 g/L	78.86
4	Ms_HCl_2PC + 6TC	52.63	4	Ms_ H_2SO_4_CF_8 g/L	78.68
5	Ms_HCl_CF_6 g/L	52.62	5	Ms_ H_2SO_4_CF_6 g/L	77.89
6	Ms_HCl_4PC + 4CF	51.04	6	Ms_ H_2SO_4_2PC + 6TC	77.16
7	Ms_HCl_CF_8 g/L	50.79	7	Ms_ H_2SO_4_4PC + 4CF	75.16
8	Ms_HCl_PC_10 g/L	49.09	8	Ms_ H_2SO_4_6PC + 2CF	73.96
9	Ms_HCl_6PC + 2CF	48.47	9	Ms_ H_2SO_4_TC_4 g/L	73.25
10	Ms_HCl_CF_4 g/L	48.43	10	Ms_ H_2SO_4_6PC + 2TC	72.04
11	Ms_HCl_6PC + 2TC	47.04	11	Ms_ H_2SO_4_TC_10 g/L	71.71
12	Ms_HCl_TC_8 g/L	45.39	12	Ms_ H_2SO_4_TC_6 g/L	68.83
13	Ms_HCl_4PC+ 4AN	42.64	13	Ms_ H_2SO_4_CF_4 g/L	68.46
14	Ms_HCl_4PC + 4TC	42.22	14	Ms_ H_2SO_4_TC_2 g/L	68.28
15	Ms_HCl_TC_6 g/L	41.61	15	Ms_ H_2SO_4_CF_2 g/L	64.16
16	Ms_HCl_TC_10 g/L	39.00	16	Ms_ H_2SO_4_TC_8 g/L	62.28
17	Ms_HCl_PC_8 g/L	37.74	17	Ms_ H_2SO_4_6PC + 2AN	61.37
18	Ms_HCl_CF_2 g/L	37.20	18	Ms_ H_2SO_4_4PC+ 4AN	54.29
19	Ms_HCl_2PC + 6AN	35.10	19	Ms_ H_2SO_4_2PC + 6AN	53.57
20	Ms_HCl_PC_6 g/L	35.01	20	Ms_ H_2SO_4_PC_10 g/L	52.65
21	Ms_HCl_TC_4 g/L	34.23	21	Ms_ H_2SO_4_PC_8 g/L	46.92
22	Ms_HCl_PC_4 g/L	28.57	22	Ms_ H_2SO_4_AN_10 g/L	43.82
23	Ms_HCl_AN_10 g/L	23.77	23	Ms_ H_2SO_4_AN_8 g/L	43.15
24	Ms_HCl_AN_8 g/L	23.20	24	Ms_ H_2SO_4_AN_6 g/L	42.95
25	Ms_HCl_AN_6 g/L	19.30	25	Ms_ H_2SO_4_PC_6 g/L	42.89

S.No.	Description	IE%	S.No.	Description	IE%
A			B		
26	Ms_HCl_AN_4 g/L	10.94	26	Ms_ H_2SO_4_AN_4 g/L	41.73
27	Ms_HCl_AN_2 g/L	6.85	27	Ms_ H_2SO_4_PC_4 g/L	41.03
28	Ms_HCl_TC_2 g/L	6.06	28	Ms_ H_2SO_4_AN_2 g/L	38.08
29	Ms_HCl_PC_2 g/L	2.71	29	Ms_ H_2SO_4_PC_2 g/L	35.42

Table 4.3: Performance ranking of all inhibitor concentration utilized for aluminium in 0.5 M HCl and 0.5 M H_2SO_4 system

S.No.	Description	IE%	S.No.	Description	IE%
	A			B	
1	Al_HCl_4PC + 4CF	81.27	1	Al_ H_2SO_4_TC_4 g/L	78.36
2	Al_HCl_4PC + 4TC	76.38	2	Al_ H_2SO_4_4PC + 4CF	78.35
3	Al_HCl_2PC + 6CF	75.18	3	Al_ H_2SO_4_TC_6 g/L	78.22
4	Al_HCl_2PC + 6TC	71.04	4	Al_ H_2SO_4_2PC + 6CF	78.06
5	Al_HCl_PC_10 g/L	66.7	5	Al_ H_2SO_4_TC_10 g/L	77.26
6	Al_HCl_6PC + 2TC	66.37	6	Al_ H_2SO_4_4PC + 4TC	77.17
7	Al_HCl_6PC + 2CF	66.06	7	Al_ H_2SO_4_6PC + 2AN	76.72
8	Al_HCl_6PC + 2AN	63.55	8	Al_ H_2SO_4_CF_10 g/L	76.54
9	Al_HCl_TC_2 g/L	55	9	Al_ H_2SO_4_CF_4 g/L	76.1
10	Al_HCl_CF_2 g/L	54.79	10	Al_ H_2SO_4_TC_2 g/L	75.67
11	Al_HCl_CF_8 g/L	54.51	11	Al_ H_2SO_4_TC_8 g/L	75.27
12	Al_HCl_4PC+ 4AN	54.24	12	Al_ H_2SO_4_2PC + 6TC	75.07
13	Al_HCl_TC_4 g/L	54.06	13	Al_ H_2SO_4_CF_6 g/L	70.89
14	Al_HCl_TC_6 g/L	53.9	14	Al_ H_2SO_4_6PC + 2CF	70.71
15	Al_HCl_PC_8 g/L	52.91	15	Al_ H_2SO_4_CF_8 g/L	70.34
16	Al_HCl_CF_10 g/L	52.65	16	Al_H2SO4_CF_2 g/L	69.05
17	Al_HCl_TC_10 g/L	52.5	17	Al_ H_2SO_4_6PC + 2TC	68.76
18	Al_HCl_2PC + 6AN	52.22	18	Al_ H_2SO_4_AN_8 g/L	66.81
19	Al_HCl_CF_6 g/L	51.98	19	Al_ H_2SO_4_2PC + 6AN	65.92
20	Al_HCl_PC_6 g/L	51.38	20	Al_ H_2SO_4_PC_6 g/L	65.87
21	Al_HCl_TC_8 g/L	51.38	21	Al_ H_2SO_4_PC_8 g/L	65.75
22	Al_HCl_AN_8 g/L	49.96	22	Al_ H_2SO_4_AN_6 g/L	64.67
23	Al_HCl_AN_10 g/L	48.07	23	Al_ H_2SO_4_AN_2 g/L	64.33
24	Al_HCl_CF_4 g/L	47.39	24	Al_ H_2SO_4_AN_10 g/L	63.04

S.No.	Description	IE%	S.No.	Description	IE%
25	Al_HCl_PC_4 g/L	46.91	25	Al_ H_2SO_4_PC_4 g/L	62.43
26	Al_HCl_AN_6 g/L	46.82	26	Al_ H_2SO_4_AN_4 g/L	61.96
27	Al_HCl_AN_2 g/L	42.95	27	Al_ H_2SO_4_PC_10 g/L	61.75
28	Al_HCl_AN_4 g/L	40.88	28	Al_ H_2SO_4_4PC+ 4AN	57.27
29	Al_HCl_PC_2 g/L	22.78	29	Al_ H_2SO_4_PC_2 g/L	47.31

4.3 Adsorption Isotherms

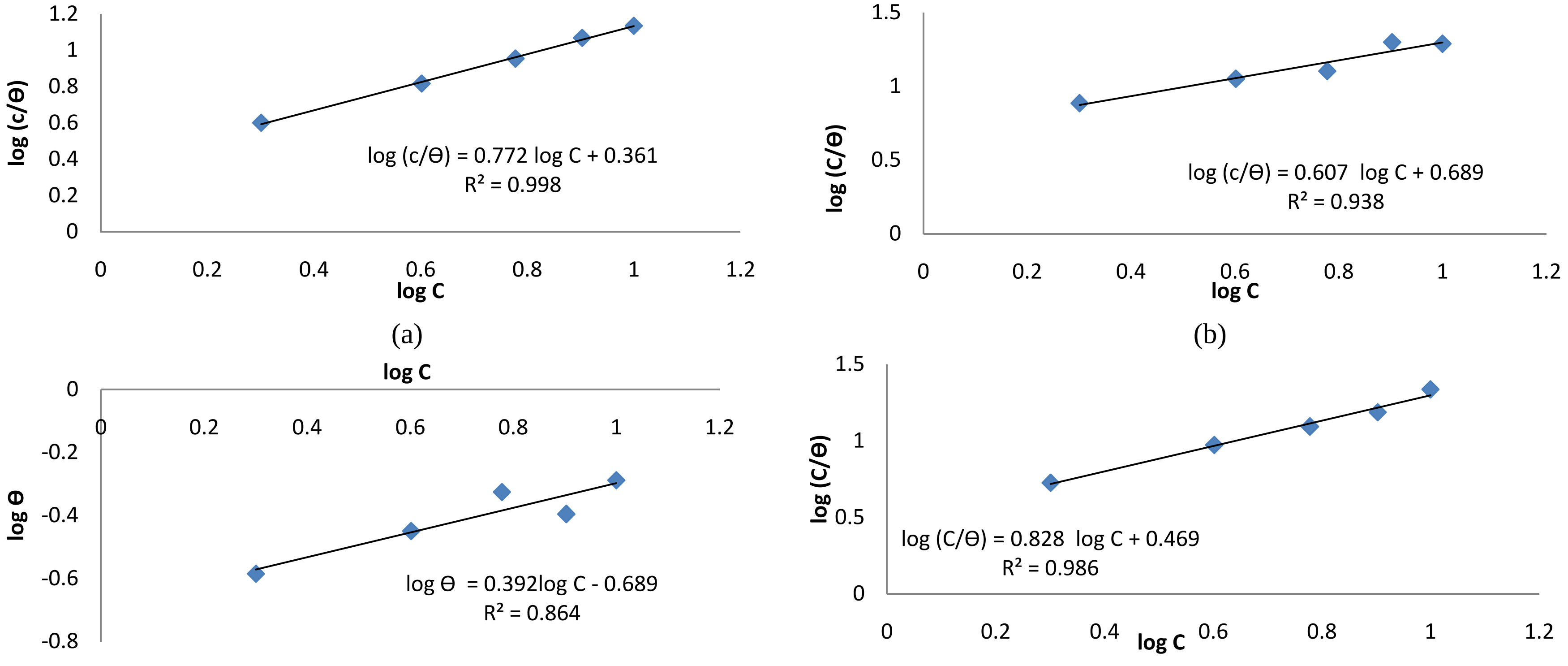
Table 4.4: *R*-values for fitting experimental data with adsorption isotherms for PC, AN, CF and TC for the immersion of mild steel in 0.5 M HCl and 0.5 M H_2SO_4 solution

S.No.	Adsorption isotherms	PC		AN		CF		TC	
		HCl	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4
1	Frumkin	0.960	0.504	0.958	0.709	0.896	0.470	0.260	0.528
2	Freundlich	0.990	0.930	0.976	0.792	0.929	0.898	0.333	0.636
3	Temkin	0.993	0.912	0.981	0.783	0.932	0.889	0.334	0.635
4	Langmuir	0.999	0.969	0.999	0.997	0.999	0.977	0.999	0.997
5	Flory-Huggins	0.987	0.766	0.978	0.733	0.924	0.720	0.306	0.583
6	Dubinin-Radushkevich	0.971	0.920	0.983	0.888	0.991	0.917	0.095	0.681
7	Bockris-Swinkel	0.987	0.840	0.987	0.755	0.940	0.809	0.337	0.634
8	El-Awady	0.993	0.920	0.982	0.787	0.934	0.879	0.334	0.635

Table 4.5: R-values for fitting experimental data with adsorption isotherms for PC, AN, CF and TC during the immersion of aluminium in 0.5 M HCl and in 0.5 M H_2SO_4 solution

S.No.	Adsorption isotherms	PC		AN		CF		TC	
		HCl	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4
1	Frumkin	0.721	0.687	0.926	0.375	0.045	0.694	0.679	0.702
2	Freundlich	0.930	0.867	0.045	0.345	0.190	0.813	0.76	0.628
3	Temkin	0.763	0.850	0.164	0.342	0.210	0.815	0.757	0.622
4	Langmuir	0.158	0.993	0.573	0.999	0.984	0.997	0.997	0.998
5	Flory-Huggins	0.518	0.764	0.913	0.359	0.045	0.778	0.704	0.651
6	Dubinin-Radushkevich	0.818	0.889	0.205	0.219	0	0.683	0.772	0.435
7	Bockris-Swinkel	0.880	0.808	0.170	0.335	0.265	0.812	0.745	0.610
8	El-Awady	0.836	0.853	0	0.342	0.200	0.815	0.759	0.620

4.3.1 Langmuir adsorption isotherm



(a)

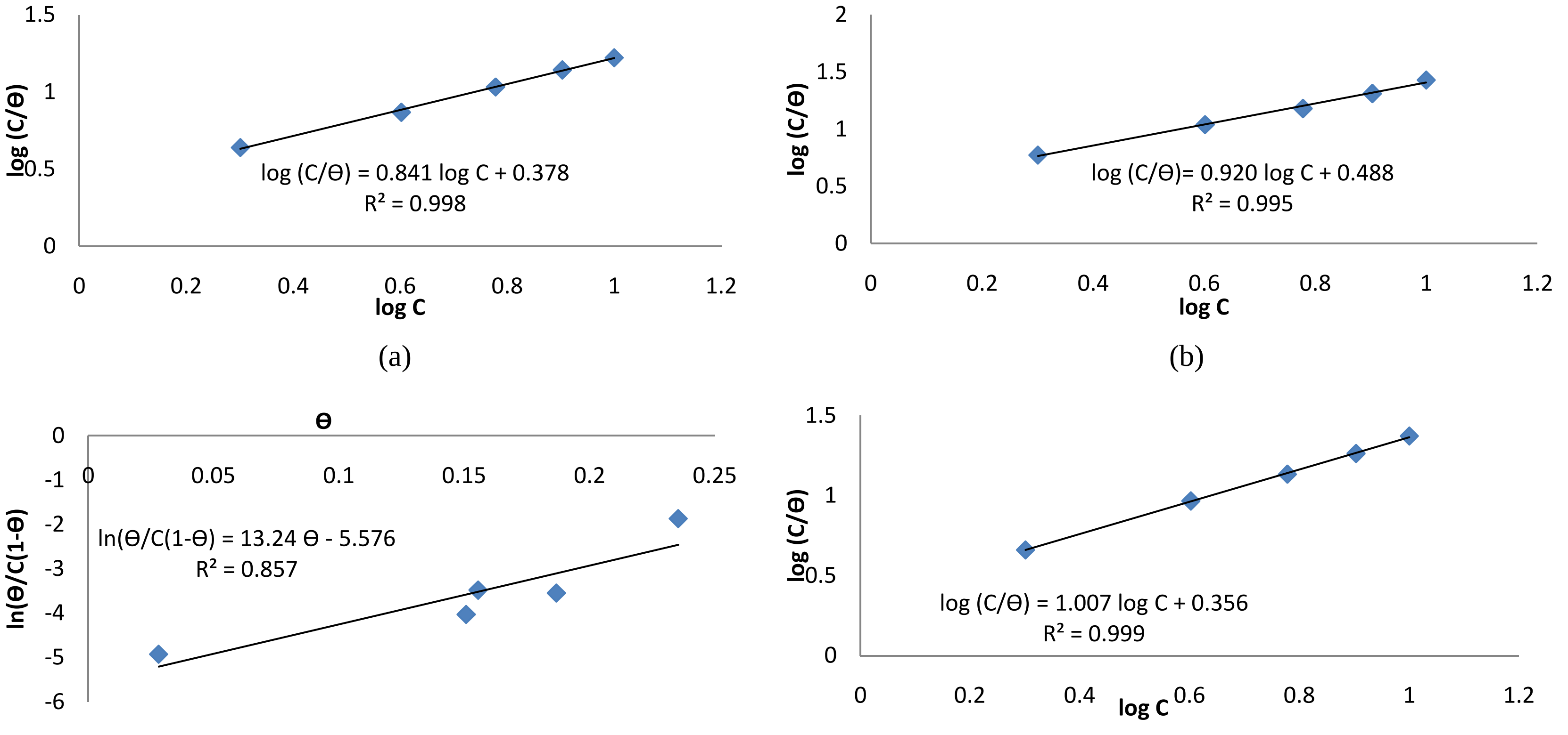
(b)

(c)

(d)

Fig. 4.11: Adsorption isotherms for mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4solution in the presence of PC

(a) mild steel in HCl showing compliance with Langmuir (b) mild steel in H_2SO_4 showing compliance with Langmuir (c) Al in HCl showing compliance with Freundlich isotherm and (d) Al in H_2SO_4 showing compliance with Langmuir.

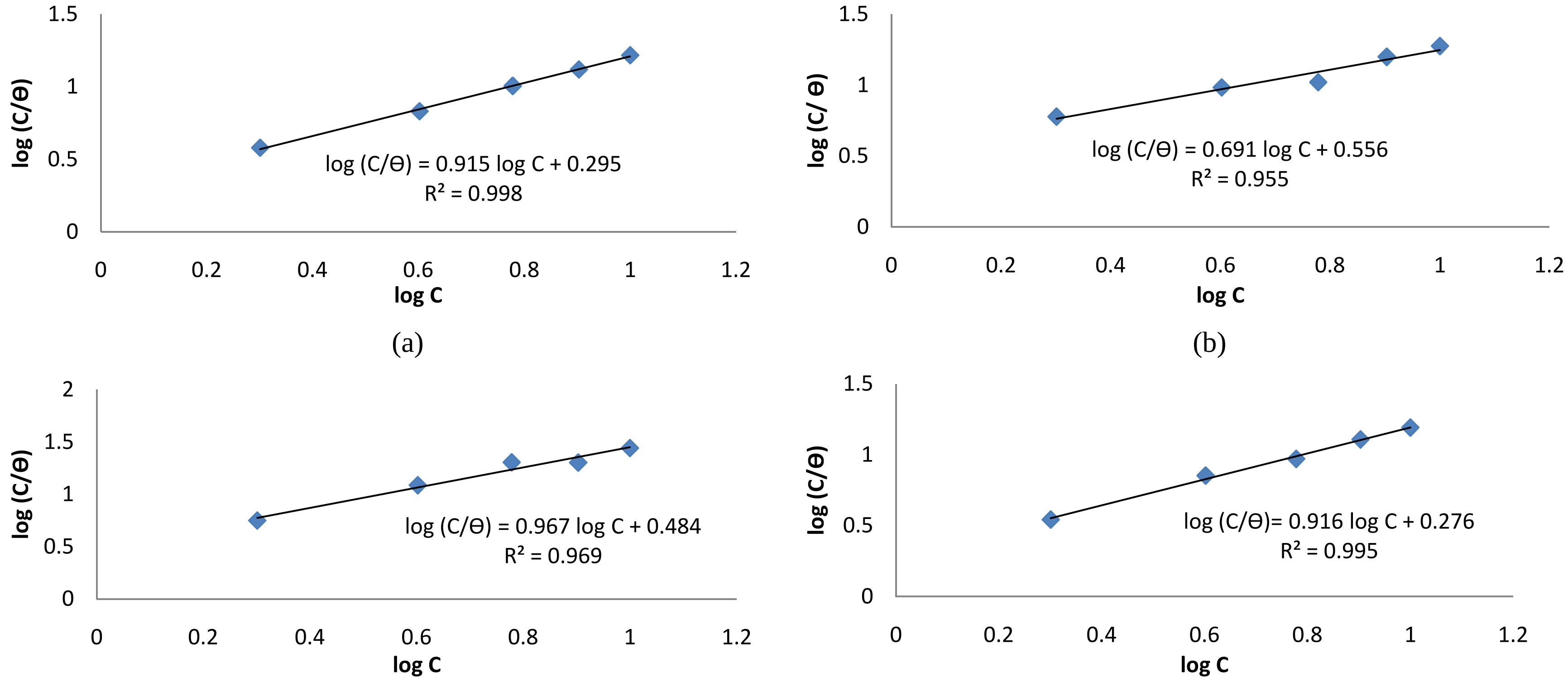


(a) (b)

(c) (d)

Fig. 4.12: Adsorption isotherms for mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 solution in the presence of AN

(a) mild steel in HCl showing compliance with Langmuir (b) mild steel in H_2SO_4 showing compliance with Langmuir (c) Al in HCl showing compliance with Frumkin isotherm and (d) Al in H_2SO_4 showing compliance with Langmuir.

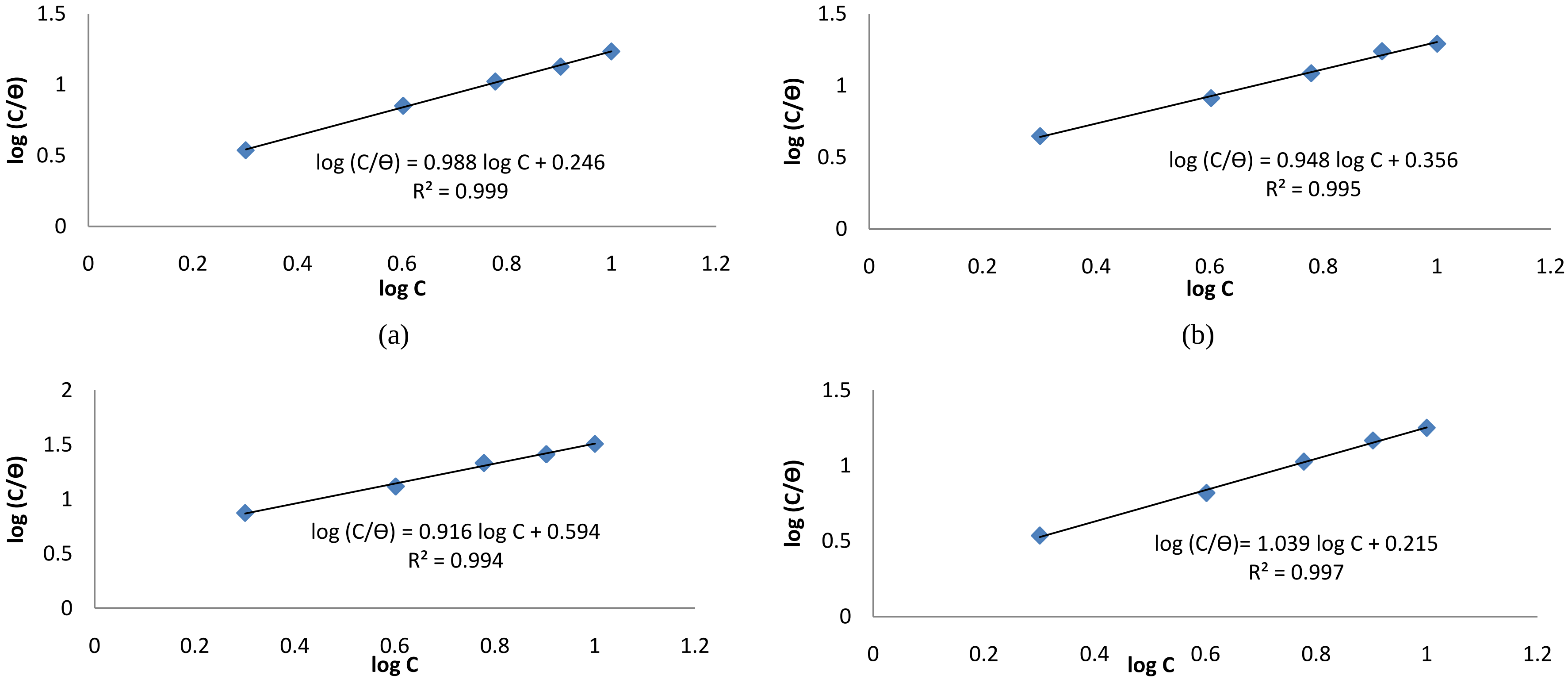


(a) (b)

(c) (d)

Fig. 4.13: Adsorption isotherms for mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 solution in the presence of CF

(a) mild steel in HCl showing compliance with Langmuir (b) mild steel in H_2SO_4 showing compliance with Langmuir (c) Al in HCl showing compliance with Langmuir and (d) Al in H_2SO_4 showing compliance with Langmuir.



(a) (b)

(c) (d)

Fig. 4.14: Adsorption isotherms for mild steel and aluminium immersed in 0.5 M HCl and 0.5 M H_2SO_4 solution in the presence of TC

(a) mild steel in HCl showing compliance with Langmuir (b) mild steel in H_2SO_4 showing compliance with Langmuir (c) Al in HCl showing compliance with Langmuir and (d) Al in H_2SO_4 showing compliance with Langmuir.

Table 4.6: Langmuir adsorption isotherm parameters showing degree of favourability.

S.No.	Description	Slope	Intercept	Q_o	K_L	R_L	Favourability condition
1	Ms_HCl_PC	0.772	0.361	1.295	2.139	0.190	Favourable
2	Ms_H_2SO_4_PC	0.607	0.689	1.647	0.881	0.362	Favourable
3	Al_H_2SO_4_PC	0.828	0.469	1.208	1.765	0.221	Favourable
4	Ms_HCl_AN	0.841	0.378	1.189	2.225	0.183	Favourable
5	Ms_H_2SO_4_AN	0.92	0.488	1.087	1.885	0.210	Favourable
6	Al_H_2SO_4_AN	1.007	0.356	0.993	2.829	0.150	Favourable
7	Ms_HCl_CF	0.915	0.295	1.093	3.102	0.139	Favourable
8	Ms_H_2SO_4_CF	0.691	0.556	1.447	1.243	0.287	Favourable
9	Al_HCl_CF	0.967	0.484	1.034	1.998	0.200	Favourable
10	Al_H_2SO_4_CF	0.916	0.276	1.092	3.319	0.131	Favourable
11	Ms_HCl_TC	0.988	0.246	1.012	4.016	0.111	Favourable
12	Ms_H_2SO_4_TC	0.948	0.356	1.055	2.663	0.158	Favourable
13	Al_HCl_TC	0.916	0.594	1.092	1.542	0.245	Favourable
14	Al_H_2SO_4_TC	1.039	0.215	0.962	4.833	0.094	Favourable

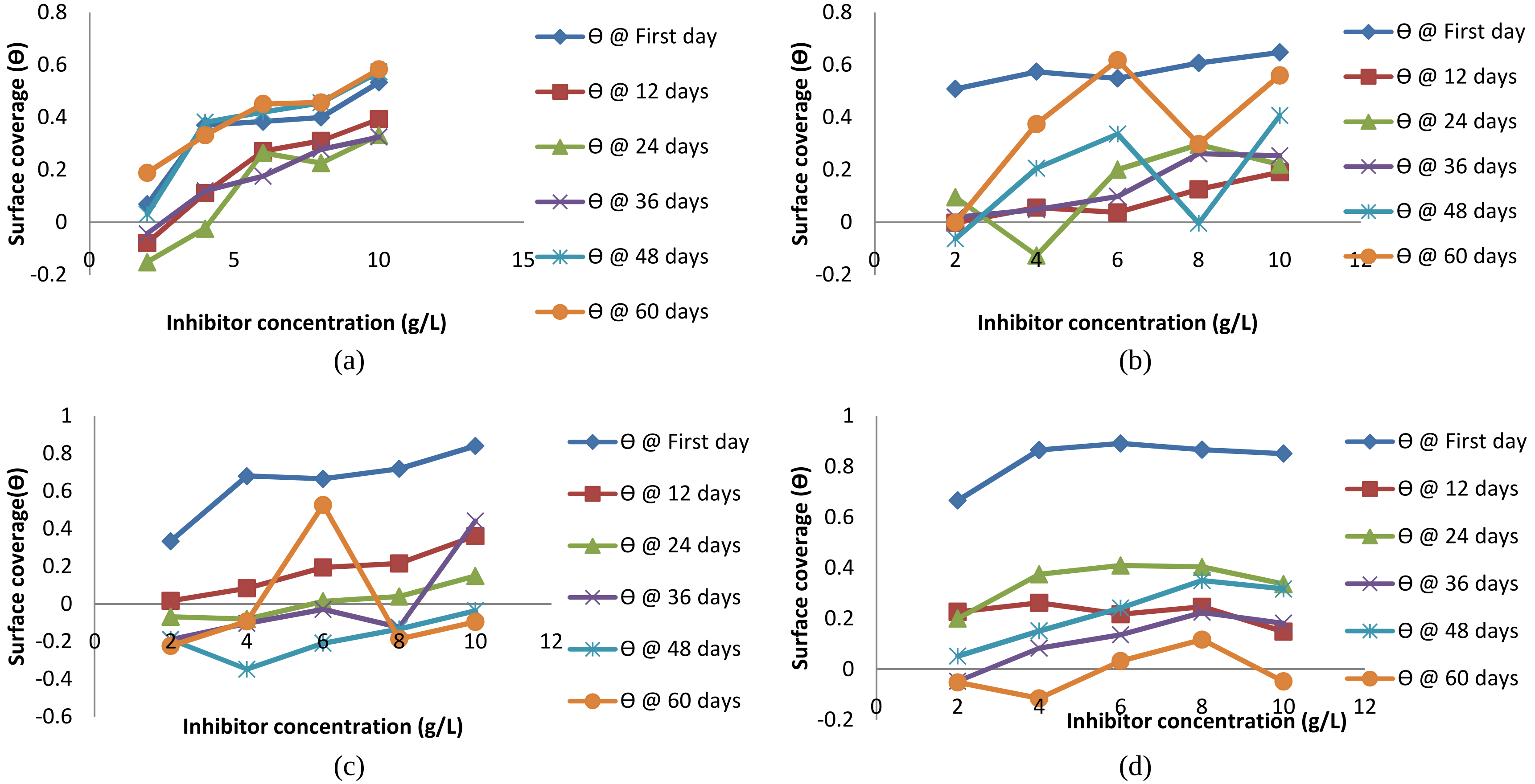
4.3.2 Freundlich adsorption isotherm

4.3.3 Frumkin adsorption isotherm

4.3.4 Dynamic surface coverage

The changes in surface coverage values as the experiment progressed for the different media-metal corrosion systems was investigated by carrying out a study of the influence of times of exposure to the relationship between θ and C. This is shown for each inhibitor used in Figures 4.15 - 4.18 and could be described as follows:

- Dynamic surface coverage for mild steel and aluminium samples immersed in HCl and H_2SO_4 in the presence of PC; In Fig 4.15a, for the mild steel samples immersed in 0.5 M HCl media, all θ behaviour showed the same trend across the inhibitor concentration. They increased as inhibitor concentration

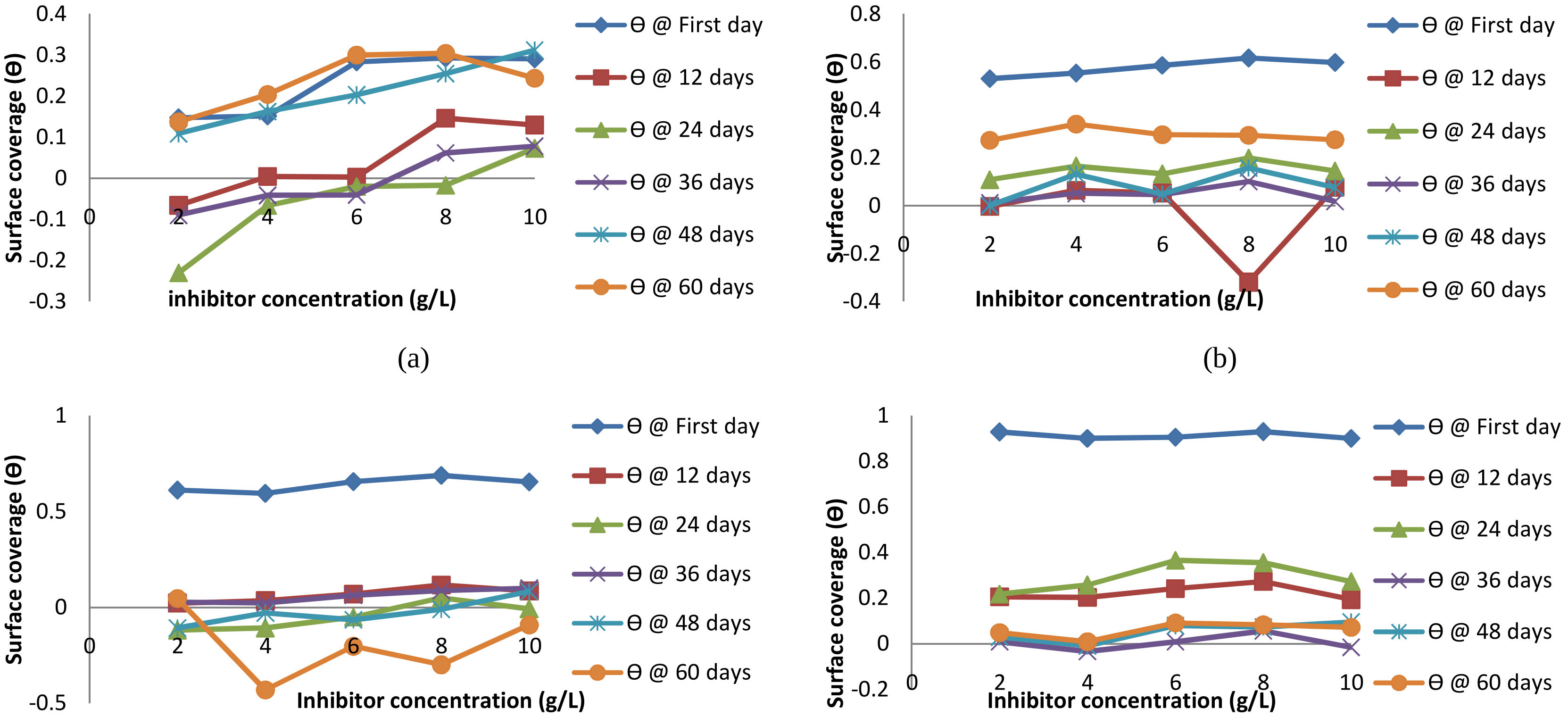


(a) (b)

(c) (d)

Fig. 4.15: Variation of surface coverage (θ) with PC concentration (g/L) at a temperature of 303K for different time intervals

(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Al in HCl (d) Al in H_2SO_4



(a)

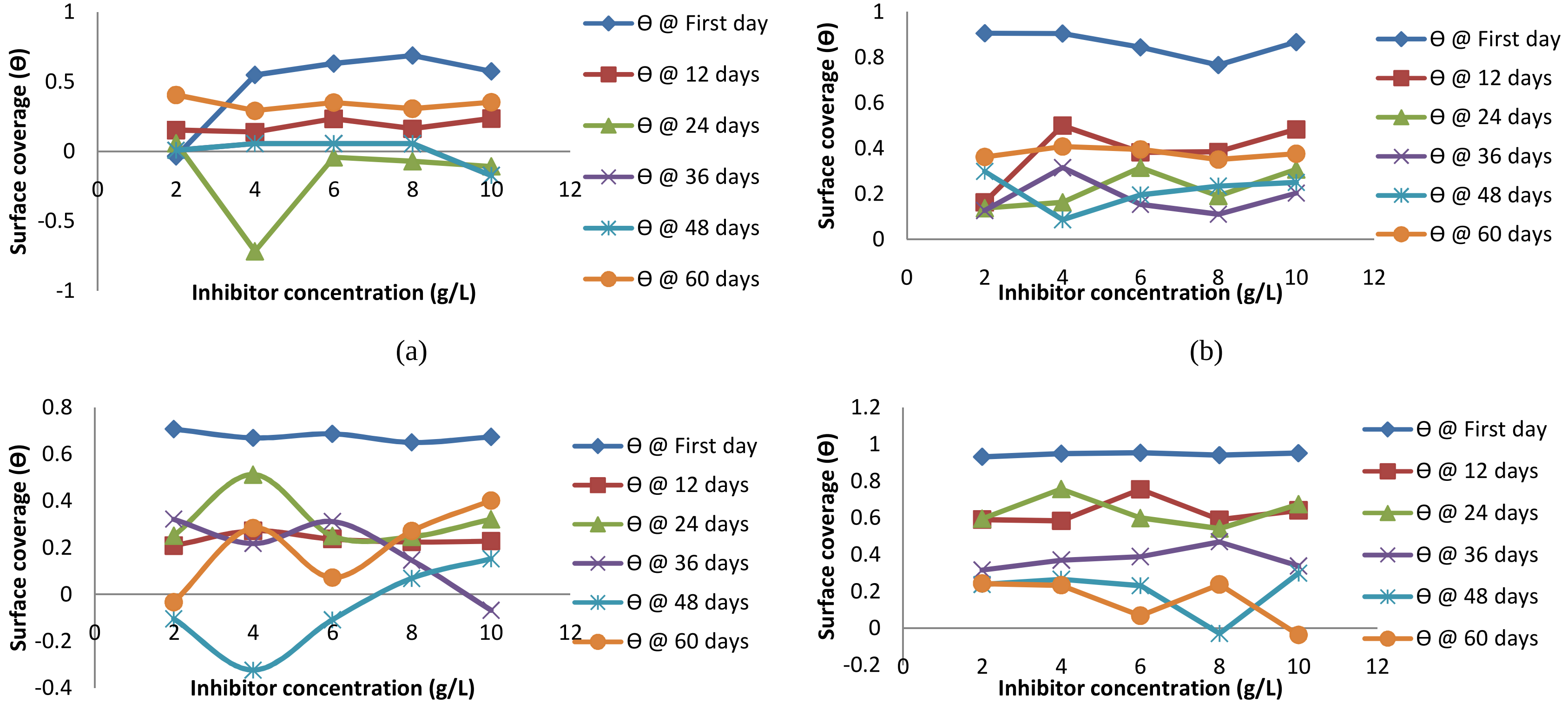
(b)

(c)

(d)

Fig. 4.16: Variation of surface coverage (θ) with AN concentration (g/L) for different time intervals.

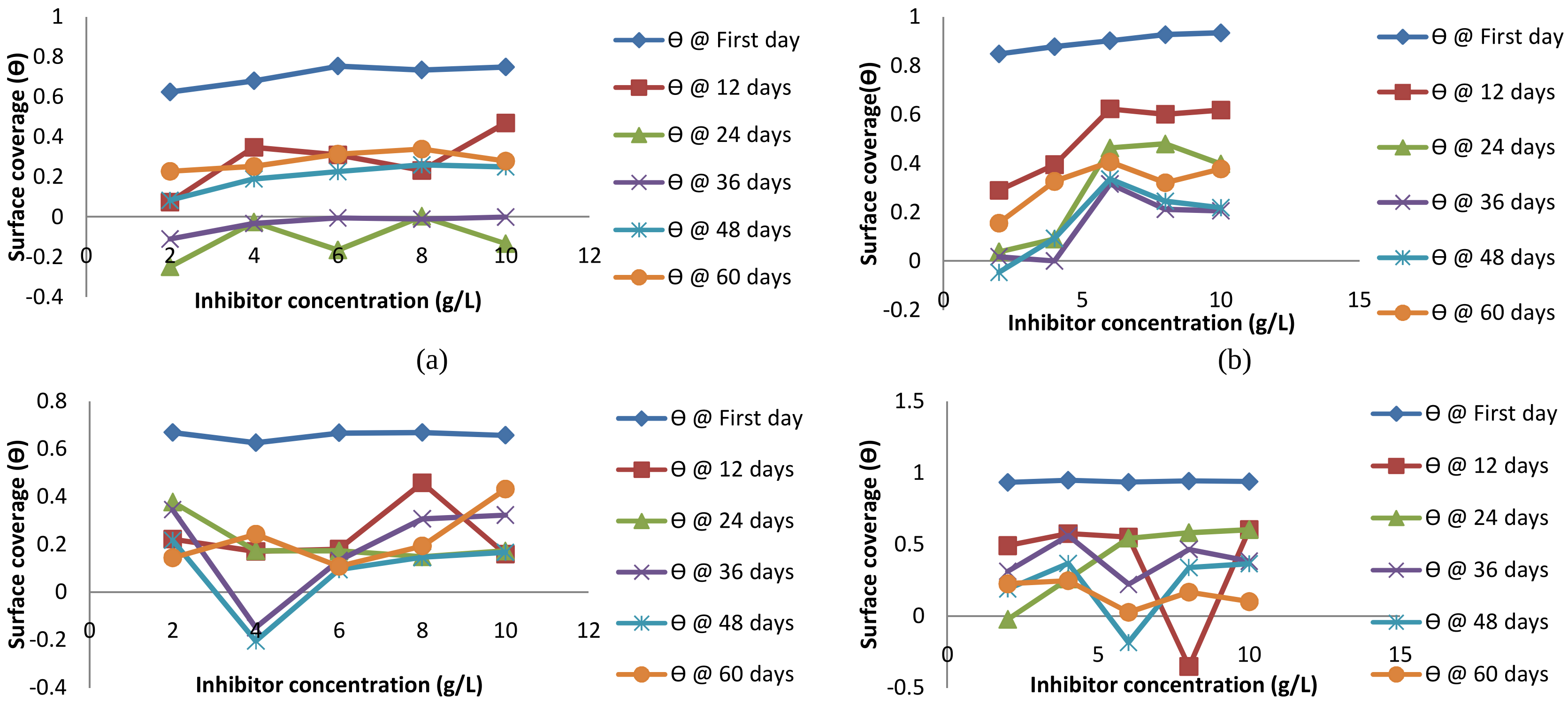
(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Al in HCl and (d) Al in H_2SO_4



(a) (b) (c) (d)

Fig. 4.17: Variation of surface coverage (θ) with TC concentration (g/L) for different time intervals.

(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Al in HCl (d) Al in H_2SO_4



(a) (b)

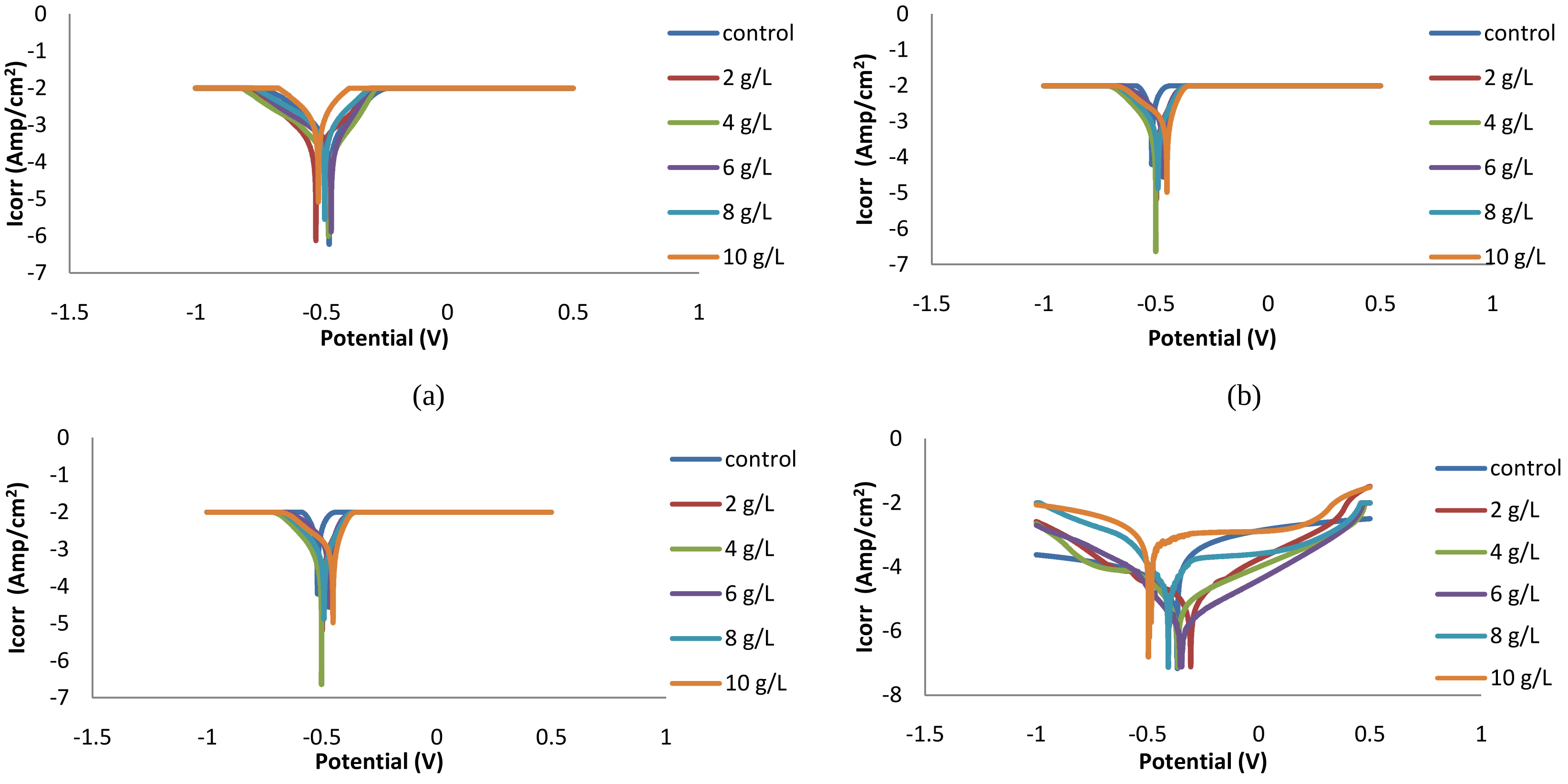
(c) (d)

Fig. 4.18: Variation of surface coverage (θ) with CF concentration (g/L) for different time intervals.

(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Al in HCl (d) Al in H_2SO_4

4.4 Electrochemical Technique: Tafel polarization studies

4.4.1 Polarization studies of mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the presence of PC



(a)

(b)

(c)

(d)

Fig. 4.19: Potentiodynamic polarization curves of mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the presence of PC

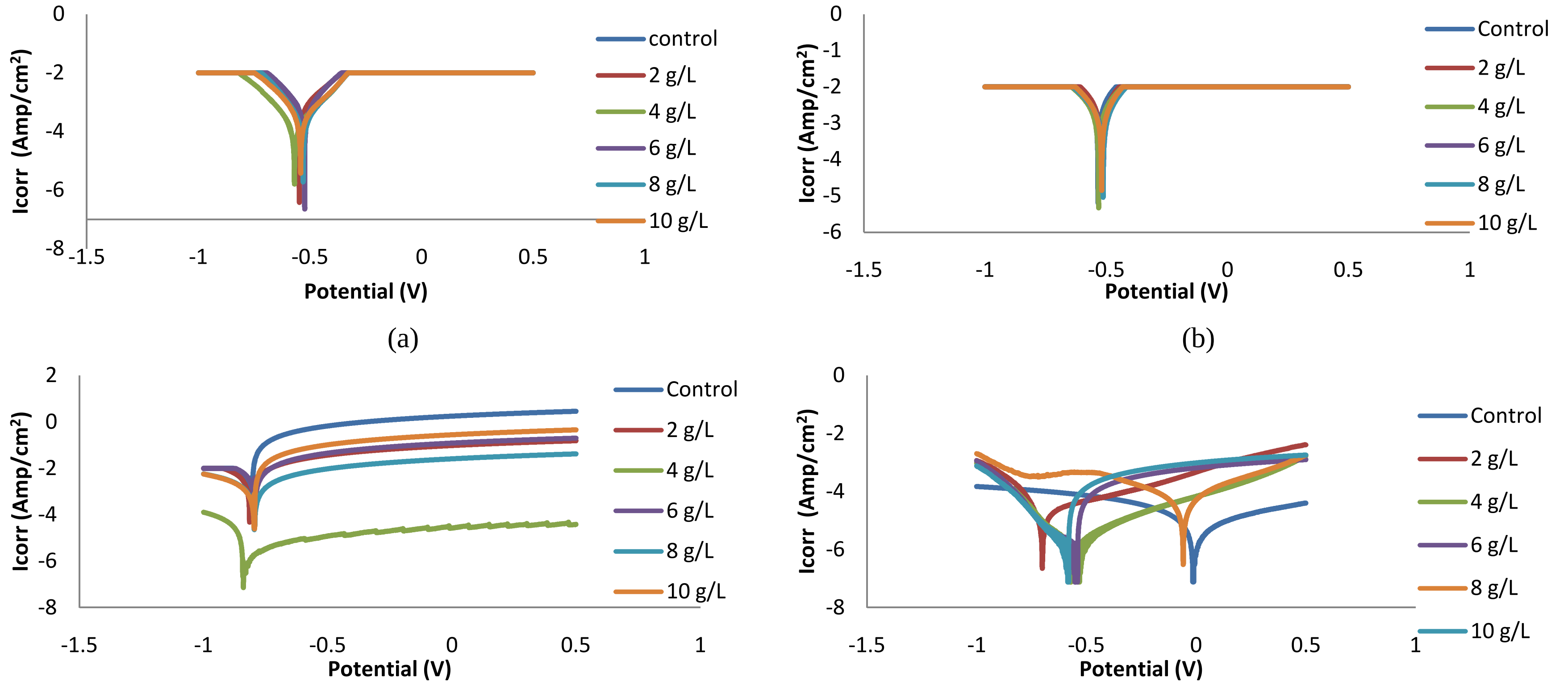
(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Al in HCl (d) Al in H_2SO_4

Table 4.7: Potentiodynamic polarization parameters for corrosion of mild steel in the absence and presence of varying concentrations of PC in 0.5 M HCl and 0.5 M H_2SO_4.

S.No.	Conc (g/L)	OCP (V)	E_{corr} (V)	b_c (A/V)	b_a (A/V)	R_{ct} (Ohm)	I_{corr} (A/cm^2)	CR (mmpy)	IE%
				0.5 M HCl					
1	control	-0.527	-0.469	-7.18E+00	7.57E+00	6.73E+01	3.82E-04	4.43E+00	
2	2	-0.557	-0.469	-6.15E+00	8.62E+00	8.50E+01	3.02E-04	3.51E+00	21.84315
3	4	-0.531	-0.493	-5.85E+00	1.05E+01	8.60E+01	3.01 E-04	3.47E+00	20.73344
4	6	-0.544	-0.461	-6.74E+00	6.23E+00	9.14E+01	2.81E-04	3.26E+00	26.36816
5	8	-0.542	-0.522	-7.17E+00	8.93E+00	1.42E+02	1.81E-04	2.09E+00	52.73632
6	10	-0.566	-0.512	-6.15E+00	7.52E+00	1.54E+02	1.67E-04	1.93E+00	56.34983
				0.5 M H_2SO_4					
1	control	-0.509	-0.519	-5.96E-01	1.20E+00	5.66E+00	4.54E-03	5.26E+01	
2	2	-0.483	-0.498	-8.60E+00	9.76E+00	3.07E+01	8.36E-04	9.69E+00	81.5849
3	4	-0.477	-0.501	-7.70E+00	1.17E+01	4.74E+01	5.42E-04	6.29E+00	88.0521
4	6	-0.476	-0.469	-5.92E+00	5.35E+00	1.35E+01	1.91E-03	2.22E+01	57.9057
5	8	-0.467	-0.491	-6.86E+00	1.11E+01	2.89E+01	8.88E-04	1.03E+01	80.4257
6	10	-0.456	-0.451	-4.62E+00	6.76E+00	1.88E+01	1.37E-03	1.59E+01	69.8404

Table 4.8: Potentiodynamic polarization parameters for corrosion of Aluminium in the absence and presence of varying concentrations of PC in 0.5 M HCl and 0.5 M H_2SO_4.

S.No.	Conc (g/L)	OCP (V)	E_{corr} (V)	b_c (A/V)	b_a (A/V)	R_{ct} (Ohm)	I_{corr} (A/cm^2)	CR (mmpy)	IE%
0.5 M HCl									
1	control	-0.772	-0.798	-4.99E+00	1.89E-01	6.97E+00	3.69E-03	4.01E+01	
2	2	-0.815	-0.838	-5.54E+00	6.05E+00	6.98E+02	3.68E-05	4.01E-01	99.00
3	4	-0.767	-0.807	-5.09E+00	1.11E+00	8.56E+00	3.00E-03	3.27E+01	18.48
4	6	-0.768	-0.805	-4.73E+00	5.80E+00	1.07E+01	2.41E-03	2.63E+01	34.53
5	8	-0.776	-0.794	-4.50E+00	6.13E+00	2.15E+01	1.20E-03	1.30E+01	67.50
6	10	-0.763	-0.8	-3.31E+00	6.05E+00	1.23E+01	2.09E-03	2.28E+01	43.30
0.5 M H_2SO_4									
1	control	-0.596	-0.367	-5.63E+00	4.25E+00	3.33E+03	7.72E-06	8.40E-02	
2	2	-0.567	-0.306	-5.10E+00	6.84E+00	4.74E+03	5.42E-06	5.90E-02	29.79
3	4	-0.516	-0.364	-8.14E+00	5.50E+00	6.07E+03	4.23E-06	4.61E-02	45.16
4	6	-0.29	-0.346	-8.71E+00	5.57E+00	1.90E+04	1.35E-06	1.47E-02	82.49
5	8	-0.24	-0.407	-8.04E+00	7.78E+00	1.03E+03	2.51E-05	1.40E-02	83.34
6	10	-0.419	-0.492	-6.17E+00	1.40E+00	3.01E+02	2.61E-05	1.35E-02	83.93



(a) (b) (c) (d)

Figure 4.20: Potentiodynamic polarization curves of mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the presence of AN

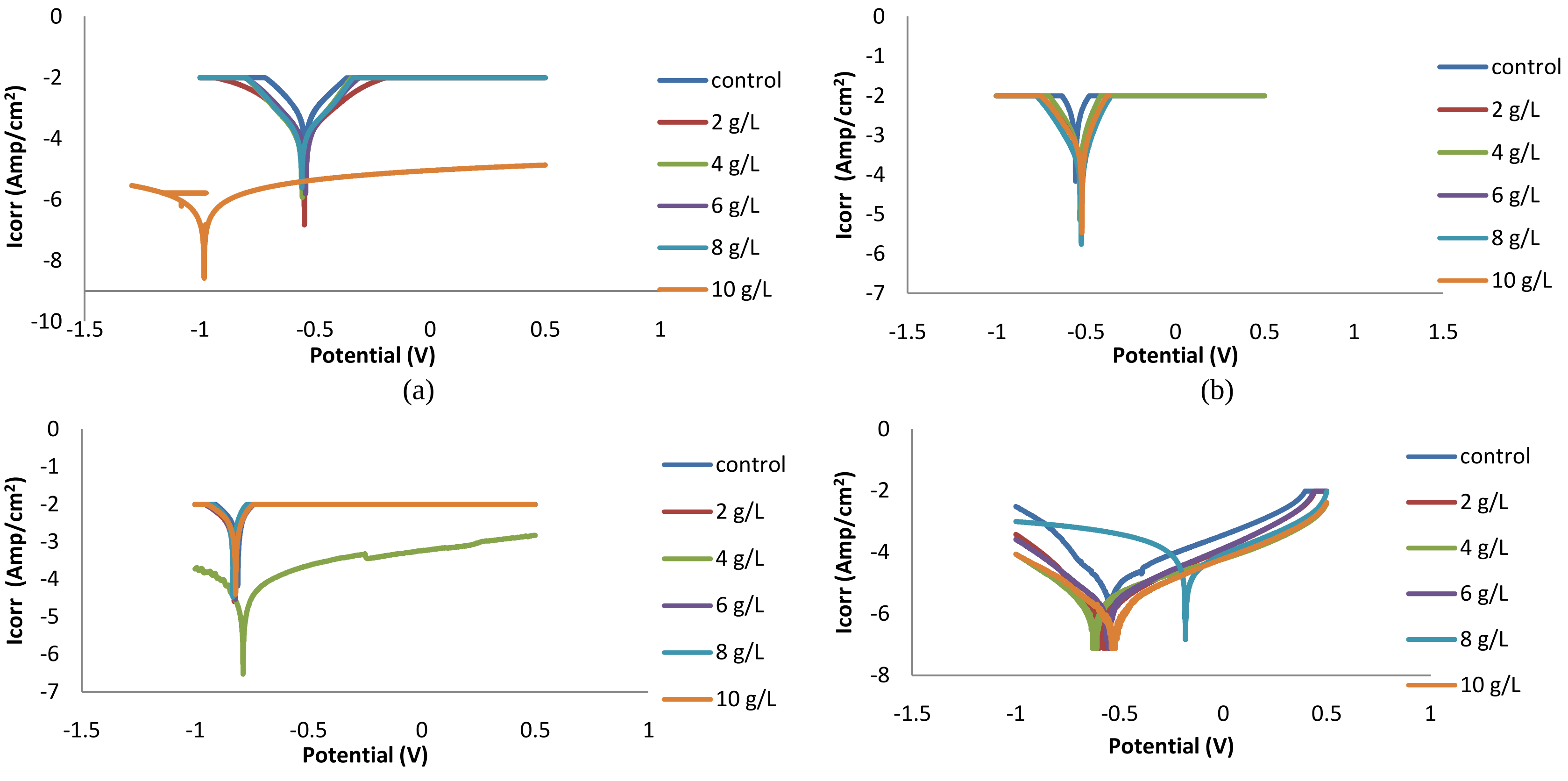
(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Al in HCl (d) Al in H_2SO_4

Table 4.9: Potentiodynamic polarization parameters for corrosion of mild steel in the absence and presence of varying concentrations of AN in 0.5 M HCl and 0.5 M H_2SO_4.

S.No.	Conc (g/L)	OCP (V)	E_{corr} (V)	b_c (A/V)	b_a (A/V)	R_{ct} (Ohm)	I_{corr} (A/cm^2)	CR (mmpy)	IE%
				0.5 M HCl					
1	control	-0.546	-0.521	-9.83E+00	8.43E+00	5.69E+01	4.52E-04	5.24E+00	
2	2	-0.541	-0.523	-8.41E+00	7.52E+00	2.58E+01	3.61E-04	4.19E+00	20.00
3	4	-0.573	-0.556	-8.76E+00	7.40E+00	7.97E+01	3.23E-04	3.74E+00	28.61
4	6	-0.535	-0.517	-8.24E+00	7.95E+00	2.41E+01	3.16E-04	3.67E+01	30.00
5	8	-0.559	-0.541	-1.06E+01	7.21E+00	1.03E+02	2.50E-04	2.89E+00	44.74
6	10	-0.568	-0.558	-9.04E+00	6.54E+00	6.43E+01	4.00E-04	4.63E+00	11.56
				0.5 M H_2SO_4					
1	control	-0.534	-0.533	-5.12E+00	3.17E+00	8.83E+00	2.91E-03	3.37E+01	
2	2	-0.519	-0.519	-7.03E+00	3.15E+00	9.46E+00	2.72E-03	3.15E+01	6.63
3	4	-0.531	-0.531	-6.94E+00	7.37E+00	1.33E+01	1.94E-03	2.24E+01	33.52
4	6	-0.508	-0.512	-7.21E+00	8.49E+00	1.55E+01	1.66E-03	1.92E+01	43.15
5	8	-0.51	-0.512	-7.36E+00	8.31E+00	1.61E+01	1.60E-03	1.85E+01	45.05
6	10	-0.516	-0.518	-7.50E+00	8.06E+00	1.34E+01	1.91E-03	2.22E+01	34.26

Table 4.10: Potentiodynamic polarization parameters for corrosion of aluminium in the absence and presence of varying concentrations of AN in 0.5 M HCl and 0.5 M H_2SO_4.

S.No.	Conc (g/L)	OCP (V)	E_{corr} (V)	b_c (A/V)	b_a (A/V)	R_{ct} (Ohm)	I_{corr} (A/cm^2)	CR (mmpy)	IE%
				0.5 M HCl					
1	control	-0.775	-0.805	-3.11E+00	3.51E-02	6.29E+00	4.08E-03	4.45E+01	
2	2	-0.783	-0.815	-4.98E+00	5.04E+00	8.61E+00	2.98E-03	3.25E+01	26.94
3	4	-0.781	-0.841	-1.12E+01	4.59E+00	2.50E+04	1.03E-06	1.12E-02	99.97
4	6	-0.765	-0.794	-3.32E+00	9.01E-01	6.63E+00	3.87E-03	4.22E+01	5.13
5	8	-0.761	-0.795	-5.53E+00	5.78E+00	3.18E+01	8.09E-04	8.81E+00	80.18
6	10	-0.769	-0.796	-5.72E+00	6.03E+00	3.36E+01	7.65E-04	8.33E+00	81.27
				0.5 M H_2SO_4					
1	control	-0.603	-0.012	-5.83E+00	5.76E+00	1.57E+04	1.64E-06	1.79E-02	
2	2	-0.56	-0.701	-1.06E+01	4.02E+00	2.14E+03	7.22E-06	7.87E-03	56.00
3	4	-0.634	-0.533	-8.93E+00	5.07E+00	4.44E+04	5.79E-07	6.31E-03	64.73
4	6	-0.622	-0.542	-6.22E+00	8.27E+00	3.06E+04	8.41E-07	9.16E-03	48.79
5	8	-0.602	-0.058	-5.80E+00	6.18E+00	1.21E+03	6.24E-07	6.79E-03	62.00
6	10	-0.61	-0.583	-7.18E+00	1.30E+01	2.08E+04	1.24E-06	1.35E-02	24.66



(a) (b) (c) (d)

Figure 4.21: Polarization curves of mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the presence of CF

(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Al in HCl (d) Al in H_2SO_4

Table 4.11: Potentiodynamic polarization parameters for corrosion of mild steel in the absence and presence of varying concentrations of CF in 0.5 M HCl and 0.5 M H_2SO_4.

S.No.	Conc (g/L)	OCP (V)	E_{corr} (V)	b_c (A/V)	b_a (A/V)	R_{ct} (Ohm)	I_{corr} (A/cm^2)	CR (mmpy)	IE%
				0.5 M HCl					
1	control	-0.553	-0.541	-8.87E+00	8.04E+00	5.31E+01	4.84E-04	5.61E+00	
2	2	-0.587	-0.546	-8.93E+00	7.69E+00	2.48E+02	1.04E-04	1.20E+00	78.55
3	4	-0.602	-0.555	-8.60E+00	8.71E+00	2.29E+02	1.12E-04	1.30E+00	76.82
4	6	-0.618	-0.541	-8.76E+00	8.68E+00	2.10E+02	1.23E-04	1.42E+00	74.64
5	8	-0.602	-0.557	-8.40E+00	7.91E+00	1.99E+02	1.29E-04	1.50E+00	73.30
6	10	-0.572	-0.972	NaN	-6.59E-15	3.03E+05	8.48E-08	9.83E-04	99.98
				0.5 M H_2SO_4					
1	control	-0.551	-0.558	-4.23E+00	3.81E+00	8.24E+00	3.12E-03	3.61E+01	
2	2	-0.529	-0.546	-7.02E+00	8.09E+00	2.69E+01	9.55E-04	1.11E+01	69.36
3	4	-0.518	-0.534	-7.87E+00	1.05E+01	3.37E+01	7.63E-04	8.85E+00	75.51
4	6	-0.525	-0.523	-7.30E+00	9.64E+00	5.77E+01	4.45E-04	5.16E+00	85.72
5	8	-0.515	-0.526	-8.17E+00	1.16E+01	1.08E+02	2.39E-04	2.77E+00	92.33
6	10	-0.521	-0.522	-6.94E+00	1.04E+01	5.02E+01	5.12E-04	5.93E+00	83.58

Table 4.12: Potentiodynamic polarization parameters for corrosion of aluminium in the absence and presence of varying concentrations of CF in 0.5 M HCl and 0.5 M H_2SO_4.

S.No.	Conc (g/L)	OCP (V)	E_{corr} (V)	b_c (A/V)	b_a (A/V)	R_{ct} (Ohm)	I_{corr} (A/cm^2)	CR (mmpy)	IE%
				0.5 M HCl					
1	control	-0.78	-0.812	-5.59E+00	1.65E-15	6.69E+00	3.84E-03	4.18E+01	
2	2	-0.793	-0.827	-4.83E+00	4.26E+00	9.16E+00	2.81E-03	3.06E+01	26.90
3	4	-0.777	-0.788	-6.53E+00	5.53E+00	1.18E+03	2.19E-05	2.38E-01	99.43
4	6	-0.787	-0.822	-4.77E+00	4.47E+00	9.11E+00	2.82E-03	3.07E+01	26.518
5	8	-0.799	-0.832	-4.85E+00	-1.65E-15	6.25E+00	1.15E-03	1.26E+01	70.00
6	10	-0.787	-0.821	-4.71E+00	2.97E+00	8.43E+00	3.05E-03	3.32E+01	20.65
				0.5 M H_2SO_4					
1	control	-0.644	-0.546	-6.53E+00	4.72E+00	2.60E+03	9.89E-06	1.15E-01	
2	2	-0.448	-0.571	-8.16E+00	5.69E+00	4.31E+04	5.97E-07	6.92E-03	93.96
3	4	-0.431	-0.613	-8.12E+00	5.36E+00	3.42E+04	7.52E-07	8.19E-03	92.85
4	6	-0.451	-0.56	-5.68E+00	6.29E+00	1.65E+04	1.55E-06	1.69E-02	85.22
5	8	-0.451	-0.182	-4.85E+00	5.86E+00	2.26E+03	5.38E-04	1.6E-02	86.00
6	10	-0.415	-0.518	-9.23E+00	7.89E+00	6.21E+04	4.14E-07	4.51E-03	96.06

It was discovered that by using the CR and I_{corr} values the maximum IE% values were 99.98 and 92.33% for mild steel in 0.5 M HCl and 0.5 M H_2SO_4 media, while for the Aluminium in 0.5 M HCl and 0.5 M H_2SO_4 media, the IE% obtained were 99.43 and 96.06% respectively. The R_{ct} values obtained showed an increase from 53.1ohms in the blank to 303000 ohms for 10 g/L inhibitor concentration for mild steel in 0.5 M HCl. For mild steel in 0.5 M H_2SO_4 media, it increased form 8.24 ohms in the blank to 108 ohms in the 8 g/L concentration. For Aluminium in 0.5 M HCl and 0.5 M H_2SO_4 media, the R_{ct} values increased from the blanks of 6.69 ohms (HCl) and 2600 ohms (H_2SO_4) to 1180 ohms (4 g/L) and 62100 ohms (10 g/L) respectively.

4.4.2 Polarization tests of mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the presence of TC

Tafel polarisation plots of mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the absence and presence of TC at varying concentrations (2-10 g/L) are shown in Figures 4.22a-d. The kinetic parameters deduced by tafel polarization of TC are indicated in the Tables 4.13 and 4.14. It is observed that, both cathodic and anodic reactions of mild steel working electrode corrosion process are inhibited by the increase of TC in 0.5 M H_2SO_4 media. This was achieved by the restraining action imposed on the cathodic and anodic reactions. This finding implied that the introduction of TC lowers the anodic metal dissolution and also impedes the cathodic hydrogen evolution reaction. However, in the 0.5 M HCl media this was not the case. Though there were increases when TC concentration was increased, it did not follow the trend observed in the 0.5 M H_2SO_4

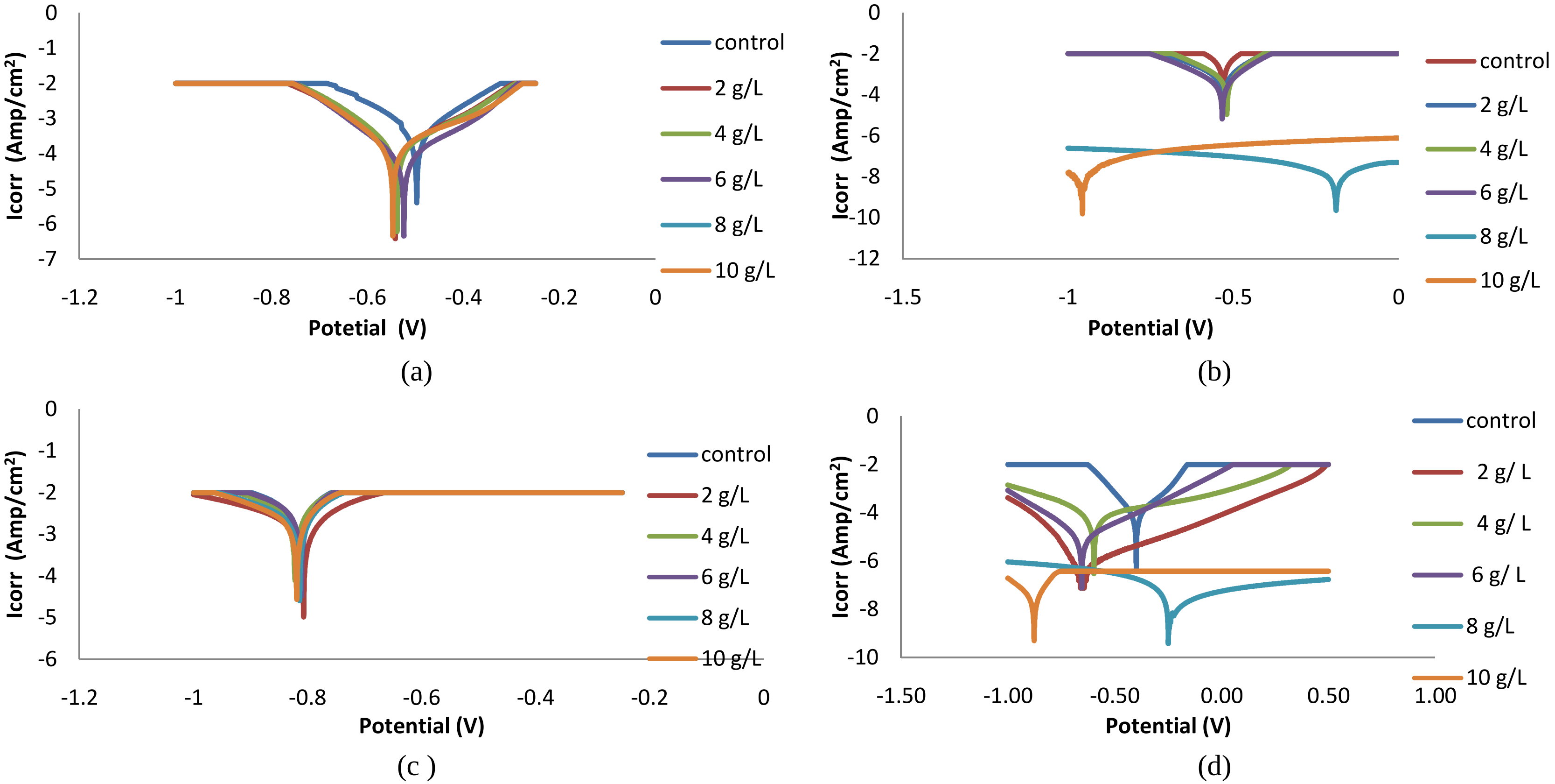


Figure 4.22: Potentiodynamic polarization curves of mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the presence of TC

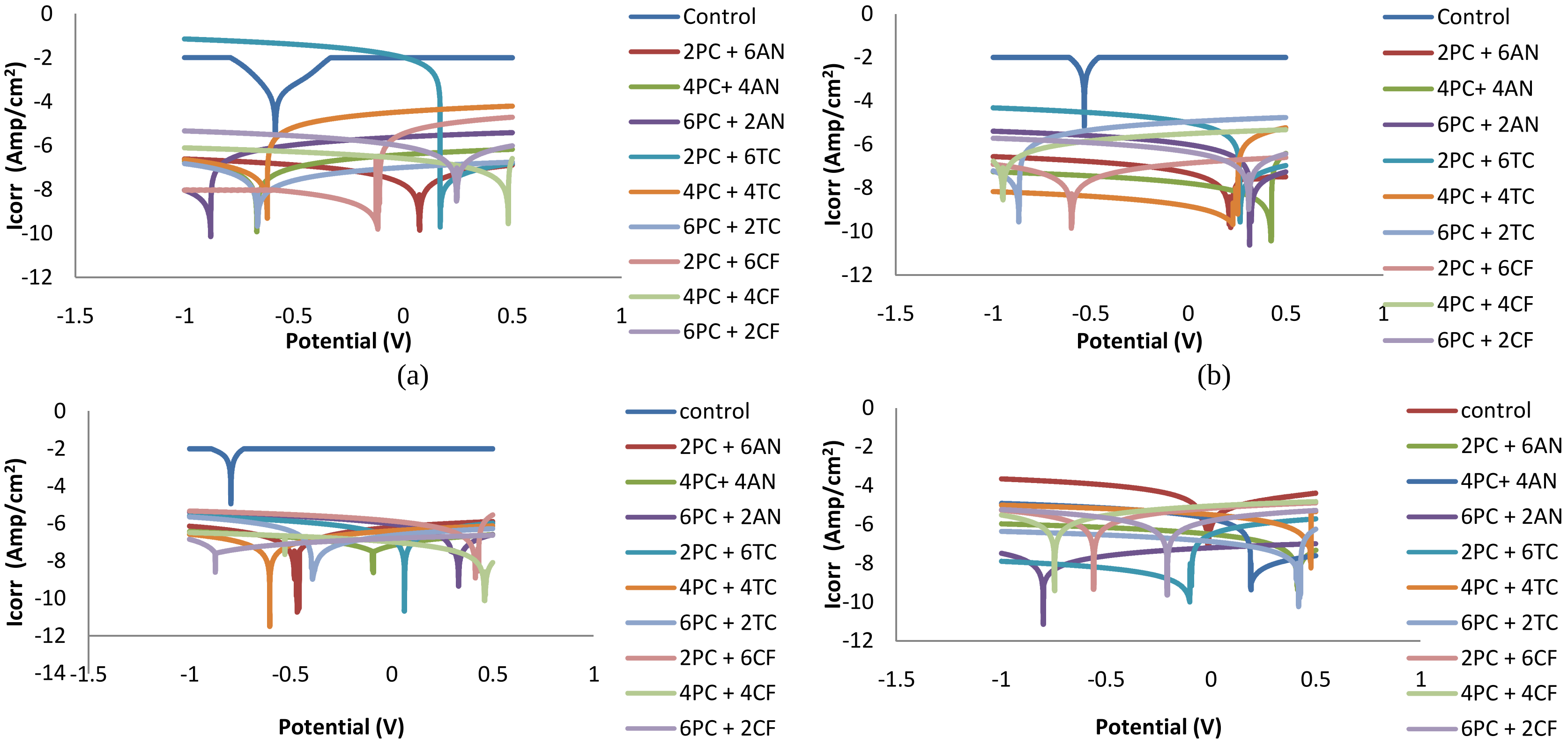
(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Al in HCl (d) Al in H_2SO_4

Table 4.13: Potentiodynamic polarization parameters for corrosion of mild steel in the absence and presence of varying concentrations of TC in 0.5 M HCl and 0.5 M H_2SO_4.

S.No.	Conc (g/L)	OCP (V)	E_{corr} (V)	b_c (A/V)	b_a (A/V)	R_{ct} (Ohm)	I_{corr} (A/cm^2)	CR (mmpy)	IE%
0.5 M HCl									
1	Control	-0.494	-0.497	-7.89E+00	8.85E+00	6.40E+01	4.02E-04	4.66E+00	
2	2	-0.568	-0.542	-9.80E+00	7.37E+00	1.59E+02	1.61E-04	1.87E+00	59.85
3	4	-0.573	-0.538	-1.03E+01	7.19E+00	1.51E+02	1.70E-04	1.98E+00	57.58
4	6	-0.554	-0.524	-1.01E+01	7.00E+00	2.92E+02	8.80E-05	1.02E+00	78.07
5	8	-0.571	-0.547	-1.02E+01	5.86E+00	1.71E+02	1.50E-04	1.74E+00	62.65
6	10	-0.559	-0.531	-8.69E+00	6.81E+00	2.77E+02	9.27E-05	1.08E+00	76.91
0.5M H_2SO_4									
1	Control	-0.529	-0.53	-1.65E-15	8.23E-16	6.03E+00	4.26E-03	4.94E+01	
2	2	-0.524	-0.529	-7.33E+00	9.59E+00	3.29E+01	7.80E-04	9.05E+00	81.67
3	4	-0.509	-0.519	-8.12E+00	1.10E+01	3.40E+01	7.55E-04	8.75E+00	82.27
4	6	-0.522	-0.533	-8.12E+00	1.08E+01	6.82E+01	3.77E-04	4.37E+00	91.15
5	8	-0.509	-0.188	-4.91E+00	5.13E+00	2.61E+06	9.83E-09	1.14E-04	99.99
6	10	-0.531	-0.956	-6.03E+00	6.51E+00	2.12E+06	1.21E-08	1.41E-04	99.99

Table 4.14: Potentiodynamic polarization parameters for corrosion of aluminium in the absence and presence of varying concentrations of TC in 0.5 M HCl and 0.5 M H_2SO_4.

S.No.	Conc. (g/L)	OCP (V)	E_{corr} (V)	b_c (A/V)	b_a (A/V)	R_{ct} (Ohm)	I_{corr} (A/cm^2)	CR (mmpy)	IE%
0.5 M HCl									
1	Control	-0.788	-0.816	-4.14E+00	0.00E+00	5.93E+00	4.33E-03	5.02E+01	
2	2	-0.781	-0.807	-4.78E+00	6.15E+00	1.62E+01	1.59E-03	1.84E+01	63.40
3	4	-0.79	-0.822	-4.90E+00	8.40E-01	7.17E+00	3.59E-03	3.90E+01	22.27
4	6	-0.784	-0.811	-5.10E+00	0.00E+00	6.22E+00	4.13E-03	4.50E+01	10.39
5	8	-0.795	-0.814	-4.93E+00	3.66E+00	9.28E+00	2.77E-03	3.02E+01	39.95
6	10	-0.785	-0.819	-5.37E+00	3.05E+00	9.60E+00	2.68E-03	2.92E+01	41.94
0.5 M H_2SO_4									
1	Control	-0.607	-0.399	2.23E+00	4.67E+00	4.70E+02	5.47E-05	5.96E-01	
2	2	-0.718	-0.647	-1.52E+01	5.57E+00	6.12E+04	4.20E-07	4.57E-03	99.23
3	4	-0.709	-0.597	-6.80E+00	4.43E+00	7.91E+02	3.25E-05	3.54E-01	40.63
4	6	-0.74	-0.653	-7.85E+00	5.64E+00	3.87E+03	6.65E-06	7.24E-02	87.85
5	8	-0.764	-0.248	-1.32E+01	1.22E+01	3.76E+06	6.83E-09	7.44E-05	99.98
6	10	-0.764	-0.877	-3.49E+00	2.95E+00	7.68E+05	3.35E-08	3.64E-04	99.93



(a) (b)

(c) (d)

Figure 4.23: Potentiodynamic polarization curves of mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the presence of SA

(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Al in HCl (d) Al in H_2SO_4

Table 4.15: Potentiodynamic polarization parameters for corrosion of mild steel in the absence and presence of varying concentrations of SA in 0.5 M HCl and 0.5 M H_2SO_4.

S.No.	Conc (g/L)	OCP (V)	E_{corr} (V)	b_c (A/V)	b_a (A/V)	R_{ct} (Ohm)	I_{corr} (A/cm^2)	CR (mmpy)	IE%
0.5 M HCl									
1	Control	-0.607	-0.584	-1.08E+01	6.63E+00	1.45E+02	1.77E-04	2.05E+00	
2	2PC + 6AN	-0.454	0.075	-4.40E+00	-8.78E+00	4.50E+06	5.71E-09	6.62E-05	99.9967735
3	4PC+ 4AN	-0.599	-0.669	-4.77E+00	7.71E+00	2.22E+08	1.16E-10	1.34E-06	99.99993453
4	6PC + 2AN	-0.541	-0.879	-5.23E+00	1.82E+00	9.48E+06	2.71E-09	3.14E-05	99.99846956
5	2PC + 6TC	-0.584	0.169	-1.03E+00	3.79E+00	2.43E+06	1.06E-08	1.22E-04	99.99403799
6	4PC + 4TC	-0.596	-0.62	-5.23E+00	-1.71E+01	4.51E+05	5.69E-08	6.60E-04	99.96785679
7	6PC + 2TC	-0.547	-0.665	-5.58E+00	4.85E+00	3.39E+06	7.57E-09	8.78E-05	99.99572577
8	2PC + 6CF	-0.574	-0.107	2.66E+00	-2.55E-01	3.14E+06	8.19E-09	9.50E-05	99.9953736
9	4PC + 4CF	-0.585	0.483	-1.03E+01	1.36E+01	1.84E+06	1.40E-08	1.62E-04	99.99211398
10	6PC + 2CF	-0.588	0.246	-5.25E-01	9.89E-01	2.77E+05	9.26E-08	1.07E-03	99.94768631
0.5 M H_2SO_4									
1	Control	-0.534	-0.533	-5.12E+00	3.17E+00	8.83E+00	2.91E-03	3.37E+01	
2	2PC + 6AN	-0.483	0.211	-3.67E+00	2.33E+00	6.55E+06	3.93E-09	4.55E-05	99.99986512
3	4PC+ 4AN	-0.488	0.428	-5.19E+00	7.32E+00	4.87E+06	5.27E-09	6.11E-05	99.99981888
4	6PC + 2AN	-0.496	0.322	-2.48E+00	-9.60E-01	2.89E+06	8.91E-09	1.03E-04	99.99969413
5	2PC + 6TC	-0.493	0.265	-4.38E+00	5.59E+00	2.32E+06	1.11E-08	1.29E-04	99.99961915
6	4PC + 4TC	-0.494	0.255	-3.66E+00	1.04E+00	1.12E+06	2.31E-08	2.67E-04	99.99920806
7	6PC + 2TC	-0.495	-0.868	-7.83E+00	3.56E+00	1.93E+06	1.33E-08	1.54E-04	99.99954298
8	2PC + 6CF	-0.397	-0.598	-3.44E+00	2.15E+00	4.77E+06	5.39E-09	6.24E-05	99.999815
9	4PC + 4CF	-0.495	-0.951	-5.12E+00	1.44E+00	2.99E+05	8.59E-08	9.95E-04	99.99705009
10	6PC + 2CF	-0.497	0.311	-7.30E+00	1.71E+00	6.41E+05	4.01E-08	4.65E-04	99.99862241

Table 4.16: Potentiodynamic polarization parameters for corrosion of aluminium in the absence and presence of varying concentrations of SA in 0.5 M HCl and 0.5 M H_2SO_4.

S.No.	Conc. (g/L)	OCP (V)	E_{corr}(V)	b_c(A/V)	b_a(A/V)	R_{ct} (Ohm)	I_{corr}(A/cm^2)	CR (mmpy)	IE%
				0.5 M HCl					
1	Control	-0.772	-0.798	-4.99E+00	1.89E-01	6.97E+00	3.69E-03	4.01E+01	
2	2PC + 6AN	-0.803	-0.481	1.22E+01	2.16E+00	7.77E+05	3.31E-08	3.60E-04	99.99910217
3	4PC+ 4AN	-0.769	-0.09	-8.65E+00	4.11E+00	1.07E+07	2.39E-09	2.61E-05	99.99993506
4	6PC + 2AN	-0.753	0.29	-1.20E+00	2.30E+01	4.93E+05	5.21E-08	5.67E-04	99.99858659
5	2PC + 6TC	-0.768	0.064	-7.62E+00	1.48E+01	1.14E+08	2.25E-10	2.45E-06	99.9999939
6	4PC + 4TC	-0.786	-0.752	-1.64E-01	-1.44E+00	6.97E+06	3.69E-09	4.01E-05	99.99989998
7	6PC + 2TC	-0.797	-0.397	-2.60E+00	7.57E+00	5.72E+06	4.49E-09	4.89E-05	99.99987817
8	2PC + 6CF	-0.767	0.43	-1.32E+00	8.17E+00	8.73E+06	2.94E-09	3.21E-05	99.99992013
9	4PC + 4CF	-0.769	0.462	7.76E+00	1.44E+01	9.83E+06	2.61E-09	2.85E-05	99.99992908
10	6PC + 2CF	-0.764	-0.872	-1.25E+00	4.87E+00	1.05E+07	2.45E-09	2.67E-05	99.99993354
				0.5 M H_2SO_4					
1	Control	-0.603	-0.012	-5.83E+00	5.76E+00	1.57E+04	1.64E-06	1.79E-02	
2	2PC + 6AN	-0.598	0.412	-4.11E+00	6.05E+00	1.70E+06	1.51E-08	1.65E-04	99.08
3	4PC+ 4AN	-0.586	0.19	4.11E-01	6.14E+00	2.66E+06	9.66E-09	1.05E-04	99.41
4	6PC + 2AN	-0.599	-0.8	-1.41E+01	7.76E+00	3.50E+09	7.34E-12	7.99E-08	99.99
5	2PC + 6TC	-0.665	-0.095	-2.19E+00	3.98E+00	4.41E+06	5.83E-09	6.35E-05	99.65
6	4PC + 4TC	-0.645	0.477	-9.11E+00	-2.53E-01	3.91E+06	6.58E-09	7.16E-05	99.60
7	6PC + 2TC	-0.625	0.426	-4.69E+00	-9.31E+00	3.41E+06	7.54E-09	8.21E-05	99.54
8	2PC + 6CF	-0.642	-0.56	6.09E+00	4.07E+00	2.21E+06	1.16E-08	1.27E-04	99.29
9	4PC + 4CF	-0.669	-0.747	8.94E-02	5.61E+00	2.21E+06	1.16E-08	1.27E-04	99.29
10	6PC + 2CF	-0.488	-0.209	1.03E+00	4.36E+00	3.60E+06	7.14E-09	7.78E-05	99.57

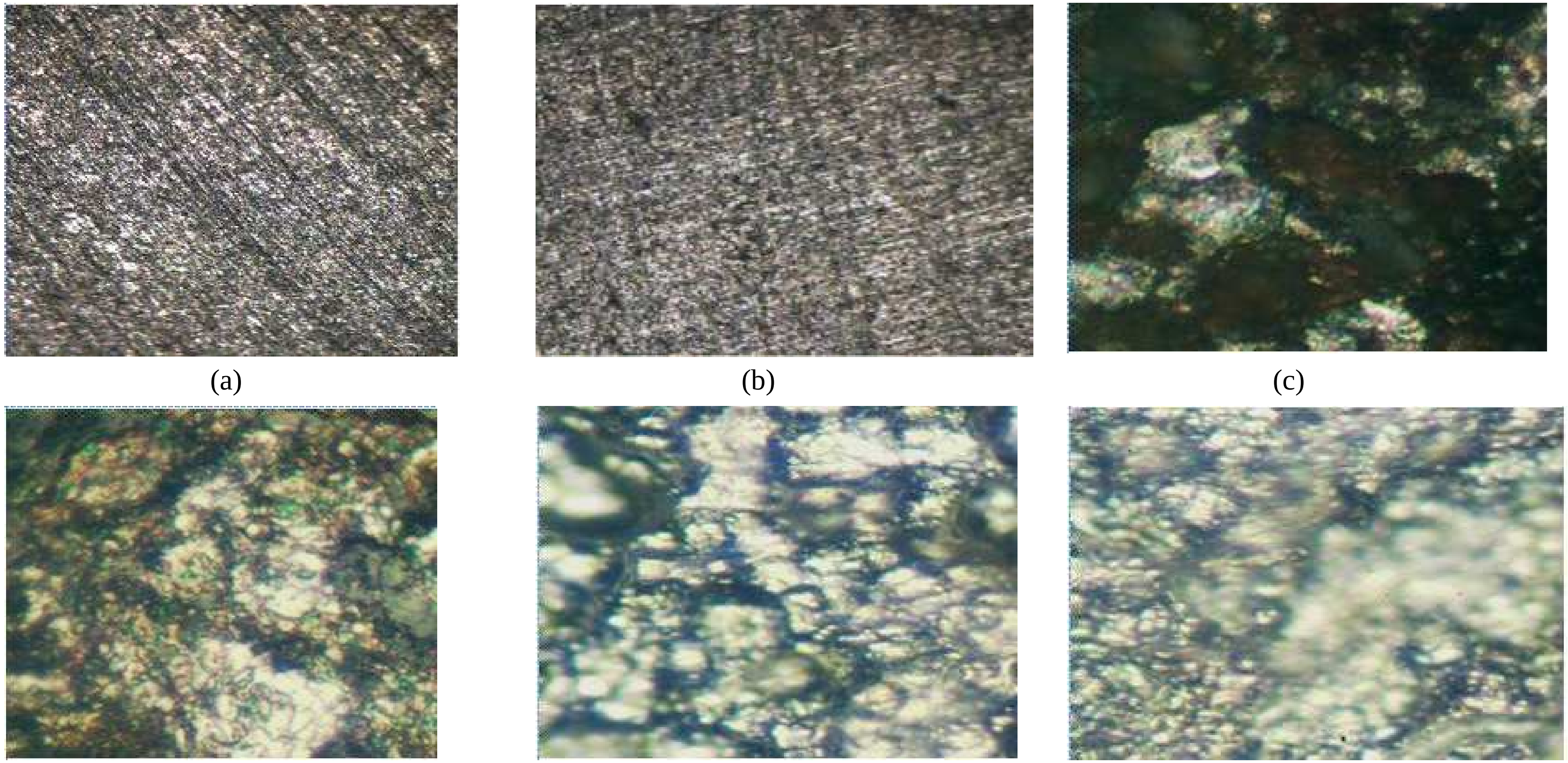
interfacial reaction taking place for the synergetic admixtures when compared to the stand alone systems.

4.5 Chemical/Phytochemical Constituent Inhibition Mechanism

4.6 Metal Surface Studies

4.6.1 Surface studies of unimmersed mild steel and aluminium samples

In Figure 4.24a the photomicrograph of unimmersed mild steel sample is observed to be smooth with no indication of corrosion. The microstructure of plain carbon steel sample is observed to have three phases namely; the ferrite, pearlite and oxide of iron phase



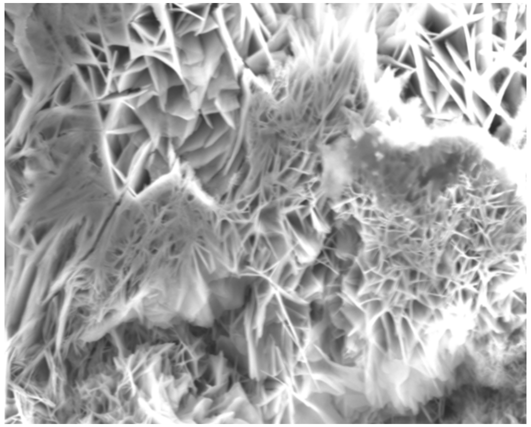
(a) (b) (c)

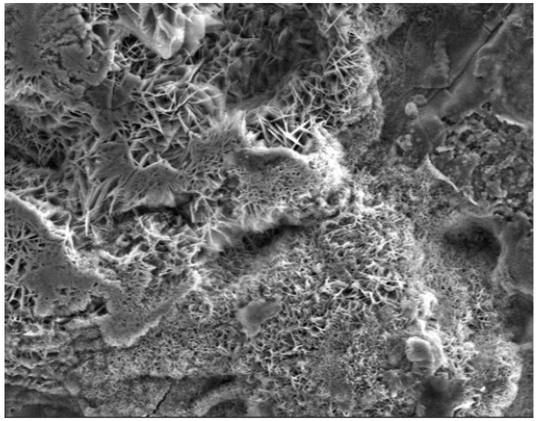
(d) (e) (f)

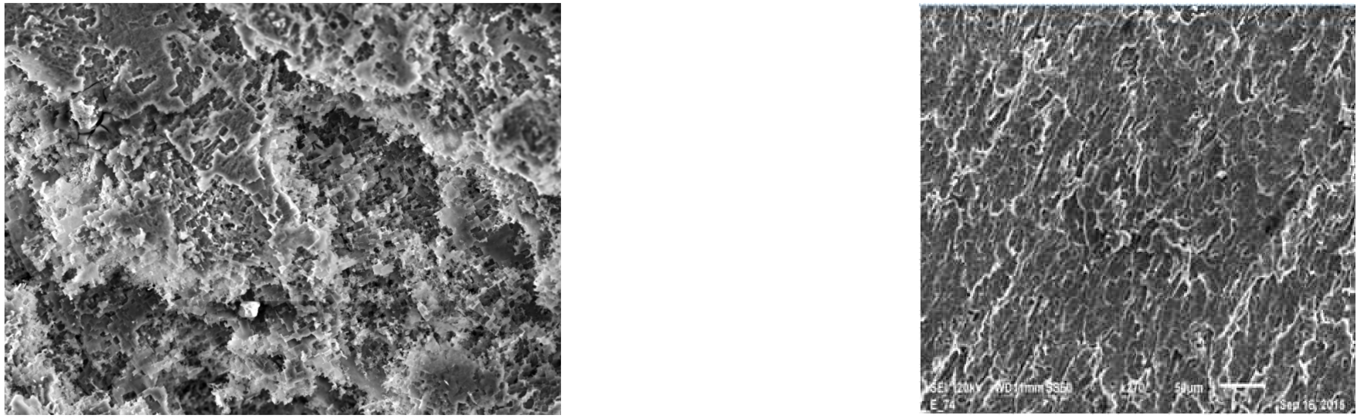
Figure 4.24: Photomicrograph of Mild steel and Al samples in the absence and presence HCl and H_2SO_4 at room temperature of 30^oC

(a) Unimmersed MS (b) Unimmersed Al (c) MS in HCl (d) MS in H_2SO_4 (e) Al in HCl (f) Al in H_2SO_4

4.6.2 Surface studies for the inhibited mild steel and aluminium samples immersed in HCl and H_2SO_4 solution at room temperature of 30^0C


(a)

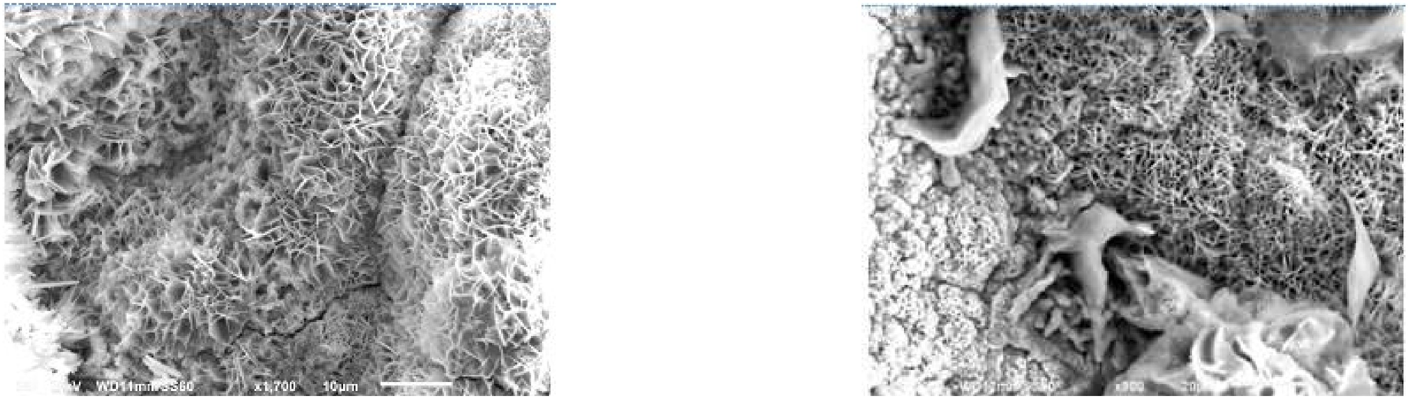

(b)



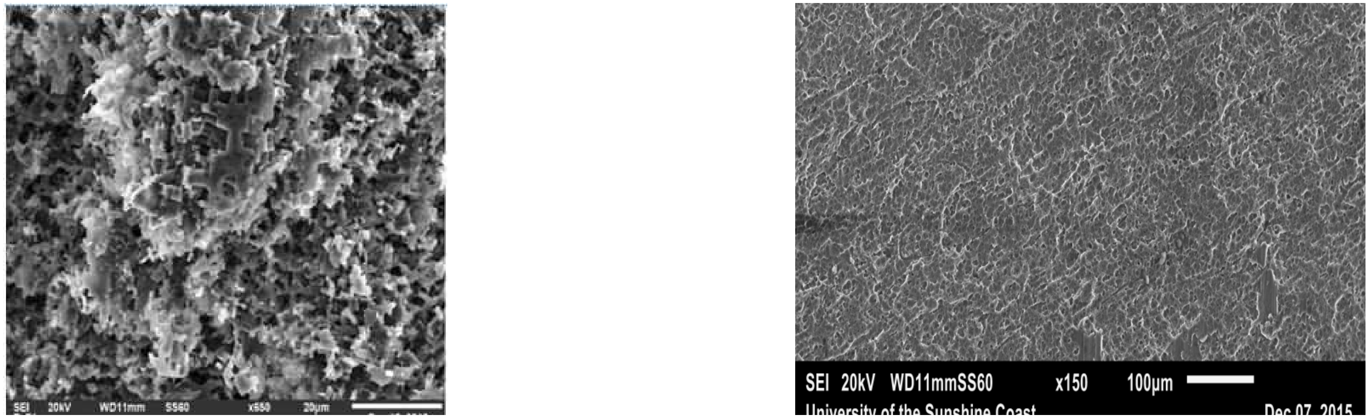
(c) (d)

Figure 4.25: SEM images of MS and Al immersed in acid in the presence of PC

(a) MS in 10 g/L PC-HCl (b) MS in 10g/L PC-H_2SO_4 (c) Al in 10 g/L PC-HCl (d) Al in 6 g/L PC-H_2SO_4



(a) (b)



(c) (d)

Figure 4.26: SEM images of MS and Al immersed in acid in the presence of AN

(a) MS in 10 g/L AN-HCl (b) MS in 10g/L AN-H_2SO_4 (c) Al in 8 g/L AN-HCl (d) Al in 8 g/L AN-H_2SO_4

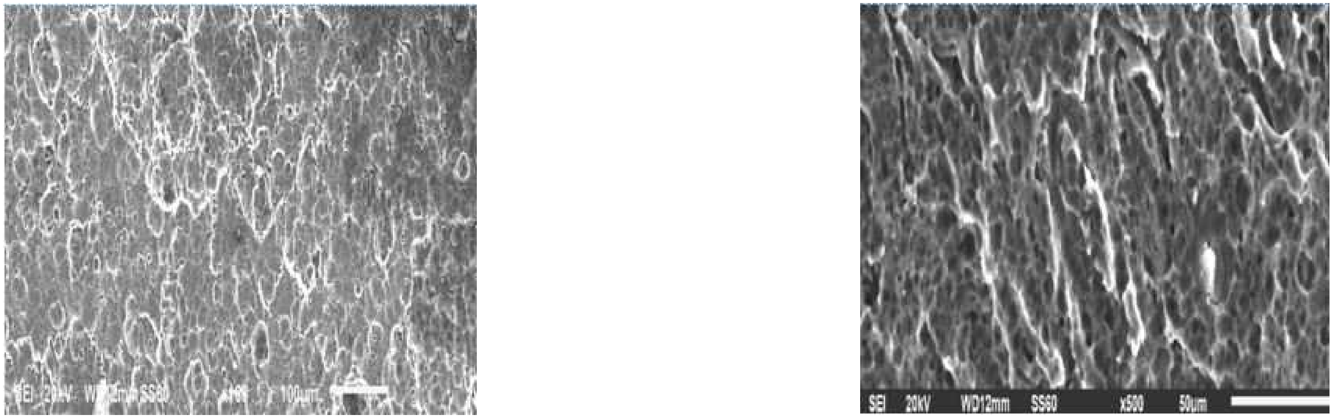
(a) (b)

(c) (d)

Figure 4.27: SEM images of MS and Al immersed in acid in the presence of CF

(a) MS in 10 g/L-HCl (b) MS in 10g/L-H_2SO_4 (c) Al in 2 g/L-HCl (d) Al in 10 g/L-H_2SO_4

(a) (b)



(c)

(d)

Figure 4.28: SEM images of MS and Al immersed in acid in the presence of TC

(a) MS in 8 g/L TC-HCl (b) MS in 4 g/L TC-H_2SO_4 (c) Al in 2 g/L TC-HCl (d) Al in 4 g/L TC-H_2SO_4.

(a)

(b)

(c) (d)

Figure 4.29: SEM images of MS and Al immersed in acid in the presence of SA

(a) MS in 6PC+2AN-HCl (b) MS in 2PC+6CF-H_2SO_4 (c) Al in 4PC+4CF-HCl (d) Al in 4PC+4CF-H_2SO_4.

4.7 ANN Modelling of Corrosion Rate

4.7.1 ANN modelling results

system

Table 4.17: Mean Square Error (MSE) and correlation data for ANN modeled metal-inhibitor- media system

			Correlation coefficient (R-value)			Mean Square Error (MSE)		
S.No	Description	No. of iterations	Training	Validation	Testing	Training	Validation	Testing
1	HCl_MS_PC	75	0.99819	1	1	0.0046181	0	0
2	H_2SO_4_MS_PC	95	0.99863	1	1	0.0034560	0	0
3	HCl_Al_PC	11	0.99908	1	1	0.0039745	0	0
4	H_2SO_4_Al_PC	37	0.99945	1	1	0.0033605	0	0
5	HCl_MS_AN	42	1	1	1	0	0	0
6	H_2SO_4_MS_AN	46	0.99974	1	1	0.0056547	0	0
7	HCl_Al_AN	28	0.99937	1	1	0.0040663	0	0
8	H_2SO_4_Al_AN	61	0.99967	1	1	0.0029294	0	0
9	HCl_MS_CF	69	0.99759	1	1	0.0022525	0	0
10	H_2SO_4_MS_CF	25	0.99998	1	1	0.0028051	0	0
11	HCl_Al_CF	26	1	1	1	0	0	0
12	H_2SO_4_Al_CF	9	0.92947	1	1	0.0050268	0	0
13	HCl_MS_TC	98	0.99979	1	1	0.0007957	0	0
14	H_2SO_4_MS_TC	79	0.99905	1	1	0.0008423	0	0
15	HCl_Al_TC	85	0.9989	1	1	0.0009850	0	0
16	H_2SO_4_Al_TC	66	0.99005	1	1	0.0007815	0	0
17	HCl_MS_SA	36	0.95032	0.90628	0.99995	0.0006509	0.0001675	0.0007968
18	H_2SO_4_MS_SA	472	1	0.99664	0.98393	0	0.0008404	0.0007728
19	HCl_Al_SA	1000	1	0.99489	0.96302	0	0.0009024	0.0008407
20	H_2SO_4_Al_SA	9	0.93748	0.9996	0.99038	0.0008127	0.0009067	0.0007939

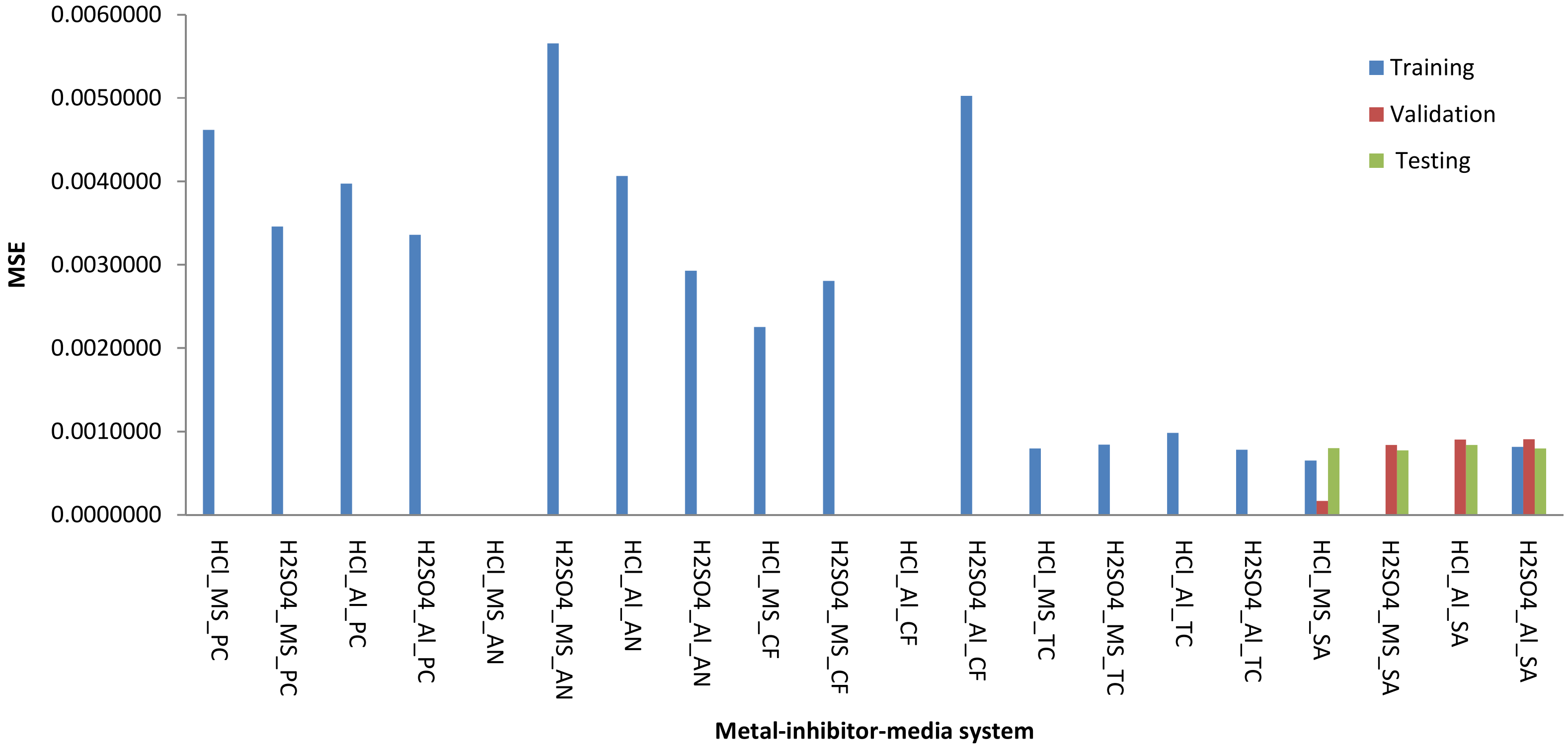
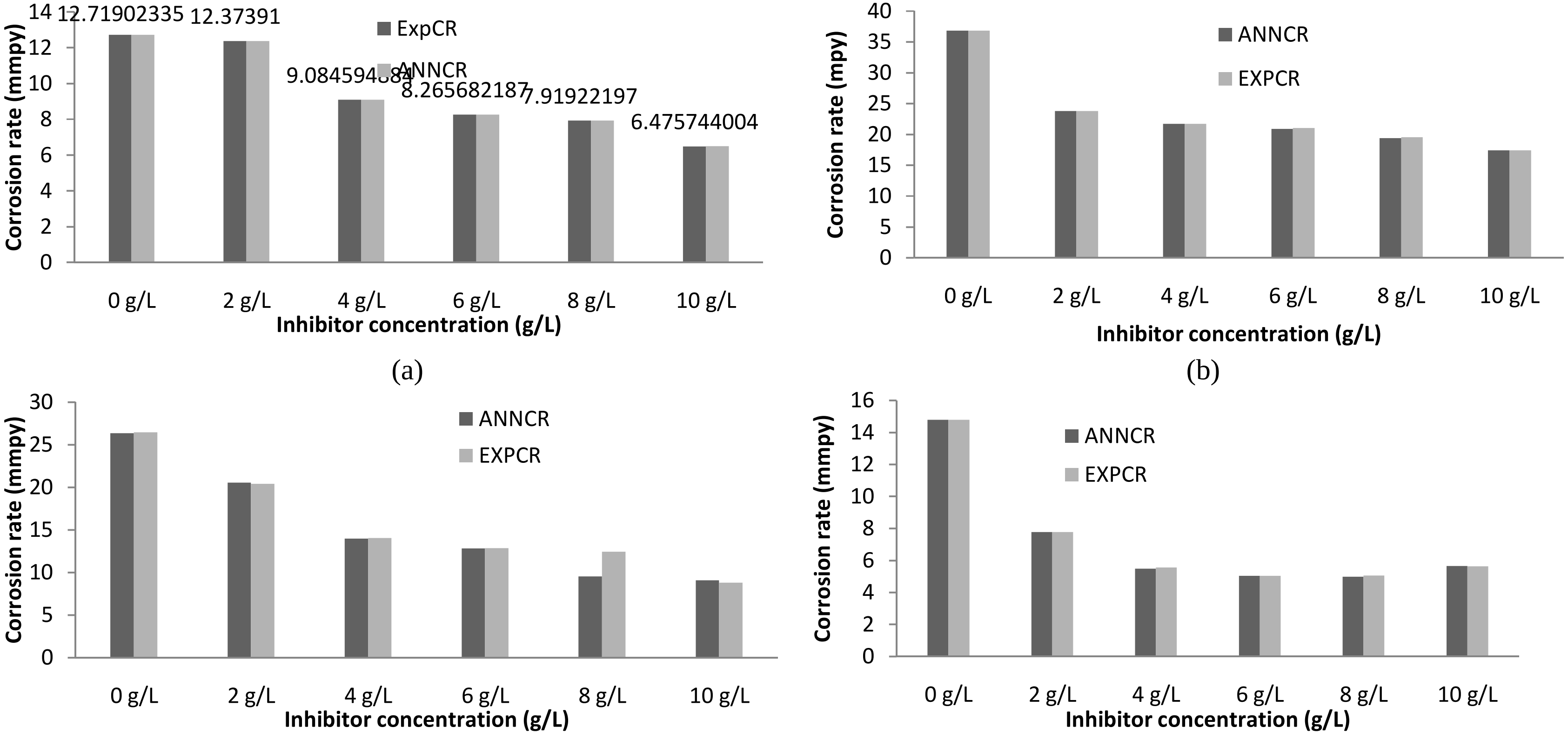


Figure 4.30: Bar chart showing the Mean Square Error for each of the training, validation and testing parameter for the network structure for each metal-inhibitor-media system.



(a)

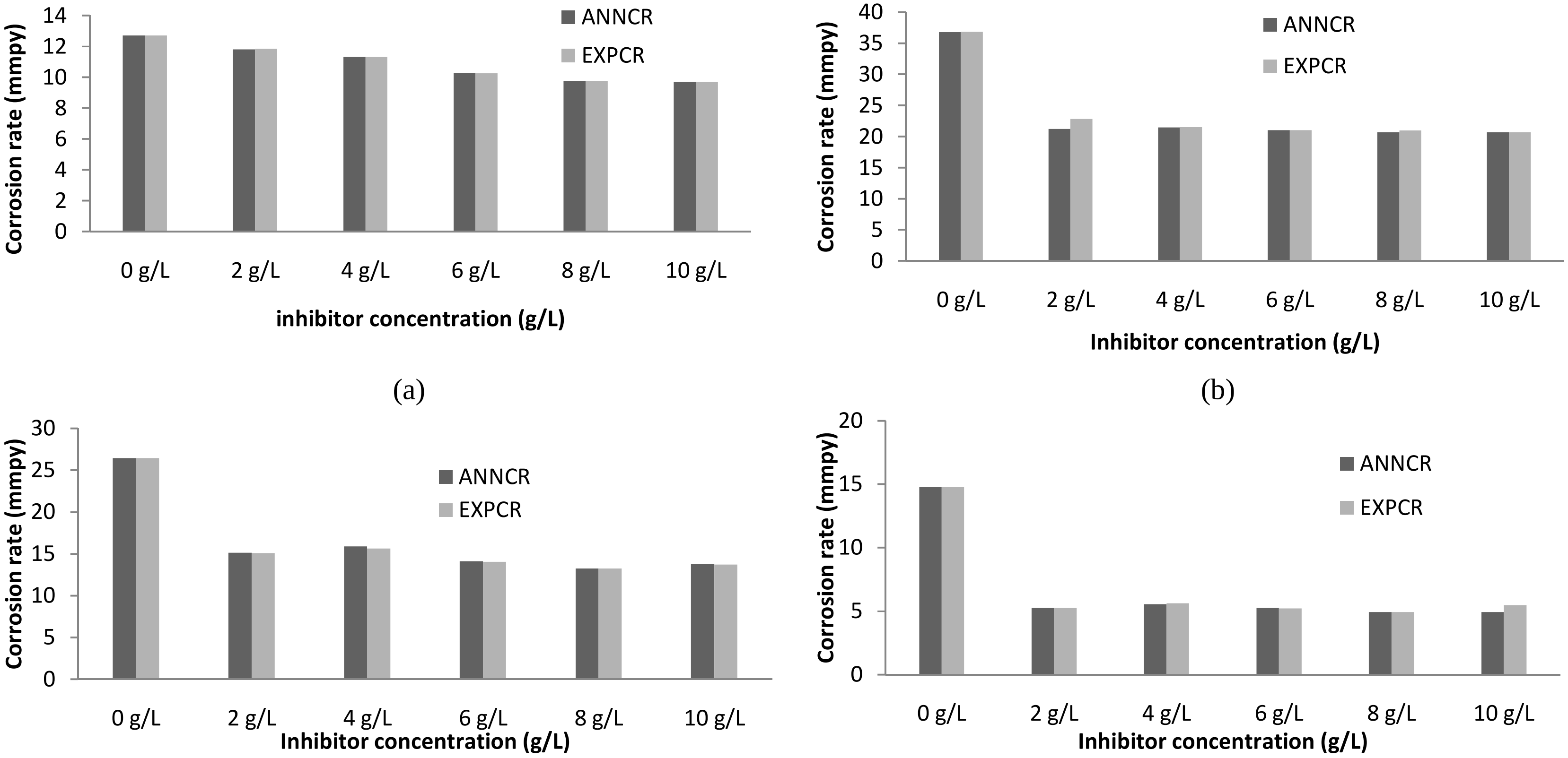
(b)

(c)

(d)

Figure 4.31: Comparison of ANN modeled result with experimental result for mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the presence of PC

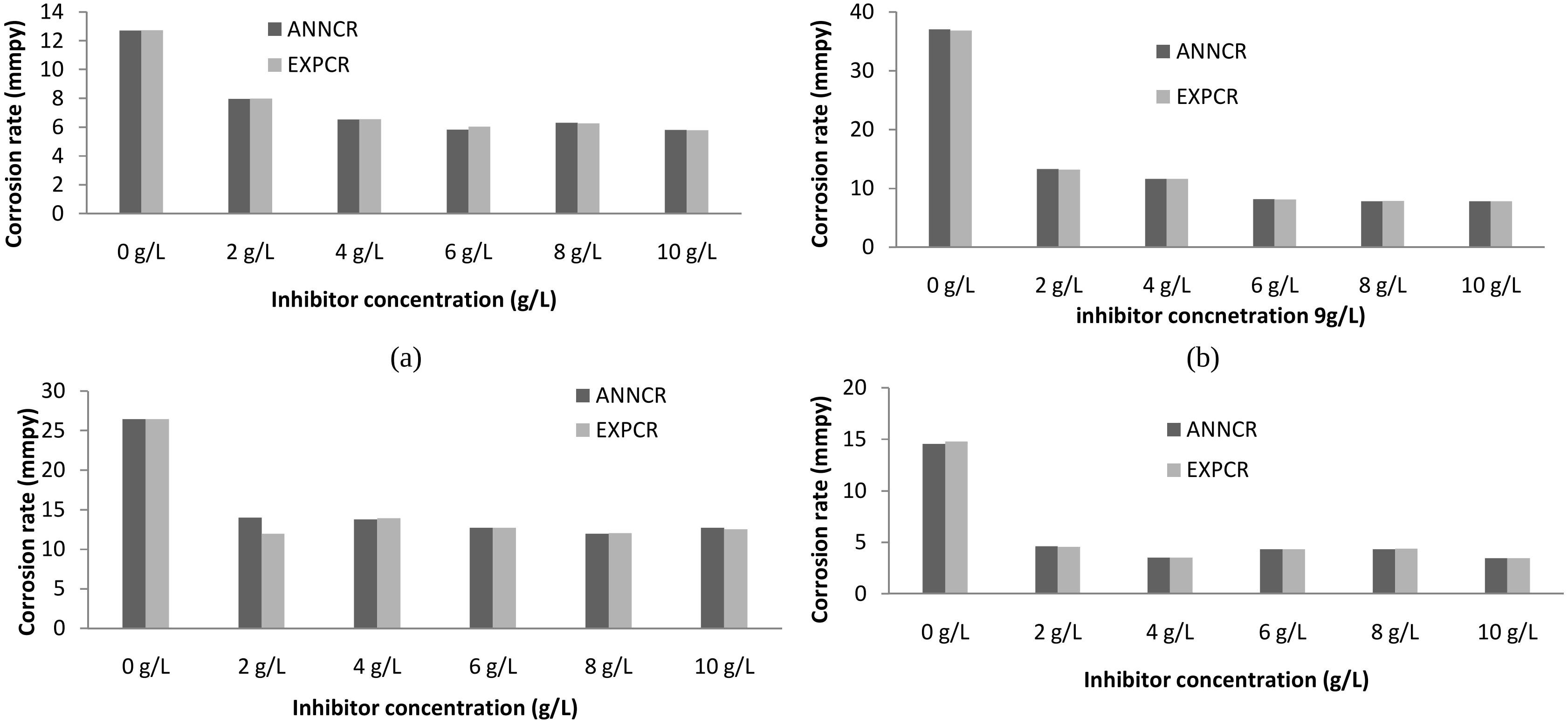
(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Al in HCl (d) Al in H_2SO_4



(a) (b) (c) (d)

Figure 4.32: Comparison of ANN modeled result with experimental result for mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the presence of AN

(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Al in HCl (d) Al in H_2SO_4

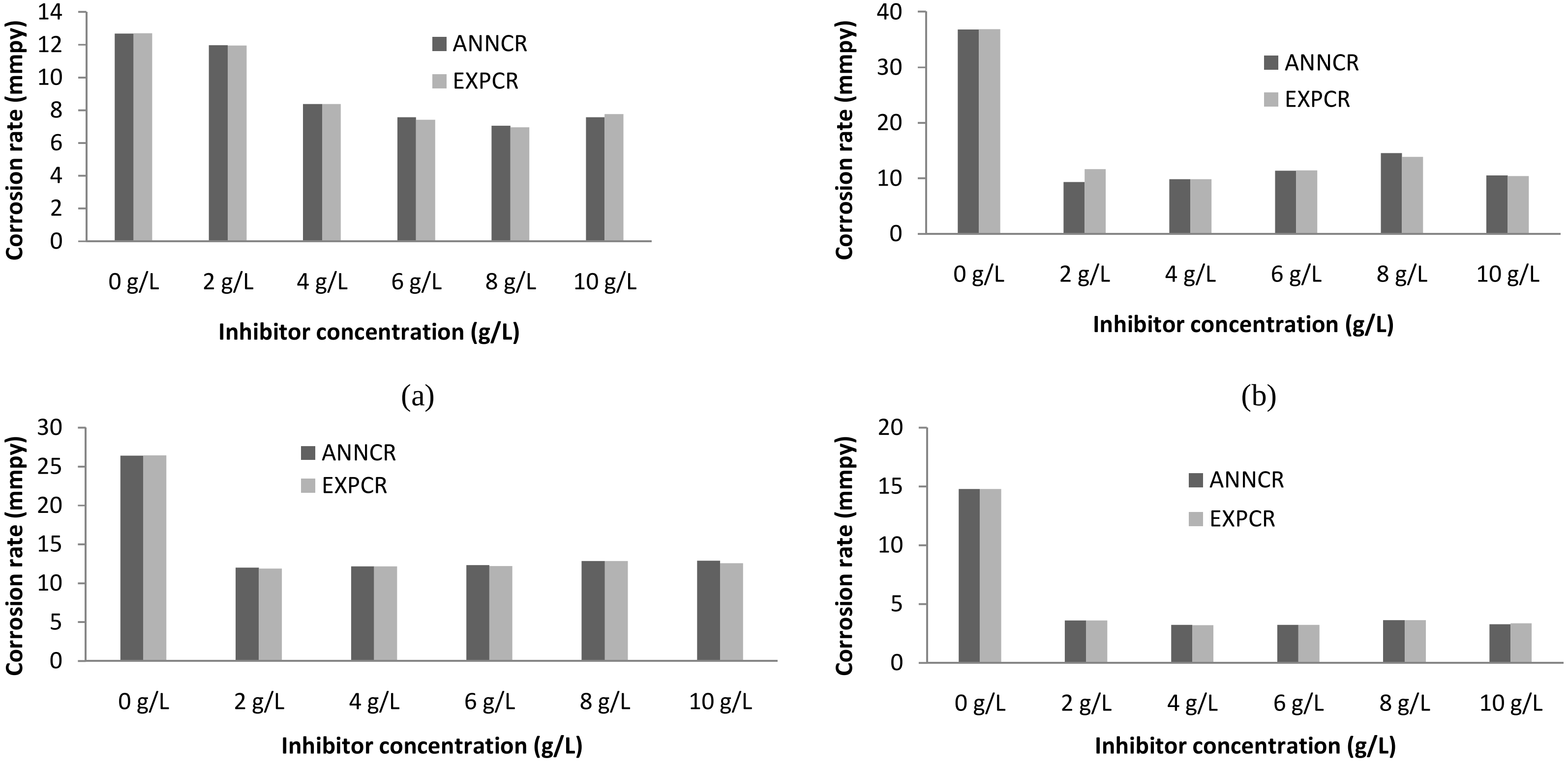


(a) (b)

(c) (d)

Figure 4.33: Comparison of ANN modeled result with experimental result for mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the presence of CF

(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Al in HCl (d) Al in H_2SO_4

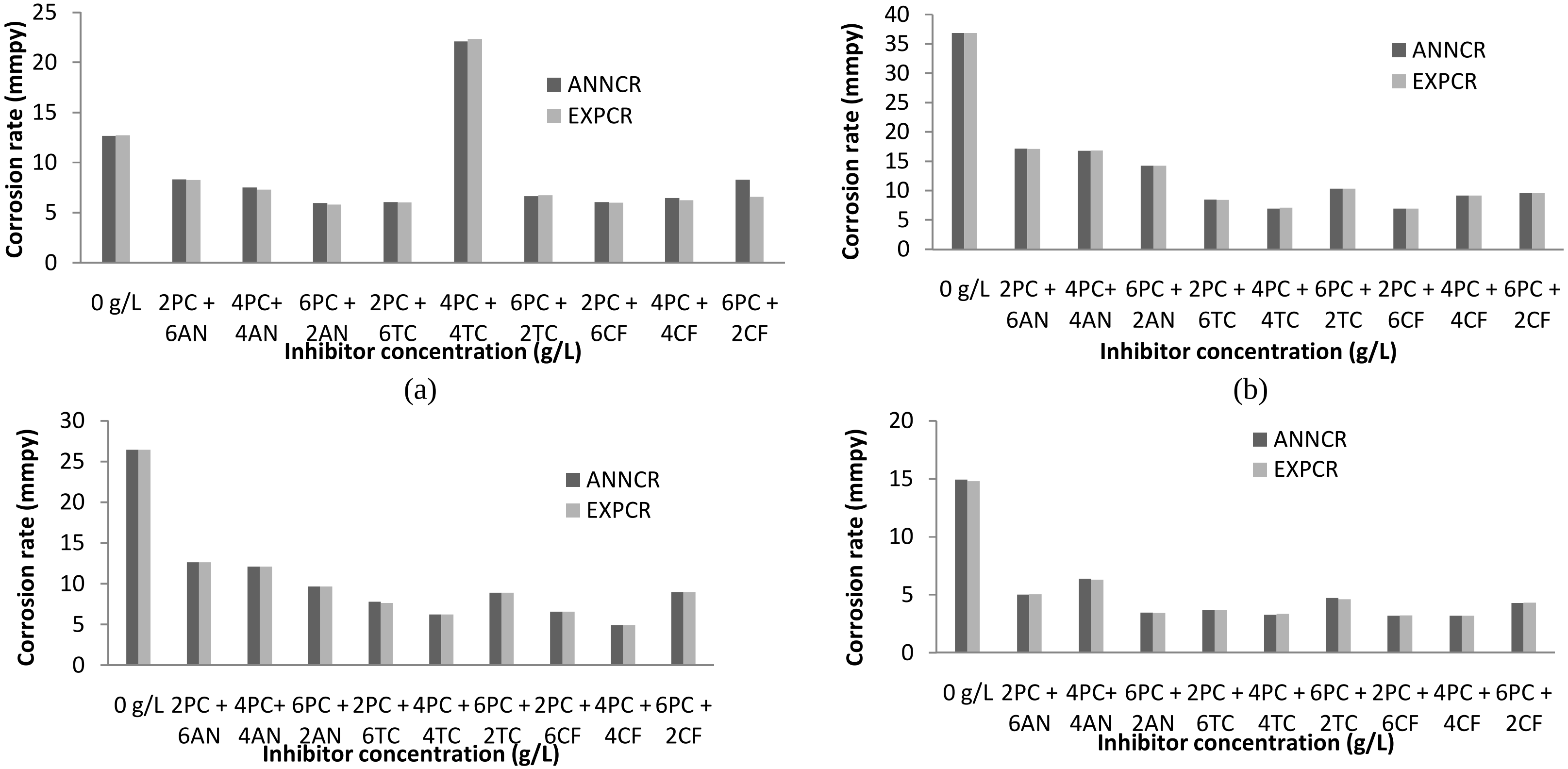


(a) (b)

(c) (d)

Figure 4.34: Comparison of ANN modeled result with experimental result for mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the presence of TC

(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Al in HCl (d) Al in H_2SO_4



(a) (b) (c) (d)

Figure 4.35: Comparison of ANN modeled result with experimental result for mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 in the presence of SA

(a) mild steel in HCl (b) mild steel in H_2SO_4 (c) Al in HCl (d) Al in H_2SO_4

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study investigated the problems associated with the effect of corrosion on industrial chemical environments usually found in the chemical and allied petrochemical industries. Metal wastage which usually happens when entire facilities are in operational service has been associated with aggressive acidic environments like HCl and H_2SO_4. Though, there are other sources of metal wastage like wearing of machine components under tensile, compressive and shearing stresses, the aggressive nature of hydrochloric and sulphuric acid cannot be said to be non-contributors to the corrosion process. Since engineering facilities (pressure vessels, hold-up tanks) have been designed to support certain load specifications in service they will ordinarily function well, but the introduction of aggressive process reagents in the petrochemical industries identified in the literature survey leads to drastic metallic wastage. This wastage ensures that metal thickness or diameter is reduced below the effective load carrying capacity. Therefore, while in service metals fail catastrophically resulting in injuries to the work force, product spillage, lost production hours and maintenance problems. By reducing the rate of metal wastage in an environmentally friendly way it is possible to prolong the service life of the machine component. This saves money and reduces incidencies of down time.

Specifically, the use of inhibitors apart from being the cheapest amongst the several techniques available, offers a versatile and viable approach. However, the over reliance on the use of chemical inhibitors have brought to the fore the problems of pollution, litigation, contamination of plant and animal life as well as the burden of disposal. Therefore, this makes the use of environmentally friendly inhibitors viable and appropriate. The reason being that plant extracts are clean, cheap and sustainable sources of addressing metal wastage arising from aggressive environment. In order to properly situate a basis of comparison for the green inhibitors, the use of inorganic inhibitor (potassium chromate) and organic inhibitors (aniline) were investigated. Furthermore, the green inhibitors (*Cassia fistula* and *Terminalia cattapa*) were also used as stand alone systems and to totally substitute or replace the chemical inhibitors. In addition, the inorganic inhibitor was partially replaced with the organic and green inhibitors. That is they were used in combination otherwise called synergy. This fractional replacement model is a novel way of tailoring the inhibitor to a desired ouput.

The aim of this study was initiated to generate measurable and testable data towards the control of corrosion induced wastage of infrastructure through the development of new inhibitor systems. This was achieved through the following objectives; determination of inhibitors performance by Weight loss and potentiodynamic polarization techniques; determination of metal-inhibitor interaction mechanism using several adsorption isotherms; inhibitor classification as either as cathodic, anodic or mixed type inhibitor using the kinetic parameters from the potentiodynamic polarization technique and ANN modelling of the complex corrosion process through the use of exposure time, inhibitor concentration, chemical composition of the respective metals used, media concentration, temperature and initial weight of metal as the input parameter, whilst using the corrosion rate as the ouput. The various indices that characterized the inhibitor behaviour in curtailing metallic deterioration and essentially prolonging the lifespan of the metal are presented in the research conclusion as follows:

- The inorganic inhibitor (potassium chromate) had the best IE of 49.09 and 52.65 at a concentration of 10 g/L for mild steel in 0.5 M HCl and 0.5 M H_2SO_4 media respectively. For aluminium in 0.5 M HCl media the PC inhibitor had the best IE value of 66.7 at a concentration of 10 g/L while the best IE value of 65.87 was at a concentration of 6 g/L for aluminium in 0.5 M H_2SO_4 media.
- The organic inhibitor (aniline) produced its best IE value of 23.77 and 43.82 at a concentration of 10 g/L in both 0.5 M HCl and 0.5 M H_2SO_4 media respectively for mild steel. On the other hand, its best IE value of 49.96 and 66.81 was at a concentration of 8 g/L in both 0.5 M HCl and 0.5 M H_2SO_4 media respectively for aluminium immersion.
- The green inhibitor (*Cassia fistula*) displayed its best IE at a 10 g/L concentration in the 0.5 M HCl (54.5) and 0.5 M H_2SO_4 (78.86) media for mild steel and 0.5 M H_2SO_4 (76.54) media for aluminium. Its best IE value of 54.79 was obtained in the aluminium for 0.5 M HCl media at 2 g/L concentration.

- The other green inhibitor (*Terminalia cattappa*) utilized in this study showed excellent IE values at a concentration of 4 g/L in the mild steel for 0.5 M H_2SO_4 (73.25) media and aluminium for 0.5 M H_2SO_4 (78.36) media respectively. The best IE values of 45.39 and 55 were obtained at concentration of 8 and 2 g/L respectively for the mild steel and aluminium in the 0.5 M HCl media.
- The novel synergetic admixtures of 6PC+2AN and 2PC+6CF obtained by tailoring the inhibitor combinations through a fractional substitution model produced its best IE value of 54.32 and 81.26 for mild steel in 0.5 M HCl and 0.5 M H_2SO_4 media respectively. The SA of 4PC+4CF produced IE values of 81.27 and 78.35 for aluminium in the 0.5 M HCl and 0.5 M H_2SO_4 media respectively.
- It was discovered that of the sixteen (16) systems investigated for adsorption isotherm fitting, fourteen (14) fitted well to the Langmuir adsorption isotherm.
- The metal-inhibitor surface interaction mechanisms of all the green inhibitor systems were characterized by the Langmuir adsorption isotherm.
- The separation factors R_L obtained for all the inhibitor systems characterized by the Langmuir adsorption isotherm showed a favourable adsorption.
- The dynamic surface coverage of each of the inhibitor systems over the entire sixty day duration of the experiment showed that the best surface coverage values were obtained on the first day of the experiment.

- The value of G obtained for the adsorption of PC on the aluminium metal surface in HCl is negative. This is an indication of a spontaneous adsorption of the inhibitor molecules on the aluminium surface.
- Four PC systems and three AN systems showed mixed inhibition behaviour that were predominantly anodic. All the synergetic admixture systems showed anodic inhibition behaviour.

- Majority of the the green inhibition systems showed mixed type inhibition mechanism. The inhibitors impacted the anodic metallic dissolution and the cathodic hydrogen evolution reactions.

- The increases in the R_{ct} values can be attributed to the formation of a protective adsorption film on the mild steel and aluminium surfaces.

- Surface analysis of the mild steel and aluminium samples in the presence and absence of HCl and H_2SO_4 showed that the introduction of the inhibitors generally stifled the corrosion process. The effect of corrosion on the grain boundaries was abated by the adsorption of inhibitor molecules.

- The green inhibitors generated a closely packed almost impenetrable film that stifled the cathodic and anodic reactions. The inhibited samples also showed a finer surface with pit frequency lower than those of the unihibited samples.

- An effective neural network model for all the metal-inhibitor-media system was developed by utilizing the nnfitting tool in the MATLAB® tool box. Most of the trends noticed in the experimental Weight loss data were characterized by the ANN.

- The ANN output corrosion rate predicted the experimental data closely throughout training, validation and testing of the data with excellent R-value and low mean square errors. Thus, artificial neural network can be used to predict almost exactly the corrosion rate of mild steel and aluminium in 0.5 M HCl and 0.5 M H_2SO_4 media in the presence of PC, AN, CF, TC and SA respectively.

- In essence we observe the effectiveness of the inhibitors in curtailing metallic corrosion when compared to the uninhibited solutions which is actual situation in the chemical and allied chemical industries (petrochemical). By reducing corrosion rate, the service life and by extension the load carrying capacity of the facilities is extended.

5.1.1 *Contributions to knowledge*

- The study yielded new inhibitor systems namely:

✓ *Cassia fistula* at 10 g/L concetration produced the best result when mild steel was immersed in 0.5 M HCl (54.5%)

✓ Synergetic admixture of 2PC + 6CF produced the best result when Mild steel was immersed in 0.5 M H_2SO_4 (81.29%)

✓ Synergetic admixture of 4PC + 4CF produced the best result when Al was immersed in 0.5 M HCl (81.27%) and

- ✓ *Terminalia catappa* at 4 g/L concetration produced the best result when Al was immersed in 0.5 M H_2SO_4 (78.36%).

  The synthesized systems could be impregnated as pigments in coating systems and used in particular environments.

- The recourse to ANN modelling rather than costly experimentation is another contribution of the research. Each of the twenty corrosion systems were modelled using ANN and a high accuracy was obtained from the predicted values. This essentially eliminates costly and time wasting experimentation.

5.2 Recommendations

The present work has opened up some issues that might be of interest for future studies. The following issues are suggested for future focus:

- Detailed study of the effect of the inhibitors on the corrosion of other metals in related or varied media systems;
- Fuzzy inference systems, genetic algorithm and their composite forms are worth investigating for the development of predictive models.

- More ANN experiments can be conducted using a larger data set introducing other neural network techniques to test their performance over the Levenberg Marquadt technique and

- The development of correlation models between weight loss and potentiodynamic polarization technique.

REFERENCES

Abd El Rehim, S.S., Magdy, Ibrahim, A.M., & Khaled, K.F. (1999). 4-Aminoantipyrine as an Inhibitor Mild Steel Corrosion in HCl Solution. *Journal of Applied Electrochemistry, 29,* 593.

Abdel-Gaber, A.M., Khamis, E., Abo-ElDahab, H., & Adeel, S.H. (2008). Inhibition of Aluminium Corrosion in Alkaline Solutions using Natural Compound. *Materials Chemistry and Physics, 109 (2-3),* 297-305.

Abdel-Graber, A.M., Abd-El-Nabey, B.A., Sidahmed, I.M., El-Zayady A.M., & Saadawy, .M. (2006). Inhibitive Action of Some Plant Extracts on the Corrosion of Steel in Acidic Media. *Corrosion Science, 48 (9),* 2765-2779.

Abdel-Rehim, S.S., Khaled, K.F., & Al-Mobarak, N.A. (2011). Corrosion Inhibition of Iron in Hydrochloric Acid using Pyrazole. *Arabian Journal of Chemistry, 4,* 333–337.

Abiola, O.K., & James, A.O. (2010). The Effects of *Aloe vera* Extract on Corrosion and Kinetics of Corrosion Process of zinc in HCl Solution. *Corrosion Science, 52 (2),* 661-664.

Abiola, O.K., Oforka, N.C., Ebenso, E.E., & Nwinuka, N.M. (2007). Ecofriendly Corrosion Inhibitors: the Inhibitive Action of *Delonix regia* Extract for the corrosion of Aluminium in acidic media. *Anti-Corrosion Methods and Materials, 54 (4),* 219-224.

Achenbach, E. (1995). Response of a Solid Oxide Fuel Cell to Load Change, *Journal of Power Sources, 57, (1-2),* 105–109.

Adejo, S. O., Yiase, S. G., Ahile, U. J., Tyohemba, T. G., & Gbertyo, J. A. (2013). Inhibitory Effect and Adsorption Parameters of Extract of Leaves of *Portulaca oleracea* of corrosion of aluminium in H_2SO_4 solution. *Archives of Applied Science Research, 5 (1),* 25-32.

Afolabi, A.S. (2007). Synergistic inhibition of potassium and sodium nitrite on mild steel in chloride and sulphide media. *Leonardo Electronic Journal of Practices and Technologies (11),* 143-154.

Ajayi, O.O., Omotosho, O.A., Ajanaku, K. O., & Olawore, B. O. (2011). Failure Evaluation of Aluminium Alloy in 2 M HCl in the presence of *Cola acuminata*. *Environmental Research Journal, 5 (4),* 163-169.

Ajayi, O.O., Omotosho, O.A., & Ifepe, V.O. (2011a). Acid Failure of Mild Steel in 2 M Sulphuric Acid in the Presence of *Vernonia amygdalina*. *Journal of Material and Environmental Science, 2,* 186-195.

Ajayi, O.O., Omotosho, O.A., Ajanaku, K.O., & Olawore, B.O. (2011b). Degradation Study of Aluminium Alloy in 2M HCl in the Presence of *Chromolaena odorata*. *Journal of Engineering and Applied Science, 6 (1),* 10-17.

Akpabio, E.J., & Neeka, J.B. (2013). Review of Petroleum Refinery Acid Catalyzed Alkylation Processes: A Message to Nigerian Refineries. *Petroleum Technology Development Journal, 3(1),* 84-97.

Ali Volkan Akkaya, B. S., & Erdem, H. H. (2009). Thermodynamic Model for Exegetic Performance of a Tubular SOFC Module. *Renewable Energy*, 1, 1–8.

Al-Turkustani, A. M., & Al-Marhabi, N. M. (2012). Inhibition of Mild Steel Corrosion using *Plectranthus tenuiflorus* (shara) Plant as Safe and Green Inhibitor in Acidic Solutions. *Global Journal of Science Frontier Research Chemistry, 12 (1),* 73-84.

Al-Turkustani, A.M., (2010). Effect of *Ajowan* Seeds as Safe Inhibitor on the Corrosion of Steel in 2.0 M Sulfuric Acid. *Modern Applied Science, 4 (10),* 52-61.

Al-Turkustani, A.M., Arab, S.T., & Al-Qarni, L.S.S. (2010a). The use of *Ruta chalepensias* Corrosion Inhibitor for Steel Corrosion in 2 M Sulphuric Acid Solution. *Oriental Journal of Chemistry, 26 (2),* 437-454.

Al-Mhyawi, S.R. (2014). Inhibition of mild steel corrosion using Juneperus plants as green inhibitor. *African Journal of Pure and Applied Chemistry, 8 (1),* 9-22.

Anca, C., Ioana, M., Vaireanu, D.I., Iosif, L., Carmen, L., & Simona, C. (2009). Estimation of Inhibition Efficiency for Carbon Steel Corrosion in Acid Media by using Natural Plant Extracts. *Revista de Chimie, 60 (11),* 1175-1180.

Aprael, S.Y. (2008). Prediction of Zinc Consumption as Sacrificial Anode in Cathodic Protection of Steel in Sea Water using Artificial Neural Network. *Journal of Engineering, 14 (2),* 2495-2508.

Arab, S.T., Al-Turkustani, A.M., & Al-Dhahiri, R.H. (2008). Synergistic Effect of *Azadirachta indica* Extract and Iodide Ions on the Corrosion Inhibition of Aluminium in Acid Media. *Journal of the Korean Chemical Society, 52 (3),* 281-294.

Ating, E.I., Umoren, S.A., Udousoro, I.I., Ebenso, E.E., & Udoh, A.P. (2010). Leaves Extract of *Ananas sativum* as Green Corrosion Inhibitor for Aluminium in Hydrochloric Acid Solutions. *Green Chemistry Letters and Reviews, 3 (2),* 61-68.

Awad, G.H. (1985). Effect of some plant extracts on the corrosion of mild steel in 0.1N Hydrochloric acid solutions. *Proc. 6th European Symp. On corrosion inhibitors 1,* 385.

Ayeni, F.A., Aigbodion, V.S., & Yaro, S.A. (2007). Non-toxic Plant Extract as Corrosion Inhibitor for Chill Cast Al-Zn-Mg Alloy in Caustic Soda Solution. *Eurasian Chemico-Technological Journal, 9 (2),* 91-96.

Badiea, A.M., & Mohana, K.N. (2009). Corrosion Mechanism of Low-Carbon Steel in Industrial Water and Adsorption Thermodynamics in the Presence of Some Plant Extracts. *Journal of Materials Engineering and Performance, 18 (9),* 1264-1271.

Bahorun, T., Neergheen, V.S., & Aruoma, O.I. (2005). Phytochemical constituents of *Cassia* fistula. *African Journal of Biotechnology 4 (13),* 1530 – 1540.

Barakat, Y.F., Hassan, A.M., & Baraka, A.M. (1998). Corrosion inhibition of mild steel in aqueous solution containing H_2S by some naturally occurring substances. *Materialwissenchaft und Werkstofftechnik,* 29 *(7),* 365-370.

Bouyanzer, A., Hammouti, B., & Majidi, L. (2006). Pennyroyal Oil from *Mentha pulegium* as Corrosion Inhibitor for Steel in 1 M HCl. *Materials Letters, 60 (3),* 2840 - 2843.

Bouyanzer, A., & Hammouti, B. (2004), Naturally occurring ginger as corrosion inhibitor for steel in molar hydrochloric acid at 353 K. *Bulletin of Electrochemistry, 20 (2),* 63-65.

Bruna, M., & Sladek, A. (2011). Hydrogen Analysis and Effect of Filtration on Final Quality of Castings from Aluminium Alloy $AlSi_7MgO_{3.}$ *Archives of Foundry Engineering, 11(1),* 5-10.

Buchweishaija, I., & Mhinzi, G.S. (2008). Natural products as a source of environmentally friendly corrosion inhibitors: The case of gum exudates from *Acacia seyal var.Seyal. Portugaliae Electrochimica Acta, 26 (3),* 257-265.

CAS, (2010). *Chemical book-CAS database list.* Retrieved from http://www.chemicalbook.com/ChemicalProductProperty_EN_cb6398284.htm

Chauhan, J.S. (2009). Anticorrosion Behaviour of *Zenthoxylum alatum* Extract in Acidic Media. *Asian Journal of Chemistry, 21 (3),* 1975-1978.

Cheung, T., & Gates, B. (1997). Strong Acid Catalyst for Paraffin Conversion. *Chemtech, 27 (9),* 28-34.

Chowdhary, R., Jain, T., Rathoria, M.K., & Mathur, S.P. (2004). Corrosion inhibition of mild steel by acid extracts of *Prosopis juliflora*. *Bulletin of electrochemistry 20 (2),* 67-75.

Christy, A.A. (2012). Effect of Heat on the Adsorption Properties of Silica Gel. *IACSIT International Journal of Engineering and Technology, 4 (4),* 484-488.

CIA, (2006). *CIA world factbook.* Retrieved from www.cia.gov/cia/publications/factbook/geos/ni.html

CSB, (2002). *Investigation report. U.S chemical safety and hazard investigation board Report No. 2001-05-1-DE.* Retrieved from http://www.csb.gov/assets/1/19/Motiva_Final_Report.pdf

CSPC, (1977). CPSC Announces Final Ban On Lead-Containing Paint. Retrieved from http://www.cpsc.gov/en/Recalls/1977/CPSC-Announces-Final-Ban-On-Lead-Containing-Paint/

Dakmouche, M., Ladjel, S., Gherraf, N., Saidi, M., Hadjaj, M., & Ouahrani, M.R. (2009). Inhibition Effect of Some Plant Extracts on the Corrosion of Mild steel in H_2SO_4 medium. *Asian Journal of Chemistry, 21 (8),* 6176-6180.

Damm, D. L., & Fedorov, A. G. (2005). Radiation Heat Transfer in SOFC Materials and Components. *Journal of Power Sources*, *143 (1), 158–165.*

De Souza, F.S., & Spinelli, A. (2009). Caffeic Acid as a Green Corrosion Inhibitor in Mild Steel. *Corrosion science, 51 (3), 642 - 649.*

Devarayan, K., Mayakrishnan, G., & Nagarajan, S. (2012). Green Inhibitors for Corrosion of Metals: a Review. *Chemical Science Review Letters*, *1,* 1-8.

Dixit, A. and Shrivastava, S. (2011). Volumetric Properties of Potassium Chromate and Potassium Dichromate in 25% Sucrose-Aqueous Solution at 303.15K. *International Journal of ChemTech Research*, *3(3),* 1265-1268.

Ebenso, E.E. & Ekpe, U.J. (1996). Kinetic Study of Corrosion and Corrosion Inhibition of Mild Steel in H_2SO_4 using *parica papaya* Leaves Extract. *West African Journal of Biology and Applied Chemistry*, *41,* 21 – 27.

Ebenso, E.E., Ekpe, U.J., & Ibok, U.J. (1998). Studies on the Inhibition of Mild Steel Corrosion by Some Plant Extracts in Acidic Medium. *Discovery and Innovation*, 10, 52 – 59.

Ebenso, E.E., Ibok, U.J., Ekpe, U.J., Umoren, S., Jackson, E., Abiola, O.K., Oforka, N.C., & Martinez, S. (2004). Corrosion Inhibition Studies of Some Plant Extracts on Aluminium in Acidic Medium. *Transactions of the SAEST (Society for advancement of Electrochemical Science and Technology), 39 (4),* 117-123.

Eddy, N.O. (2009). Inhibitive adsorption properties of ethanol extract of colocasia esculenta leaves for corrosion of mild steel in H_2SO_4. *International Journal of Physical Sciences, 4 (4),* 165-171.

Eddy, N.O., & Odiongenyi, A.O. (2010). Corrosion Inhibition and Adsorption Properties of Ethanol Extract of IT *heinsia crinata* / IT on mild steel in H_2SO_4. *Pigment and Resin Technology,* 39 (5), 288-295.

Eddy, N.O., & Odoemelam, S.A. (2009). Inhibition of Corrosion of Mild Steel in Acidic Medium using Ethanol Extract of *Aloe vera*. *Pigment and Resin Technology*, 38 (2), 111-115.

Ekpe, U.J., Ebenso, E.E., & Ibok, U.J. (1994). Inhibitory Action of *Azadirachta indica* leaves extract on the corrosion of mild steel in H_2SO_4. *Journal of West African Science Association, 37,* 13 – 30.

El-Dahan, H.A. (2006). Natural products as corrosion inhibitors for copper in saline water in presence of sulphide. *Egyptian Journal of Chemistry 49 (5),* 589-600.

El-Etre, A.Y., Abdallah, M., & El-Tantawy, Z.E. (2005). Corrosion inhibition of some metals using *lawsonia* extract. *Corrosion Science 47 (2),* 385- 395.

El-Etre, A.Y. (2003). Inhibition of aluminum corrosion using Opuntia extract. Corrosion *Science, 45 (11),* 2485-2495.

El-Etre, A.J. (2007). Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves. *Journal of Colloid and Interface Science, 314 (2),* 578-583.

El-Sayed, A., Shaker, A. M., & Abd El-Lateef, H. M. (2010). Corrosion inhibition of tin, indium and tin–indium alloys by adenine or adenosine in hydrochloric acid solution. *Corrosion Science, 52 (10),* 72-81.

Emranuzzaman, T., Kumar, Vishwanatham, S., & Udayabhanu, G. (2004). Synergistic Effects of Formaldehyde and Alcoholic Extract of Plant Leaves for Protection of N80 Steel in 15% HCl. *Corrosion Engineering Science and Technology, 39 (4),* 327- 332.

EPA, (1994). *OPPT Chemical fact sheets. Aniline Fact Sheets Support Document (CAS No. 62-53-3).* Retrieved from http://www.epa.gov/chemfact/anali-sd.pdf

Febrianto, J., Kosasih, A.N., Sunarsob, J., Ju, Y., Indraswati, N., & Ismadji, S. (2009). Equilibrium and Kinetic Studies in Adsorption of Heavy Metals using Biosorbent: A Summary of Recent Studies. *Journal of Hazardous Materials, 162 (2-3),* 616-645.

Fekry. A.M., & Mohamed, R.R. (2010). Acetyl thiourea chitosan as an eco-friendly inhibitor for mild steel in sulphuric acid medium. Electrochimica Acta, 55 (6), 1933-1939.

Feng, Y., Siow, K.S., Teo, W.K., & Hsieh, A.K. (1999). The synergistic effects of propargyl alcohol and potassium iodide on the inhibition of mild steel in 0.5 M sulfuric acid solution. *Corrosion Science, 41,* 829-859.

Fontana, M.G. (1987). *Corrosion Engineering.* 3 rd ed. McGraw-Hill, New York.

Foo, K.Y., & Hameed, F.H. (2010). Insights into the Modelling of Adsorption Isotherm Systems. *Chemical Engineering Journal*, *156,* 2-10.

Fouda, A.S., Elmorsi, M.A. and Elmekkawy, A. (2013). Eco-friendly Chalcones Derivatives as Corrosion Inhibitors for Carbon Steel in Hydrochloric Acid Solution. *African Journal of Pure and Applied Chemicstry, 7 (10),* 337-349.

Gunasekaran, G., & Chauhan, L.R. (2004). Eco-friendly inhibitor for corrosion inhibition of mild steel in phosphoric acid medium. *Electrochimica Acta, 49 (25),* 4387-4395.

Gunasekaran, G., & Chauhan, L.R. (2007). Corrosion inhibition of mild steel by plant extract in dilute HCl medium. *Corrosion Science 49 (3),* 1143-1161.

Gundersen, O., Kluken, A.O., & Myhr, O.R. (2001). *Mathematical Modelling of Weld Phenomena* 5, Edited by H. Cerjak, Institute of Materials, London, UK.

Hameurlaine, S., Gherraf, N., benmnine, A., & Zellagui, A. (2010). Inhibition effect of Methanolic Extract of *atractylis serretuloides* on the corrosion of mild steel in H_2SO_4 medium. *Journal of Chemical and Pharmaceutical Research 2 (4), 819-825.*

Hartley, J. (1996). *The Increasing use of aluminium: Prospects and Implications EUR/17284/EN*. Retrieved from http://ftp.jrc.es/EURdoc/eur17284en.pdf.

Ibrahim, M.E., El-Khrisy, A.M., Al-Abdallah, E.M.M., & Baraka, A. (1981). Evaluation of the Inhibitor Action of certain Natural Substances Used as Corrosion Inhibitors-1. In the Dissolution of Tin in Nitric Acid. *Mo Metalloberflanche Beschichten won Metall und Kunstsoff 35 (4),* 134-136.

I-Sayed, M.E., Mansour, O.Y., Selim, I.Z., & Ibrahim, M. M. (2001). Identification and Utilization of Banana Plant Juice and its Liquor as Anti-Corrosive Materials. *Journal of Science and Industrial Research, 60 (9), 738-747.*

Jalili, S., Jaberi, A., Malijani, M.G., & Jafarian, M. (2008). Prediction of Lead Corrosion Behaviour using Feed Forward Artificial Neural Network. *Journal of Iranian Chemical Society, 5 (4), 669 – 676.*

James, O.O., Ajanaku, K.O., Ogunniran, O.K., Ajani, O.O., & John, M.O. (2009). Adsorption Behaviour of [(4-Hydroxy-6-methyl-2-oxo-2Hpyran- 3-yl)-(4-methoxy-phenyl)-methyl]-urea on Stainless Steel in Phosphoric Media. *Portguliae Electrochimica Acta, 27 (5),* 591- 598.

Jain, T., Chowdhary, R., Arora, P., & Mathur, S.P. (2005). Corrosion inhibition of aluminum in hydrochloric acid solutions by peepal (*Ficus religeosa*) extracts. *Bulletin of Electrochemistry, 21(1),* 23- 27.

Jerkiewicz, G., Borodzinski, J.J., Chrzanowski, W., & Conway, B.E. (1995). Examination of factors influencing promotion of H absorption into metals by site-blocking elements. *Journal of Electrochemical Society,142,* 3755-3763.

Kasthuri, P.K., & Arulanantham, A. (2010). Eco-friendly extract of *Euphorbia hirta* as corrosion inhibitor on mild steel in sulphuric acid medium. *Asian Journal of Chemistry, 22 (1),* 430-434.

Kesavan, D., Gopiraman, M., & Sulochana, N. (2012). Green inhibitors for corrosion of metals: A review. *Chemical Science Review and Letters, 1(1),*1-8.

Khamis, E., & Alandis, N. (2002). Herbs as new type of green inhibitors for acidic corrosion of steel. *Materialwissenschaf tund Werkstoffiechnik, 33 (9),* 550-554.

Kiselev, V. D., Ukhlovtsev, S. M., Podobaev, A. N., & Reformatskaya, I. I. (2006). Analysis of Corrosion Behavior of Steel 3 in Chloride Solutions by using Neural Networks. *Protection of Metals, 42 (5), 452-458.*

Koch, G.H., Brongers, M.P.H., Thompson, N.G., Virmani, Y.P., & Payer, J.H. (2002). Corrosion Costs and Preventive Strategies in the United States. NACE Intl PHWA-RD-01-156.

Kumar, S., Arora, S., Sharma, M., Arora, P., & PrakashMathur, S. (2009). Synergistic Effect of Calotropis Plant in Controlling Corrosion of Mild Steel in Basic Solution. *Journal of the Chilean Chemical Society, 54 (1),* 83-88.

Lebrini, M., Robert, F., & Roos, C. (2010). Inhibition effect of alkaloids extract from *annona squamosa* plant on the corrosion of C38 steel in normal hydrochloric acid medium. *International Journal of Electrochemical Science, 5 (11),* 1678 - 1712.

Lebrini, M., Robert, F., Lecante, A., & Roos. C. (2011). Corrosion Inhibition of C38 Steel in 1M Hydrochloric Acid Medium by Alkaloids Extract from *oxandra asbeckii* plant. *Corrosion Science, 53 (2),* 687-695.

Li, P., & Chyu, M. K. (2003). Simulation of the Chemical/Electrochemical Reactions and Heat/Mass Transfer for a Tubular SOFC in a Stack. *Journal of Power Sources, 124, (2),* 487–498.

Lingvay, I., Vaireanu, D.I., Cojocaru, A., Parvu, L., Major, I., Nita, S., & Lingway. C. (2009). Evaluation of Inhibitive Properties of Environmentally Friendly Plant Extracts using Polarization Curves. *European Corrosion Congress 2009, EUROCORR 2009 3,* 1490.

Liu, Z., & Xiong, G.l. (2003), Preparation and application of plant inhibitors. Corrosion *and Protection 24 (4),* 146-150.

Loto, C.A. (2001). The Effect of Mango Bark and Leaf Extract Solution Additives on the Corrosion Inhibition of Mild Steel in Dilute Sulphuric Acid – part I. *Corrosion Prevention and Control, 48 (1),* 38-41.

Loto, C.A. (2001a). The Effect of Mango Bark and Leaf Extract Solution Additives on the Corrosion Inhibition of Mild Steel in Dilute Sulphuric Acid – part 2. *Corrosion Prevention and Control, 48 (2),* 59-64.

Loto, C.A. (2003). The Effect of Bitter Leaf Extract on the Inhibition of Mild Steel in HCl and H_2SO_4. *Corrosion Prevention control, 50 (1),* 43-49.

Loto, C.A., & Mohammed, A.I. (2000). The Effect of Cashew Juice Extract on Corrosion Inhibition of Mild Steel in HCl. *Corrosion Prevention and Control, 47 (2),* 50-56.

Loto, C.A., & Mohammed, A.I. (2003). Inhibition Evaluation of Mango Juice Extracts on the Corrosion of Mild Steel in HCl. *Corrosion Prevention and Control 50 (3),* 107-118.

Loto, R.T., Loto, C.A., & Popoola, A.P. (2015). Inhibition effect of phenylamine on the corrosion of austenitic stainless steel type 304 in dilute sulphuric acid. Canadian Journal of Pure and Applied Sciences, 9 (2), 3409-3422.

Lu, N., Li, Q., Sun, X., & Khaleel, M. (2006). The Modelling of a Standalone Solid-Oxide Fuel Cell Auxiliary Power unit. *Journal of Power Sources, 161 (2),* 938–948.

Malinov, S. & Sha, W. (2004). Application of Neural Networks for Modelling Correlations in Titanium Alloys. *Materials Science and Engineering A, 365 (1-2),* 202-211.

Malinov, S., Sha, W., & Guo, Z. (2000). Artificial Neural Network Modelling of Crystallization Temperatures of Ni-P Based Amorphous Alloys Material. *Materials Science and Engineering A, 283*, 1-218.

Malinov, S., Sha, W., & Mckeown, J.J. (2001). Modelling the Correlation Between Processing parameters and properties in titanium alloys using artificial neural network. *Computational materials science, 21 (3),* 375-394.

McShane, S., Malinov, S., Mckeown, J.J., & Sha, W. (2001). Computational modelling of materials, minerals and metals processing, TMS, Easton, Pa, USA.

Metzbower, E.A., DeLoach, J.J., Lalam, S.H., & Bhadeshia, H.K.D.H. (2001). Neural Network Analysis of Strength and Ductility of Welding Alloys for High Strength Low Alloy Shipbuilding Steels. *Science and Technology of Welding and Joining, 6 (2),* 116-124.

Minhaj, A., Saini, P.A., Quraishi, M.A., & Farooqi, I.H. (1999). A Study of Natural Compounds as Corrosion Inhibitors for Industrial Cooling Systems. *Corrosion Prevention and Control, 46 (2),* 32-38.

NACE, (2002). *Corrosion cost and preventive strategies in the United States. Publication No. FHWA-RD-01-156.* Retrieved from https://www.nace.org/uploadedFiles/Publications/ccsupp.pdf.

Nappi, C. (2013). *The global aluminium industry 40 years from 1972.* Retrieved from http://www.worldaluminium.org/media/filer_public/2013/02/25/an_outlook_of_the_global_aluminium_industry_1972_-_present_day.pdf.

Neelavathi, P., venkatalakshmi, P., & Brindha, P. (2013). Anti bacterial activities of aqueous ethanolic extracts of *Terminalia catappa* leaves and back against some pathogenic bacteria. *International Journal of Pharmacy and Pharmaceutical Sciences, 5 (1),* 114-120.

Nigam, N., & Srivastava, K. (1998). Role of amaranthus-A wild plant on the dissolution of mild steel in acidic medium. *Journal of the Institution of Engineers (India) Chemical Engineering Division, 68(3),* 89-92.

Njoku, V.O., & Oguzie, E.E. (2009). Inhibitory properties of *Baphia nitida* extract in acid mild steel corrosion. *European Corrosion Congress 2009, EUROCORR 2009, 2,* 849-870.

Noor, E.A. (2009). Potential of aqueous extract of *Hibiscus sabdariffa* leaves for inhibiting the the corrosion of aluminum in alkaline solutions. *Journal of Applied Electrochemistry, 39 (9),* 1465-1475.

Obot, I.B., & Obi-Egbedi. N.O. (2010). An interesting and efficient green corrosion inhibitor for aluminium from extracts of *Chlomolaena odorata L.* in acidic solution. *Journal of Electrochemistry, 40 (11),* 1977-1984.

Obot, I.B., Obi-Egbedi, N.O., & Umoren, S.A. (2009). Experimental and theoretical investigation of clotrimazole as corrosion inhibitors for Aluminium in hydrochloric acid and effect of iodide ion addition. *Der Pharma Chemica, 1 (1),* 151-166.

Obot, I.B., Obi-Egbedi, N.O., Umoren, S.A., & Ebenso, E.E. (2010). Synergistic and antagonistic effects of anions and *Ipomoea invulcrata* as green corrosion inhibitor for aluminium dissolution in acidic medium. *International Journal of Electrochemical Science, 5(7),* 994-1007.

Obot, I.B., Ebenso, E.E., Obi-Egbedi, N.O., Ayo, S.A., & Zuhair, M.G. (2012). Experimental and theoretical investigations of adsorption characteristics of itraconazole as green corrosion inhibitor at a mild steel/hydrochloric acid interface. *Research in Chemical Intermediates, 38,* 1761-71.

Oguzie, E.E. (2006). Adsorption and corrosion inhibitive properties as *Azadirachta indica* in acid solutions, *Pigment and Resin Technology, 35 (6),* 334-340.

Oguzie, E.E. (2008). Corrosion inhibitive effect and adsorption behaviour of *Hibiscus sabdariffa* on mildsteel in acidic media. *Portugaliae Electrochimica Acta, 26 (3),* 303-314.

Oguzie, E.E., Enenebeaku, C.K., Akalezi, C.O., Okoro, S.C., Ayuk, A.A., & Ejike, E.N. (2010). Adsorption and corrosion-inhibiting effect of *Dacryodis edulis* extract on low-carbon-steel corrosion in acidic media. *Journal of Colloid and interface Science, 349 (1),* 238 - 292.

Okafor P.C., Ikpi, M.E., Uwah, I.E., Ebenso, E.E., Ekpe, U.J., & Umoren, S.A. (2008). Inhibitory action of *Phyllanthus amarus* extracts on the corrosion of mild steel in acidic media. *Corrosion Science, 50 (8),* 2310-2317.

Okafor, P.C., Ebenso, E.E., & Ekbe, U.J. (2010). *Azadirachta indica* extracts as corrosion inhibitor for mild steel in acidic medium. *International Journal of Electrochemical Science, 5 (7),* 978-993.

Okafor, P.C., Uwah, I.E., Ekerenam, O.O., & Ekpe, U.J. (2009). *Combretum bracteosum* extracts as eco-friendly corrosion inhibitor for mild steel in acidic medium. *Pigment and Resin Technology, 38 (4),* 236-241.

Okafor, P.C., Ekpe, U.J., Ebenso, E.E., Umoren, E.M., & Leizou, K.E. (2005). Inhibition of mild steel corrosion in acidic medium by *Allium sativum* extracts. *Bulletin of Electrochemistry, 21(8),* 347-352.

Okafor, P.C., & Ebenso, E.E. (2007). Inhibitive action of *Carica papaya* extracts on the corrosion of mild steel in acidic media and their adsorption characteristics. *Pigment and Resin Technology 36 (3),* 134-140.

Oluwole, O., & Idusuyi, N. (2012). Artificial Neural Network Modelling for al-zn-sn Sacrificial Anode Protection of Low Carbon Steel in Saline Media. *American Journal of Materials Science, 2(3),* 62-65.

Omotosho, O. A., Ajayi, O. O., Fayomi, O. S., & Ifepe, V. O. (2011). Assessing the Deterioration Behavior of Mild Steel in 2 M Sulphuric Acid using *Bambusa glauscescens. International Journal of Applied Engineering Research Dindigul, 2 (1),* 85-97.

Omotosho, O.A., & Ajayi, O.O. (2012). Investigating the acid failure of aluminium alloy in 2 M hydrochloric acid using *Vernonia amygdalina*. *ITB Journal of Engineering Science, 44, (1),* 77-92.

Omotosho, O.A., Ajayi, O.O., Ajanaku, K.O., & Ifepe, V.O. (2012a). Environment Induced Failure of Mild Steel in 2 M Sulphuric Acid using *Chromolaena odorata. Journal of Materials and Environmental Science, 3 (1),* 66-75.

Omotosho, O.A., Ajayi, O.O., Fayomi, O., & Ifepe, V.O. (2012b). Evaluating the Deterioration Behaviour of Mild Steel in 2 M Sulphuric Acid in the Presence of *Butyrospermum parkii*. *Asian Journal of Applied Science, 5 (2),* 74-84.

Omotosho, O.A., Ajayi, O.O., Fayomi, O., & Yussuff, O. (2012c). Degradation Evaluation of Zinc in 2 M Hydrochloric Acid in the Presence of *Bambusa bambos*. *Singapore Journal of Scientific Research, 2 (1),* 14-24.

Omotosho, O.A., Okeniyi, J.O., & Ajayi, O.O. (2010). Performance Evaluation of Potassium Dichromate and Potassium Chromate Inhibitors on Concrete Steel Rebar Corrosion. *Journal of Failure Analysis and Prevention, 10 (5),* 408 – 415.

Parker, K., Salas, M., & Nwosu, V.C. (2010). High Fructose Corn Syrup: Production, Uses and Public Health Concerns. *Biotechnology & Molecular Review, 5(5),* 71-78.

Poongothai, N., Ramachanderan, T., Natesan, M., & Murugavel, S.C. (2009). Corrosion Inhibition of Mild Steel by Essential Oils in an HCl Environment. *Materials Performance, 48 (9)*, 52-56.

Popoola, L.T., Grema, A.S., Latinwo, G.K., Gutti, B., & Balogun, A.S. (2013). Corrosion Problems During Oil and Gas Production and its Mitigation. *Internation Journal of Industrial Chemistry, 4(35),* 1-15.

Potgieler, J.H., Olubambi, P., & Thanjekwayo, N.P. (2008). The Effect of Selected Plant Extracts on the Corrosion Behaviour of Duplex Stainless Steels. *EUROCORR 2008-European Corrosion Congress: Managing Corrosion for Sustainability, Book of Abstracts*, 78-79.

Premkumar, P., Kannan, K., & Natesan, M. (2008). Thyme extract of *Thymus vulgar L.* as volatile corrosion inhibitor for mild steel in NaCl environment. *Asian Journal of Chemistry, 20 (1),* 445-451.

Priya, S.L., Chitra, A., Rajenderan, S., & Anuradha, K. (2005). Corrosion Behaviour of Aluminium in Rain Water Containing Garlic Extract. *Surface Engineering, 21(3),* 229-231.

Quraishi, M.A., Singh, A., Singh, V.K., Yadav, D.K., & Singh, A.K. (2010). Green Approach to Corrosion Inhibition of Mild Steel in Hydrochloric Acid and Sulphuric Acid Solutions by the Extract of *Murraya koenigii* Leaves. *Materials Chemistry and Physics, 122 (1),* 114-122.

Quraishi, M.A. (2004). Naturally Occurring Products as Corrosion Inhibitors. Paper No. 04411 *NACE International, Corrosion*-2004, Houston, TX.

Quraishi, M.A., Rafiquee, M.Z.A., Khan, S., & Saxena, N. (2007). Corrosion inhibition of aluminium in acid solutions by some imidazoline derivatives. *Journal of Applied Electrochemistry, 37,* 1153-62.

Raja, P. B., & Sethuraman, M.G. (2009). *Solanum tuberosum* as an inhibitor of mild steel corrosion in acid media. *Iranian Journal of Chemistry and Chemical Engineering, 28 (1),* 77-84.

Raja, P.B., & Sethuraman, M.G. (2008). Natural products as corrosion inhibitor for metals in corrosive media-A review. *Material Letters, 62,* 113-116.

Raja, P.B., & Sethuraman, M.G. (2009). Inhibition of corrosion of mild steel in sulphuric acid medium by *Calotropis procera*/IT. *Pigment and Resin Technology, 38 (1),* 33-37.

Raja, P.B., Rahim, A.A., Osman, H., & Awang, K. (2010). Inhibitory effect of *Kopsia singapurensis* extract on the corrosion behavior of mild steel in acid media. *Wuli Huaxue Xuebao/Acta Physico- Chimica Sinica, 26 (8),* 2171-2176.

Rajalakshmi, R., Subhashini, S., Leelavathi, S., & Mary, R.F. (2008). Efficacy of sprouted seed extracts of *Phaseolus aureus* on the corrosion inhibition of mild steel in 1M HCl. *Oriental Journal of Chemistry, 24 (3),* 1085-1090.

Rajalakshmi, R., Subhashini, S., Nanthini, M., & Srimathi, M. (2009). Inhibiting effect of seed extract of Abrus precatorius on corrosion of aluminium in sodium hydroxide. *Oriental Journal of Chemistry 25 (2)*, 313-318.

Rajeev, P., Surendranathan, A.O., & Murthy, C.S.N. (2012). Corrosion Mitigation of the Oil Well Steels using Organic Inhibitors-A Review. *Journal of Material and Environmental Science, 3 (5),* 856-869.

Rajenderan, S., Jeyasundari, J., Usha, P., Selvi, J.A., Narayanasamy, B., Regis, A.P.P., & Renga, P. (2009). Corrosion behaviour of aluminium in the presence of an aqueous extract of hibiscus rosasinensis. *Portugaliae Electrochimica Acta, 27 (2),* 153-164.

Rajenderan, S., Shanmugapriya, S., Rajalakshmi, T., & Amal Raj, A.J. (2005). Corrosion inhibition by an aqueous extract of rhizome powder. *Corrosion, 61 (7),* 685-692.

Ramana, K.V.S., Anita, T., & Mandal, S. (2009). Effect of Different Environmental Parameters on Pitting Behavior of AISI type 316L Stainless steel: Experimental Studies and Neural Network Modelling. *Materials and Design, 30 (9),* 3770-3775.

Ramesh, S. P., Vinod Kumar, K. P., & Sethuraman, M. G. (2001). Extract of andrographis paniculata as corrosion inhibitor of mild steel in acid medium. *Bulletin of Electrochemistry, 17 (3),* 141–144.

Rehan, H.H. (2003). Corrosion control by water-soluble extracts from leaves of economic plants. *Materialwissenschaft und Werkstofftechnik, 34 (2),* 232-237.

Riggs, O.L. & Hurd, R.M. (1967). Temperature coefficient of corrosion inhibition. *Corrosion, NACE, 33,* 252-258.

Rmila, A., Prema, A.A., & Sahayaraj, P.A. (2010). Influence of Murraya koenigii (curry leaves) extract on the corrosion inhibition of carbon steel in HCl solution. *Rasayan Journal of Chemistry, 3 (1),* 74-81.

Rocha, J.C., Cunha, J.A., Gomes, P., & D’Elia, E. (2010). Corrosion inhibition of carbon steel in hydrochloric acid solution by fruit peel aqueous extracts. *Corrosion Science ,52 (7),* 2341- 2348.

Robson, J. (1993). Steel pickling: A profile. Retrieved from http://www.epa.gov/ttn/ecas/regdata/IPs/Steel%20IP.pdf

Rocha, J.C., Gomes, J.A., Ella, E.D., Cruz, A.P., Cabral, L.M., Torres, A.G., & Monteir, M.V. (2012). Grape pomace extracts as green inhibitors for carbon steel in hydrochloric acid solutions. *International Journal of Elecrtochemical Science, 7 (12),* 11941-11956.

Sangeetha, M., Rajendran, S., Muthumegala, T.S., & Krishnaveni, A. (2011). Green Corrosion inhibitors- An overview. *Zastita Materijala, 52*, 3-19.

Saratha, R., & Vasudha, V.G. (2009). Inhibition of mild steel corrosion 1N H_2SO_4 medium by acid extract of *Nyctanthes arbortristis* leaves. *E-Journal of Chemistry, 6(4),* 1003-1008.

Saratha, R., & Vasudha, V.G. (2010). *Emblica officinalis* (Indian Gooseberry) leaves extract as corrosion inhibitor for mild steel in 1 N HCL medium. *E Journal of Chemistry, 7 (3),* 677-684.

Saratha, R., Priya, S.V., & Thilagavathy, P. (2009). Investigation of *Citrus aurantiifolia* leaves extract as corrosion inhibitor for mild steel in 1 M HCL. *E-Journal of Chemistry, 6 (3),* 785-795.

Sartorelli, P., Carvaiho, C.S., Reimao, J.Q., Ferreira, M.J.P., & Tempone, A.G. (2009). Antiparasitic activity of bioachanin A, an isolated isoflavone form fruits of *cassia fistula* (Leguminosae). *Parasitol Res.,* 104, 311-314.

Satapathy, A.K., Gunasekaran, G., Sahoo, S.C., Amit, K. & Rodrigues, P.V. (2009). Corrosion inhibition by *Justicia gendarussa* plant extract in hydrochloric acid solution. *Corrosion Science, 51 (12),* 2848-2856.

Sathiyanathan, R.A.L., Maruthamutu, S., Selvanayagam, M., Mohanan, S., & Palaniswamy, N. (2005). Corrosion inhibition of mild steel by ethanolic extracts of *Ricinus communis* leaves. *Indian Journal of Chemical Technology, 12,* 356-360.

Sethuram, M.G., & Raja, P.B. (2005). Corrosion inhibition of mild steel by *Datura metel* in acidic medium. *Pigment and Resin Technology, 34(6),* 347-352.

Shyamala, M., & Arulanantham, A. (2009). *Eclipta alba* as corrosion pickling inhibitor on mild steel in hydrochloric acid. *Journal of Materials Science and Technology, 25 (5),* 633-636.

Singh, A.K., & Quraishi, M.A. (2010). Piroxicam: A novel corrosion inhibitor for mild steel corrosion in HCl acid solution. *Journal of Materials and Environmental Science, 1(2),* 101-110.

Sivaraju, M., & Kannan, K. (2010). Eco-friendly inhibitor (*Tributes terrestris L*) for mild steel corrosion in 1N Phosphoric acid. *Asian Journal of Chemistry, 22 (1),* 233-244.

Sivaraju, P.K., & Arulanantham, A. (2010). Inhibitive properties of plant extract (*Acalypha indica L.*) on mild steel corrosion in 1N phosphoric acid. *International Journal of Chemical Technology Research, 2 (2).*

Soror, T.K. (2004). New naturally occurring product extract as corrosion inhibitor for *316* stainless steel in 5% HCl. *Journal of Materials Science Technology, 20 (4),* 463-466.

Speller, F.N., Chappel, E.L., & Russell, R.P. (1927). Practical applications of inhibitors for pickling operations. *Trans Am Inst Chem Engrs, 19,* 165.

Srinivasa, P, Mathew, M.T, Stack, M.M., & Roche, L.A. (2008). Some Thoughts on Neural Network Modelling of Micro-abrasion Corrosion process. *Tribology International, 41,* 672 – 680.

Stupnisek-Lisac, E., Meticos-Hukovic, M., Lencic, D., Vorkapic-Furac, J., & Berkovic, K. (1992). Structural investigation of N-arylpyrroles as iron corrosion inhibitors in hydrochloric acid. *Corrosion, 48,* 924-930.

Subhashini, S., Rajalakshmi, R., Prithiba, A., & Mathina, A. (2010). Corrosion mitigating effect of *Cyamopsis tetragonaloba* seed extract on mild steel in acid medium. *E-Journal of Chemistry 7 (4),* 1133-1137.

Tan, N. D., & Dao, T. T. (2011). Eco- friendly synthesis and antimicrobial activity of chalcones. *Pharmacol. Pharm., 2,* 282-297.

Tantawi, S.H., & Selim, I.Z. (1996). Improvement of concrete properties and reinforcing steel inhibition using a natural product admixture. *Journal of Materials Science and Technology, 12 (2),* 95-99.

Umoren, S.A., Obet, I.B., Akpabio, L.E., & Etuk, S.E. (2008). Adsorption and corrosive inhibitive properties of *Vigna unguiculata* in alkaline and acidic media. *Pigment and Resin Technology, 37 (2),* 98-105.

Umoren, S.A., Ogbobe, O., Okafor, P.C., & Ebenso, E. E. (2007). Polyethylene Glycol and Polyvinyl Alcohol as Corrosion Inhibitors for Aluminium in Acidic Medium. *Journal of Applied Polymer Science, 105,* 3363–3370.

Umoren, S.A., & Ebenso, E.E. (2007). The synergistic effect of polyacrylamide and iodide ions on the corrosion inhibition of mild steel in H_2SO4. *Materials Chemistry and Physics, 106,* 387–393.

Ungureanu, C.A., Das, S., & Jawahir, I.S. (2007). Life-cycle cost analysis. Retrieved from http://www.phinix.net/services/Carbon_Management/Life-cycle_Cost_Analysis.pdf

Uwah, I.E., Okafor, P.C., & Ebiekpe, V.E. (2010). Inhibitive action of ethanol extracts from Nauclea latifolia on the corrosion of mild steel in H_2SO_4 solutions and their adsorption characteristics. *Arabian Journal of Chemistry, 10.*

Waldemar, D.P. (2010). *Numerical methods, algorithms, and tools in C#.* Taylor and Francis Group, LLC, Boca Raton.

Wang C., Nehrir, M.H. & Gao, H. (2006). Control of PEM fuel cell distributed generation systems. *IEEE Transactions on Energy Conversion, 21, (2),* 586 – 595.

Webber, T.W., & Chakkravorti, R.K. (1974). Pore and solid diffusion models for fixed-bed absorbers. *American Institute of Chemical Engineers, 20,* 228.

World Steel Association, (2013). Steels contribution to a low carbon future. Retrieved Retrieved from http://www.worldsteel.org/publications/position-papers/Steel-s-contribution-to-a-low-carbon-future.html

Yang, L., Zhang, H., Tan, T., & Rahman, A. U. (2009). Thermodynamic and NMR investigations on the adsorption mechanism of puerarin with oligo-β-cyclodextrin coupled polystyrene-based matrix. *Journal of Chemical Technology and Biotechnology, 84,* 611-617.

Yescas, M.A., Bhadeshia, H. K. D.H., & Mackay, D.J. (2001). Estimation of the amount of retained austenite in austempered ductile irons using neural networks, *Materials science and engineering A, 311(1-2),* 162-173.

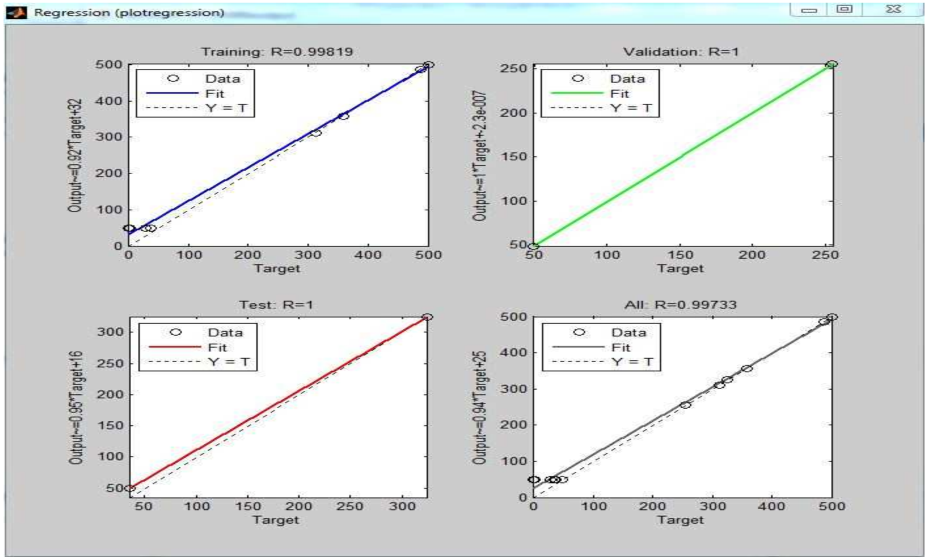
Zeleznik, F.J. (1991). Thermodynamic properties of aqueous sulfuric acid system to 350K. *American Institute of Physics and the Chemical Society, 20 (6).*

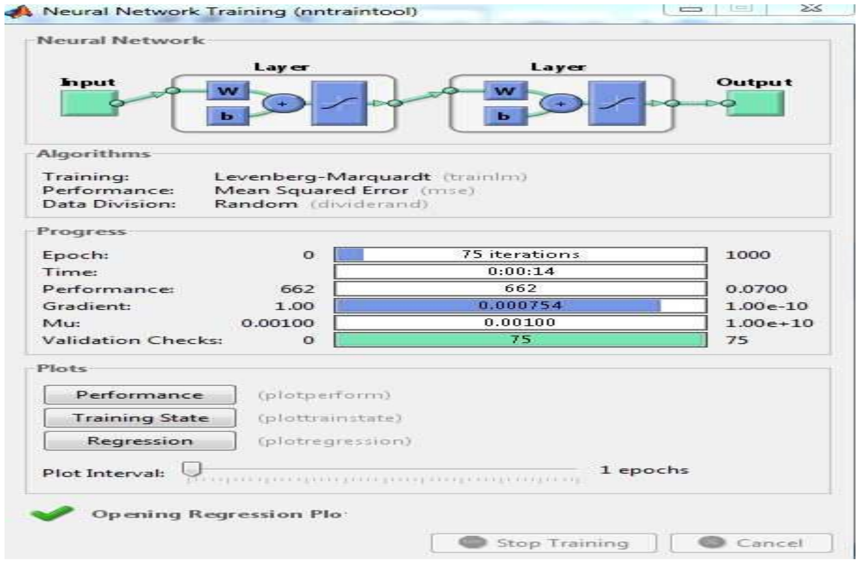
Zuchhi, F., & Omar, I. H. (1985). Plant extracts as corrosion inhibitors of mild steel in HCl solutions. *Surface Technology, 24 (4),* 391-399.

APPENDICES

APPENDIX A: ANN OUTPUT SCHEDULE FOR ENTIRE INHIBITOR SYSTEMS

ANN output Schedule for MS_HCl_PC





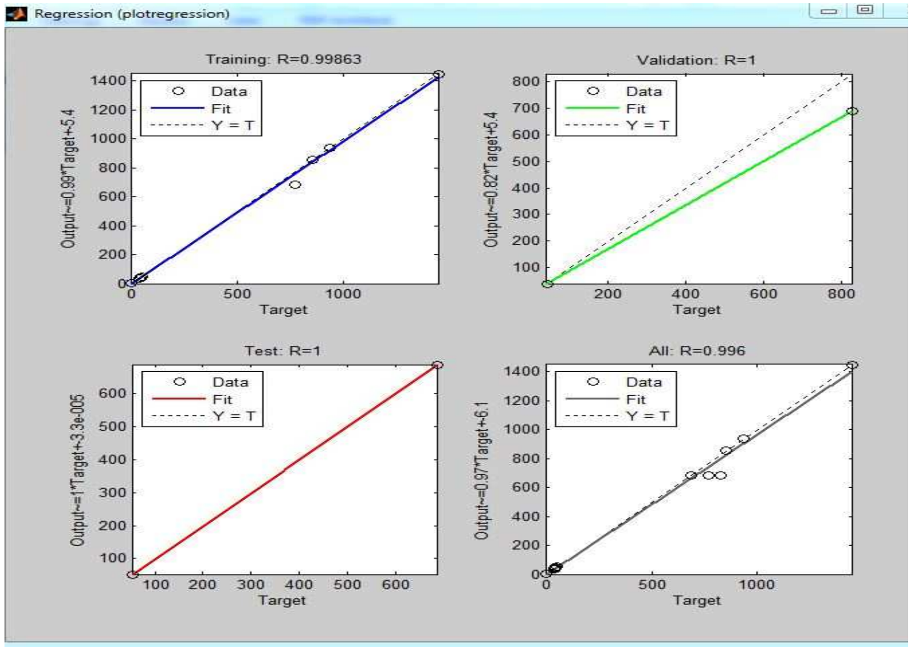
Algorithms
Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

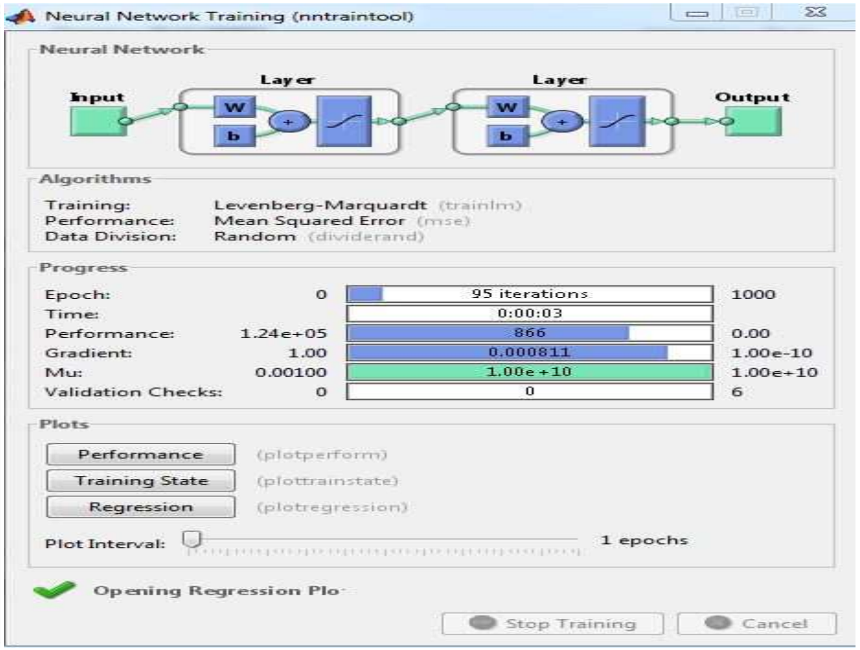
Progress
Epoch: 0 | 75 iterations | 1000
Time: 0:00:14
Performance: 662 | 662 | 0.0700
Gradient: 1.00 | 0.000754 | 1.00e-10
Mu: 0.00100 | 0.00100 | 1.00e+10
Validation Checks: 0 | 75 | 75

Plots
Performance (plotperform)
Training State (plottrainstate)
Regression (plotregression)
Plot Interval: 1 epochs

Opening Regression Plo

ANN Schedule for MS_H_2SO_4_PC





Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Progress

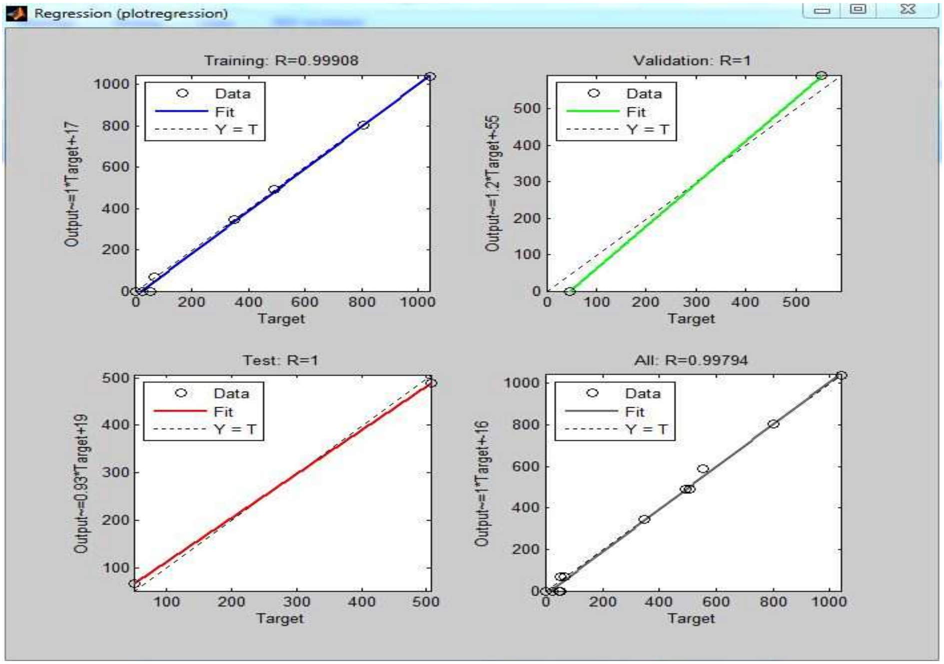
Epoch:	0	95 iterations	1000
Time:		0:00:03	
Performance:	1.24e+05	866	0.00
Gradient:	1.00	0.000811	1.00e-10
Mu:	0.00100	1.00e+10	1.00e+10
Validation Checks:	0	0	6

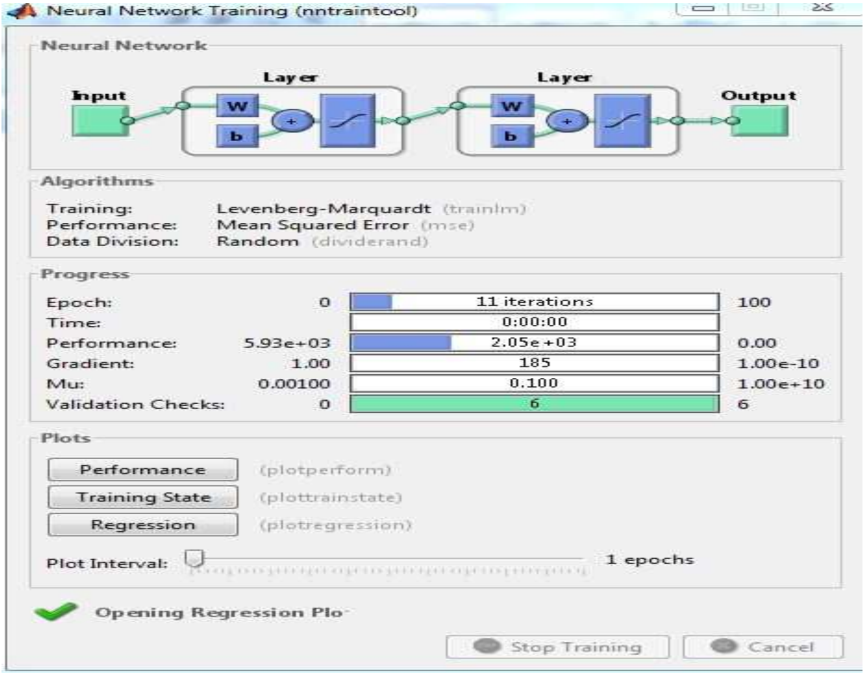
Plots

Plot Interval: 1 epochs

Opening Regression Plo·

ANN Schedule for Al_HCl_PC





Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Progress

Epoch:	0	11 iterations	100
Time:		0:00:00	
Performance:	5.93e+03	2.05e+03	0.00
Gradient:	1.00	185	1.00e-10
Mu:	0.00100	0.100	1.00e+10
Validation Checks:	0	6	6

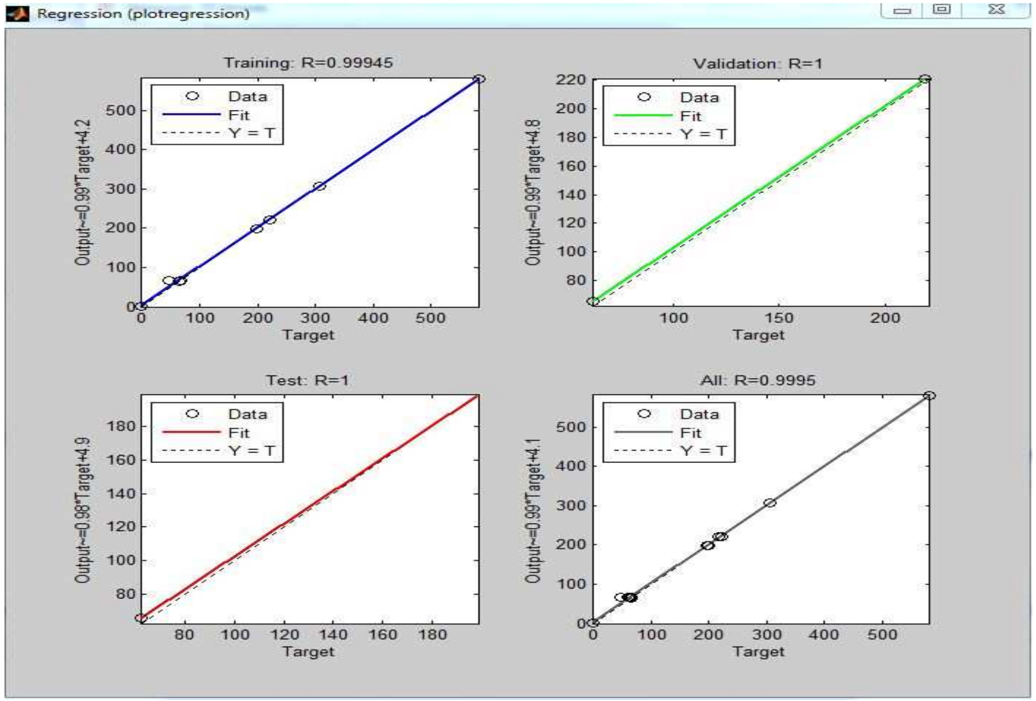
Plots

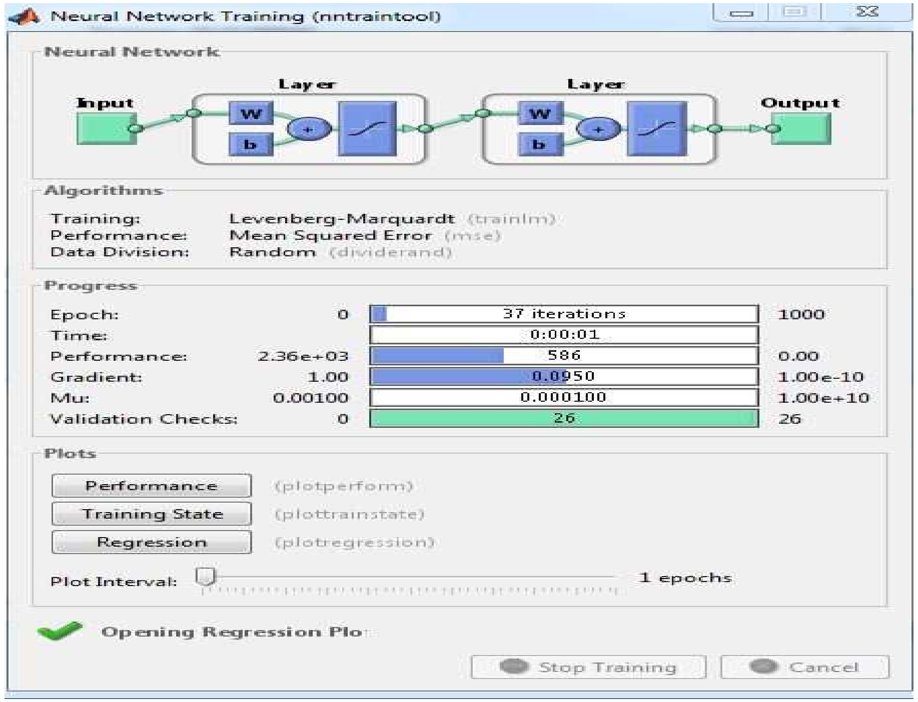
Performance (plotperform)
Training State (plottrainstate)
Regression (plotregression)

Plot Interval: 1 epochs

✓ Opening Regression Plo

ANN Schedule for Al_H_2SO_4_PC





Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Progress

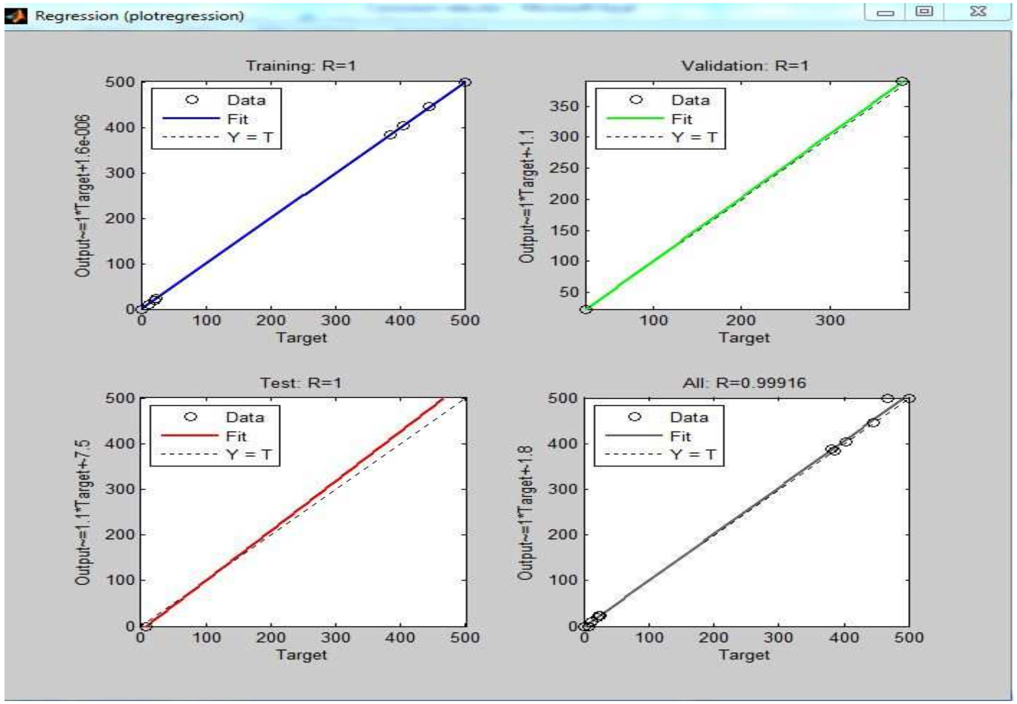
```
Epoch:                 0       37 iterations    1000
Time:                          0:00:01
Performance:     2.36e+03      586              0.00
Gradient:            1.00      0.0950           1.00e-10
Mu:               0.00100      0.000100         1.00e+10
Validation Checks:      0      26               26
```

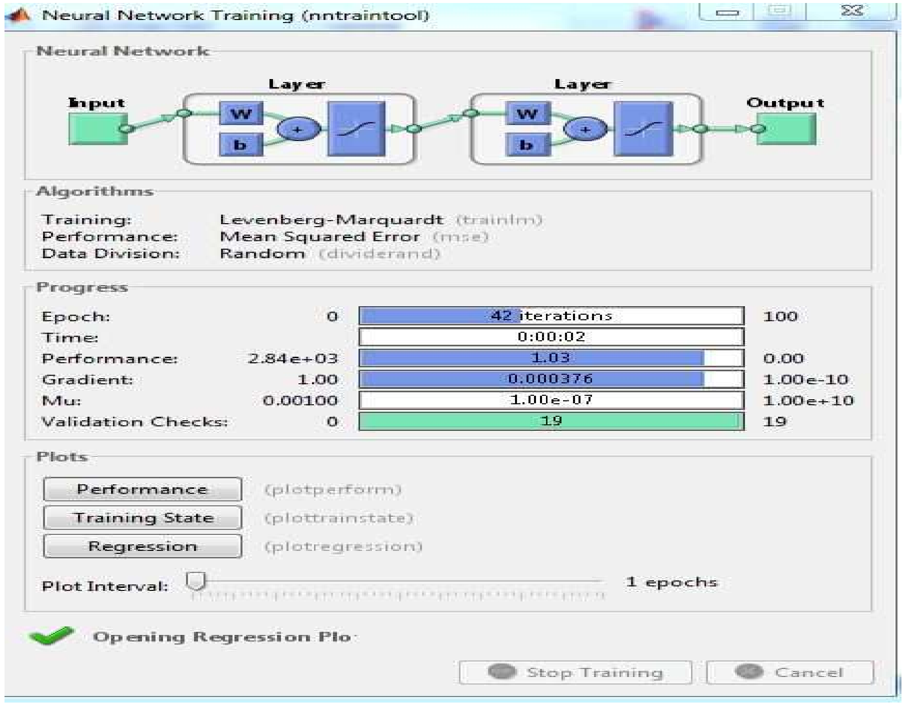
Plots

Plot Interval: 1 epochs

Opening Regression Plo

ANN Output Schedule for MS_HCl_AN





Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Progress

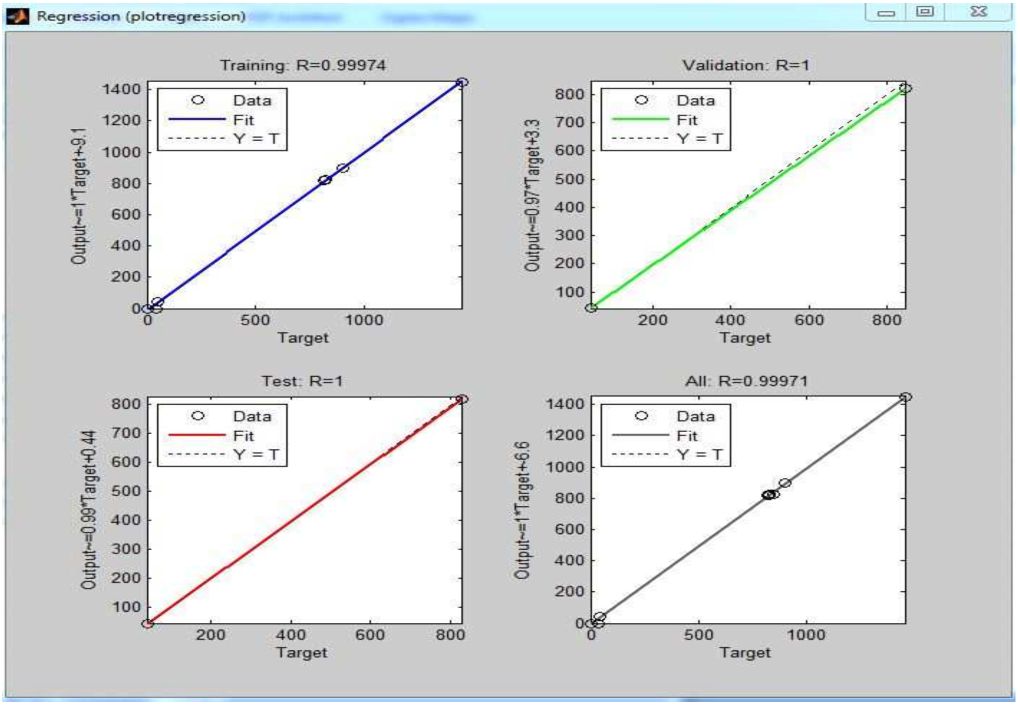
Epoch: 0 42 iterations 100
Time: 0:00:02
Performance: 2.84e+03 1.03 0.00
Gradient: 1.00 0.000376 1.00e-10
Mu: 0.00100 1.00e-07 1.00e+10
Validation Checks: 0 19 19

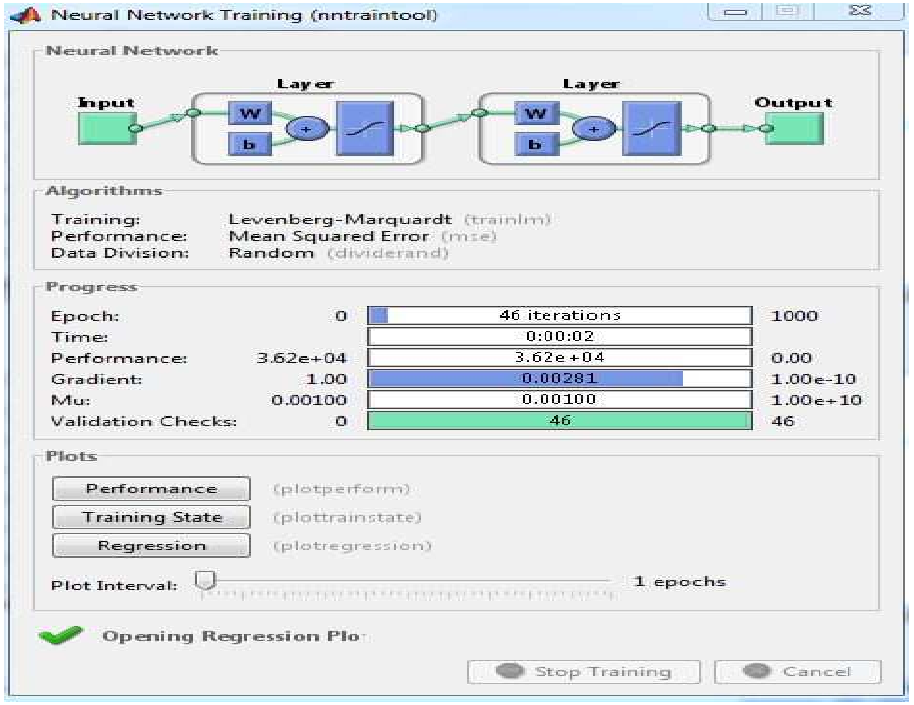
Plots

Performance (plotperform)
Training State (plottrainstate)
Regression (plotregression)
Plot Interval: 1 epochs

Opening Regression Plo

ANN Output Schedule for $MS\_H_2SO_4\_AN$





Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Progress

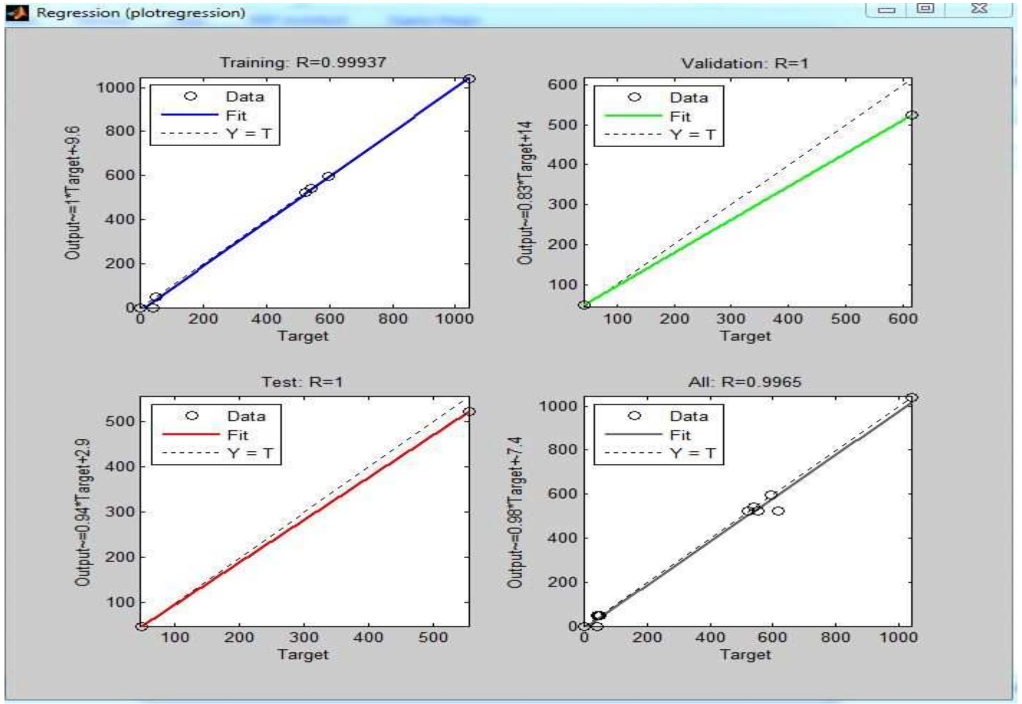
Epoch:	0	46 iterations	1000
Time:		0:00:02	
Performance:	3.62e+04	3.62e+04	0.00
Gradient:	1.00	0.00281	1.00e-10
Mu:	0.00100	0.00100	1.00e+10
Validation Checks:	0	46	46

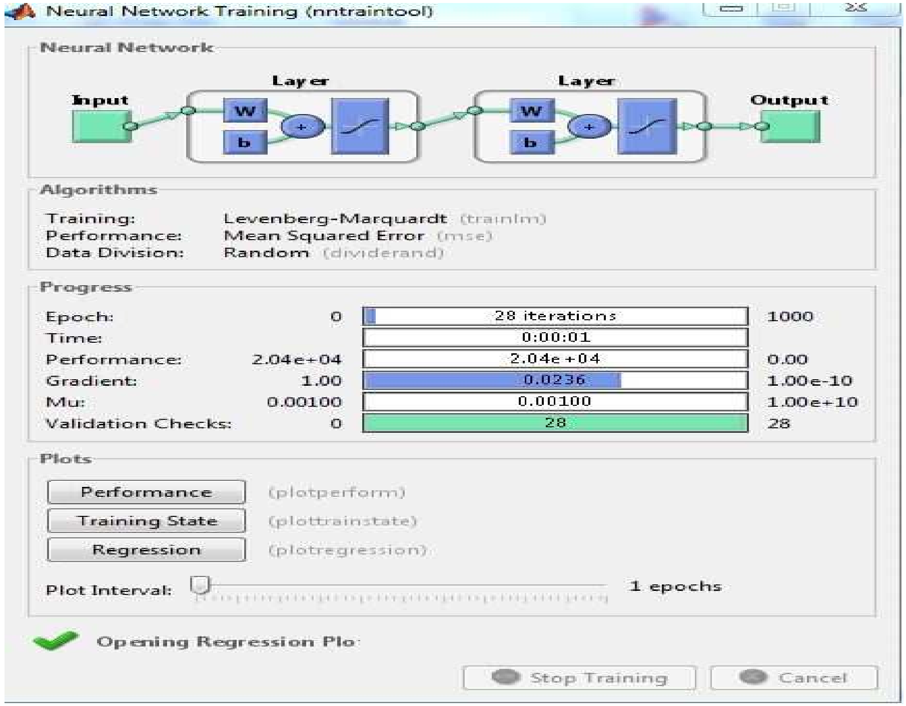
Plots

Plot Interval: 1 epochs

Opening Regression Plo

ANN Output Schedule for Al_HCl_AN





Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

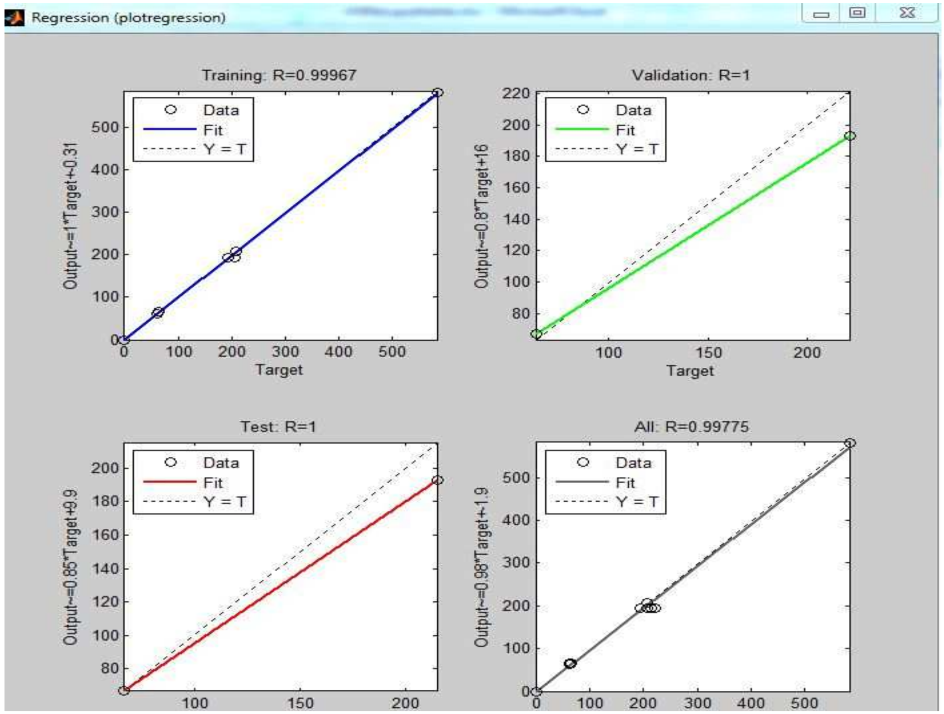
Progress

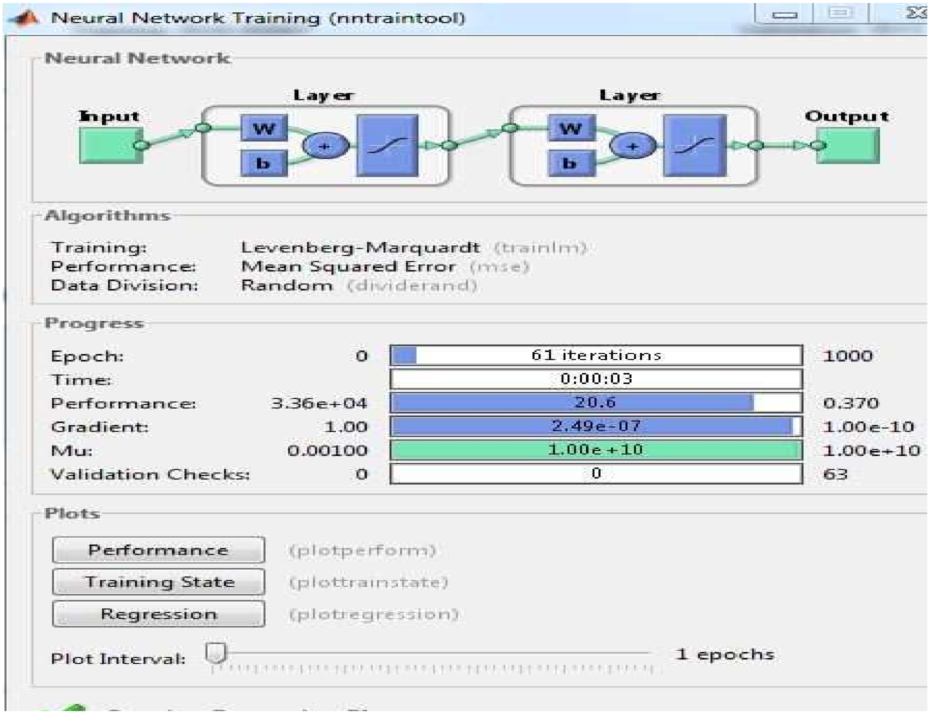
Epoch: 0 | 28 iterations | 1000
Time: 0:00:01
Performance: 2.04e+04 | 2.04e+04 | 0.00
Gradient: 1.00 | 0.0236 | 1.00e-10
Mu: 0.00100 | 0.00100 | 1.00e+10
Validation Checks: 0 | 28 | 28

Plot Interval: 1 epochs

Opening Regression Plo

ANN Output Schedule for Al_H_2SO_4_AN





Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

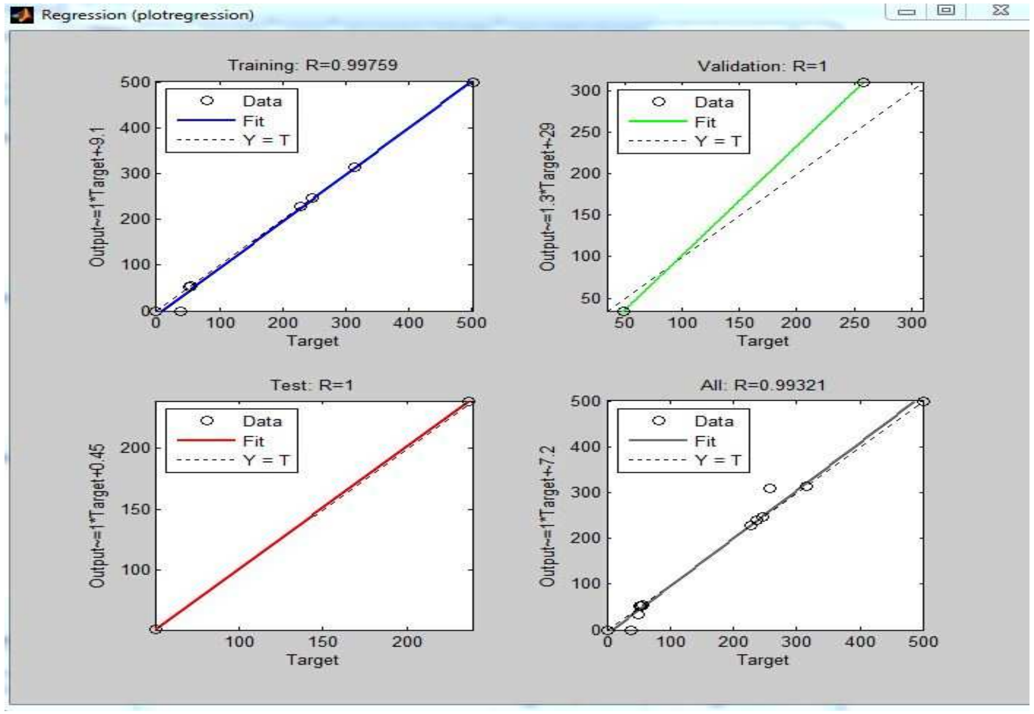
Progress

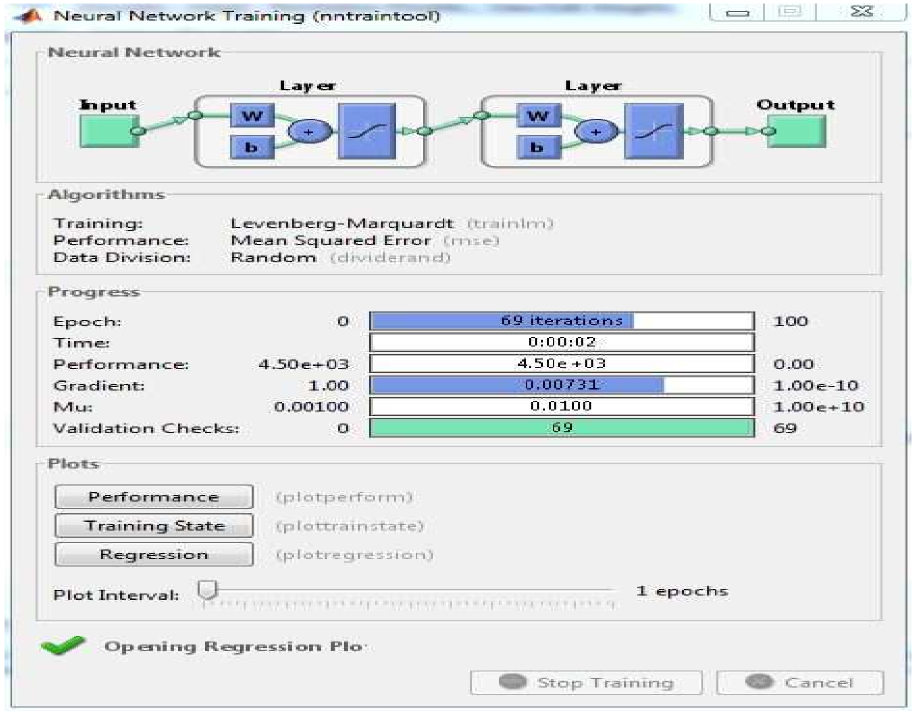
Epoch:	0	61 iterations	1000
Time:		0:00:03	
Performance:	3.36e+04	20.6	0.370
Gradient:	1.00	2.49e-07	1.00e-10
Mu:	0.00100	1.00e+10	1.00e+10
Validation Checks:	0	0	63

Plots

Plot Interval: 1 epochs

ANN Output Schedule for MS_HCl_CF




Neural Network Training (nntraintool)

Neural Network

Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Progress

Epoch:	0	69 iterations	100
Time:		0:00:02	
Performance:	4.50e+03	4.50e+03	0.00
Gradient:	1.00	0.00731	1.00e-10
Mu:	0.00100	0.0100	1.00e+10
Validation Checks:	0	69	69

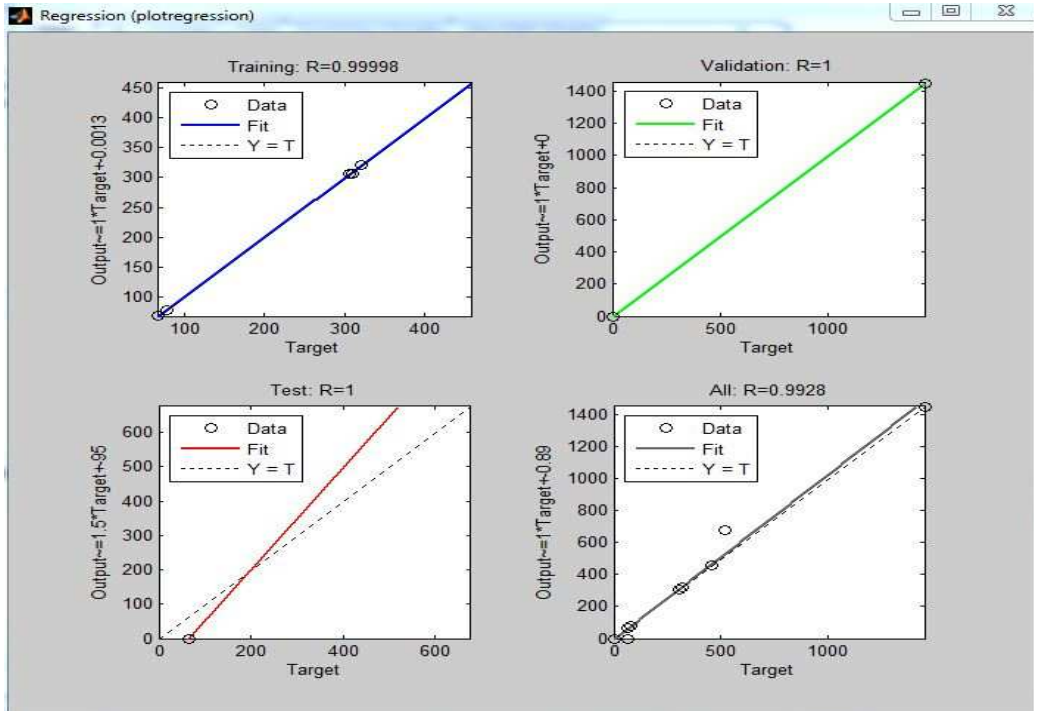
Plots

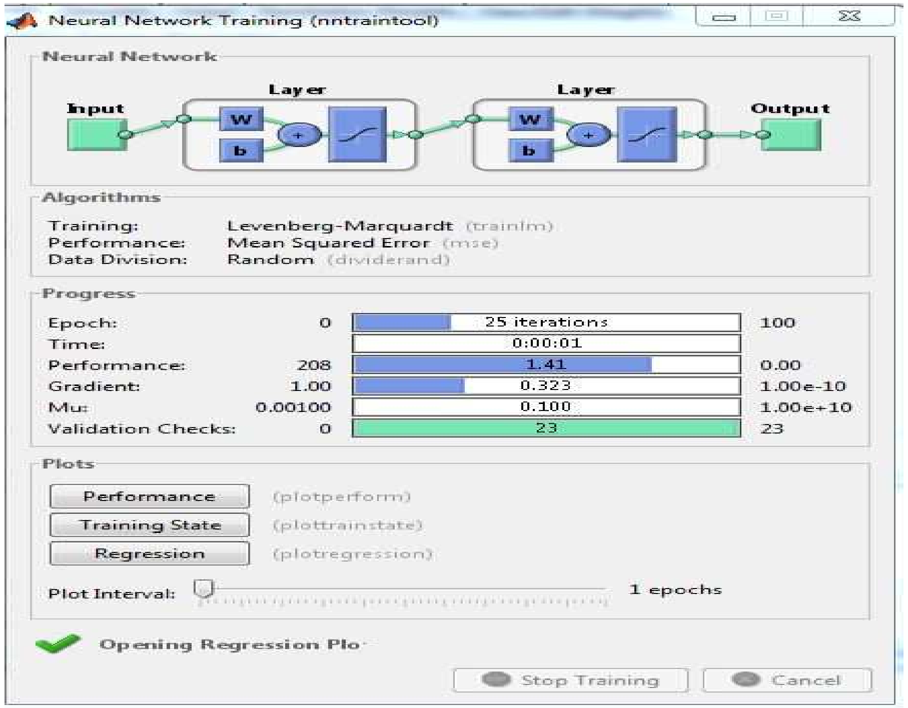
Performance (plotperform)
Training State (plottrainstate)
Regression (plotregression)

Plot Interval: 1 epochs

✓ Opening Regression Plo·

ANN Output Schedule for MS_H_2SO_4_CF





Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Progress

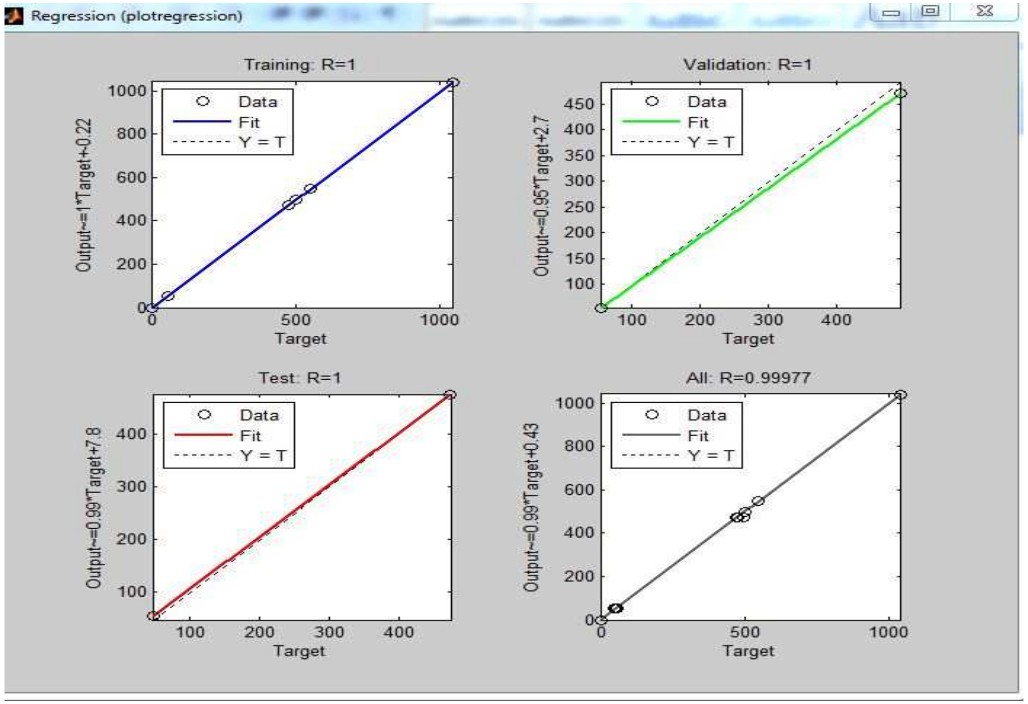
Epoch: 0 25 iterations 100
Time: 0:00:01
Performance: 208 1.41 0.00
Gradient: 1.00 0.323 1.00e-10
Mu: 0.00100 0.100 1.00e+10
Validation Checks: 0 23 23

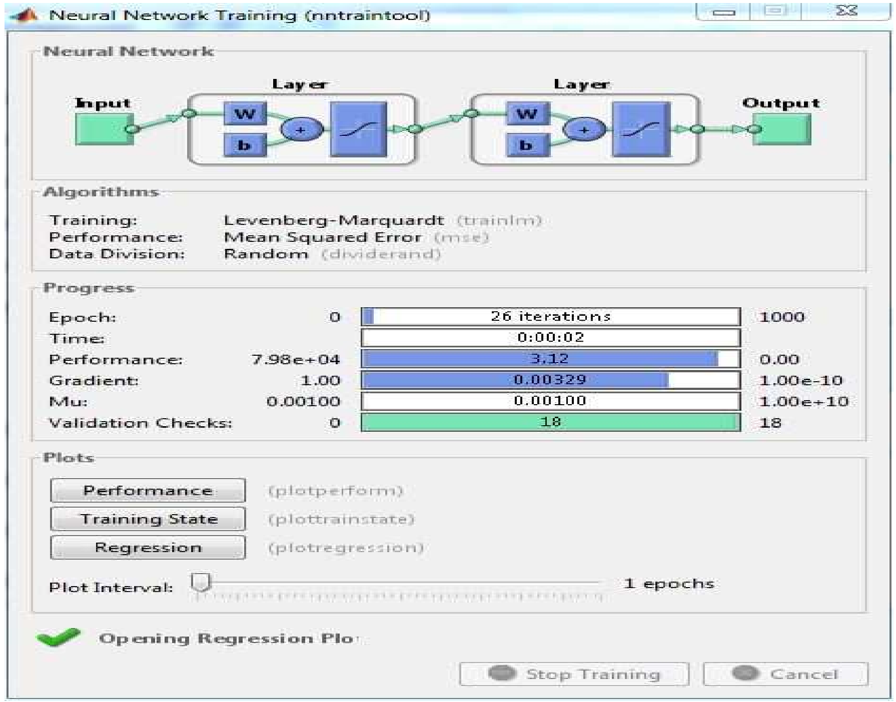
Performance (plotperform)
Training State (plottrainstate)
Regression (plotregression)

Plot Interval: 1 epochs

Opening Regression Plo

ANN Output Schedule for Al_HCl_CF





Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Progress

Epoch:	0	26 iterations	1000
Time:		0:00:02	
Performance:	7.98e+04	3.12	0.00
Gradient:	1.00	0.00329	1.00e-10
Mu:	0.00100	0.00100	1.00e+10
Validation Checks:	0	18	18

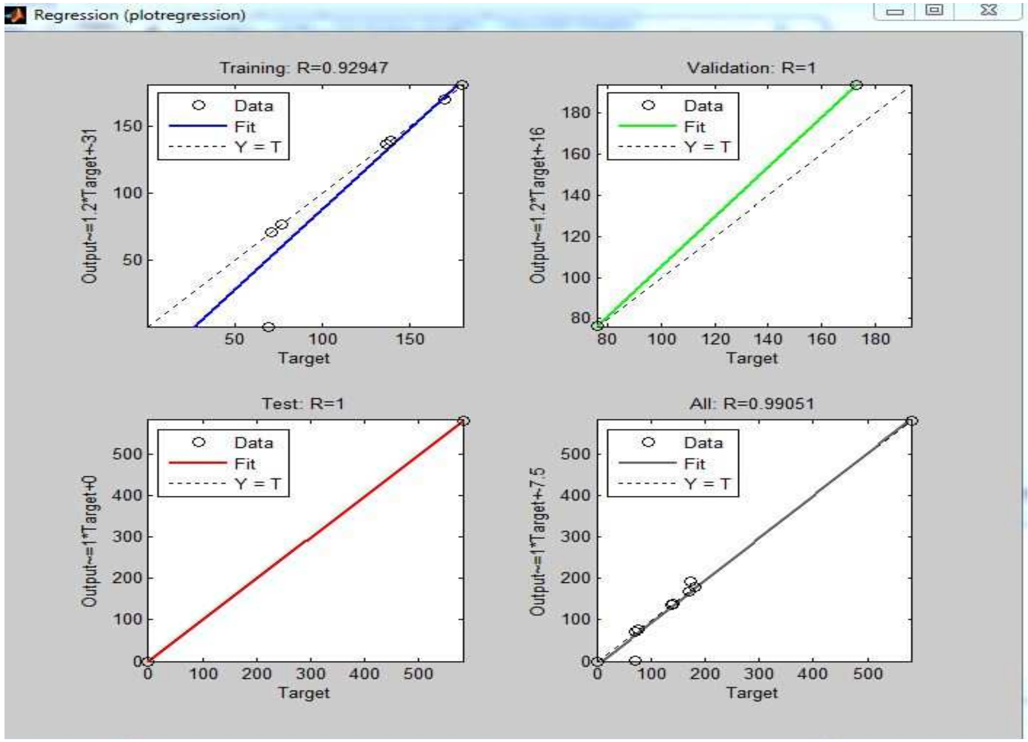
Plots

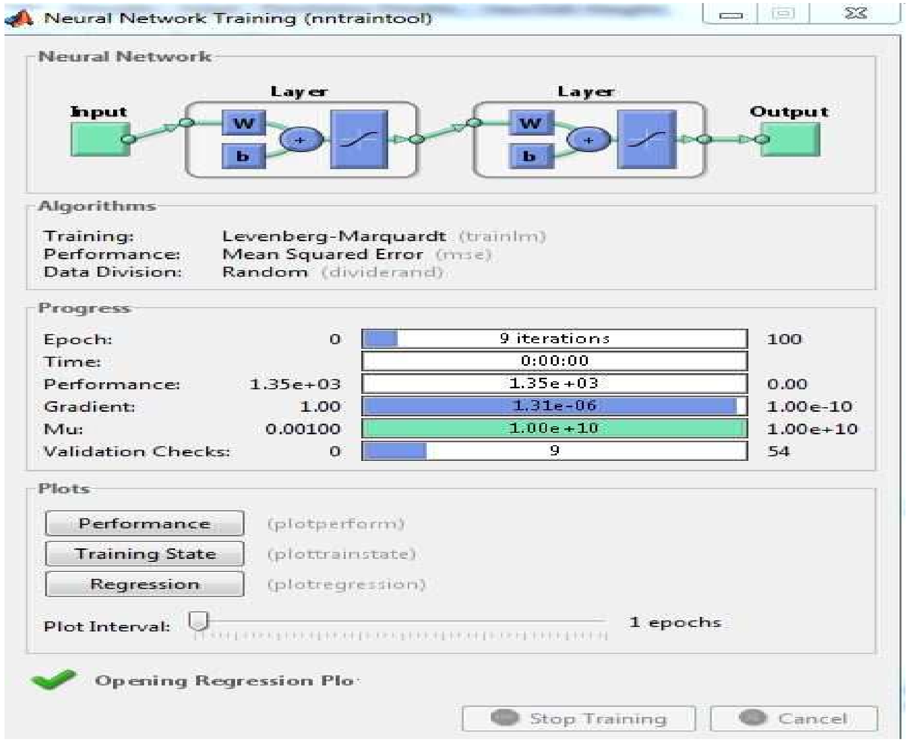
(plotperform)
(plottrainstate)
(plotregression)

Plot Interval: 1 epochs

✓ Opening Regression Plo

ANN Output Schedule for MS_H_2SO_4_CF





Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Progress

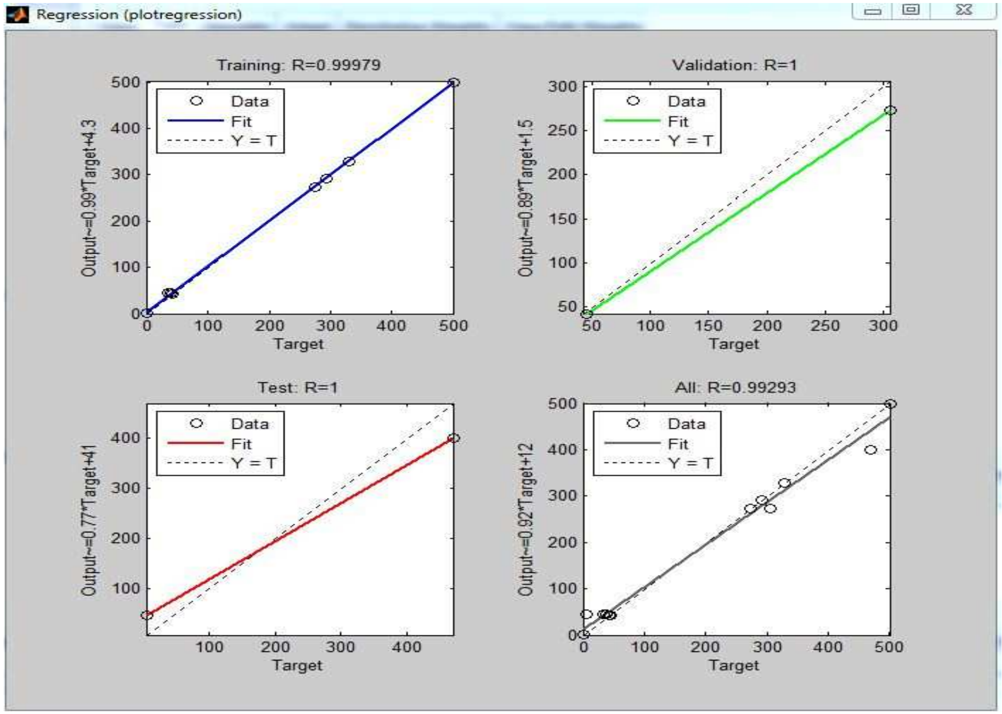
Epoch:	0	9 iterations	100
Time:		0:00:00	
Performance:	1.35e+03	1.35e+03	0.00
Gradient:	1.00	1.31e-06	1.00e-10
Mu:	0.00100	1.00e+10	1.00e+10
Validation Checks:	0	9	54

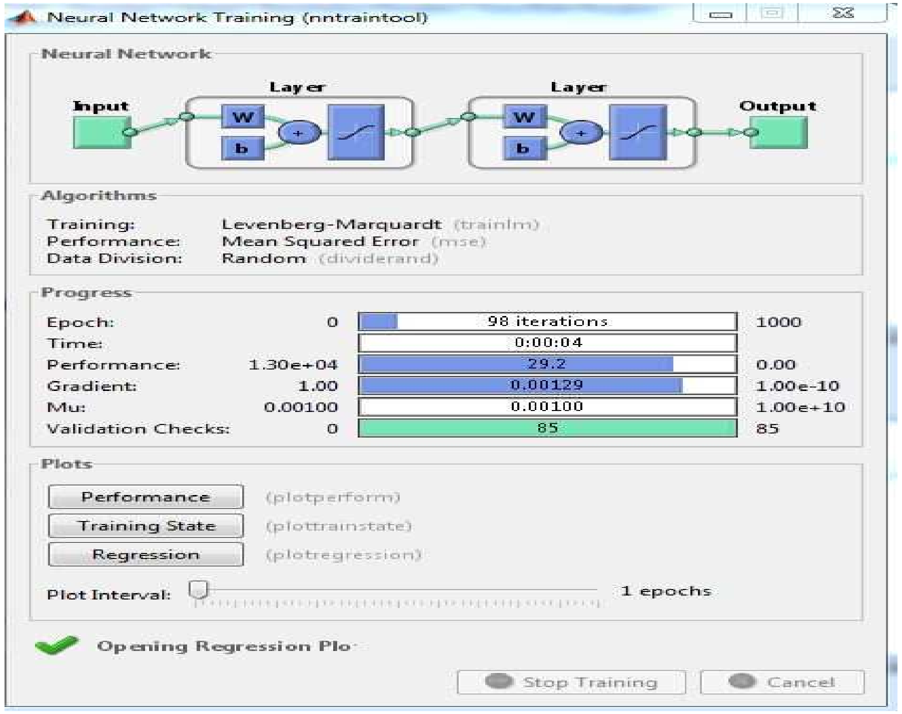
Plots

Plot Interval: 1 epochs

✓ Opening Regression Plo

ANN Output Schedule for MS_HCl_TC





Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Progress

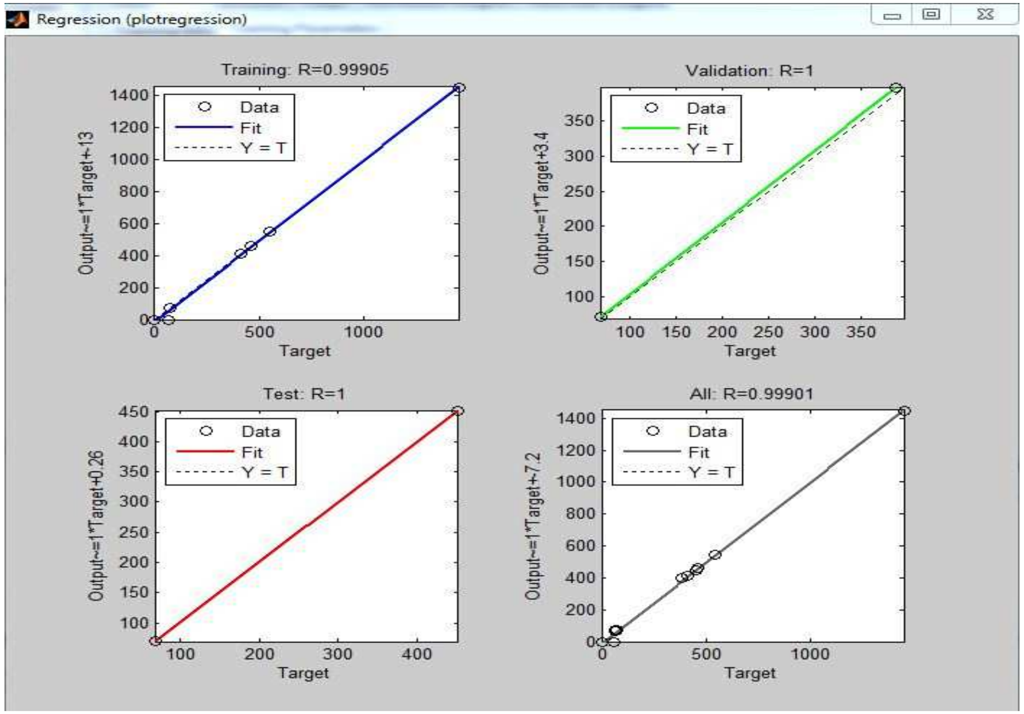
Epoch:	0	98 iterations	1000
Time:		0:00:04	
Performance:	1.30e+04	29.2	0.00
Gradient:	1.00	0.00129	1.00e-10
Mu:	0.00100	0.00100	1.00e+10
Validation Checks:	0	85	85

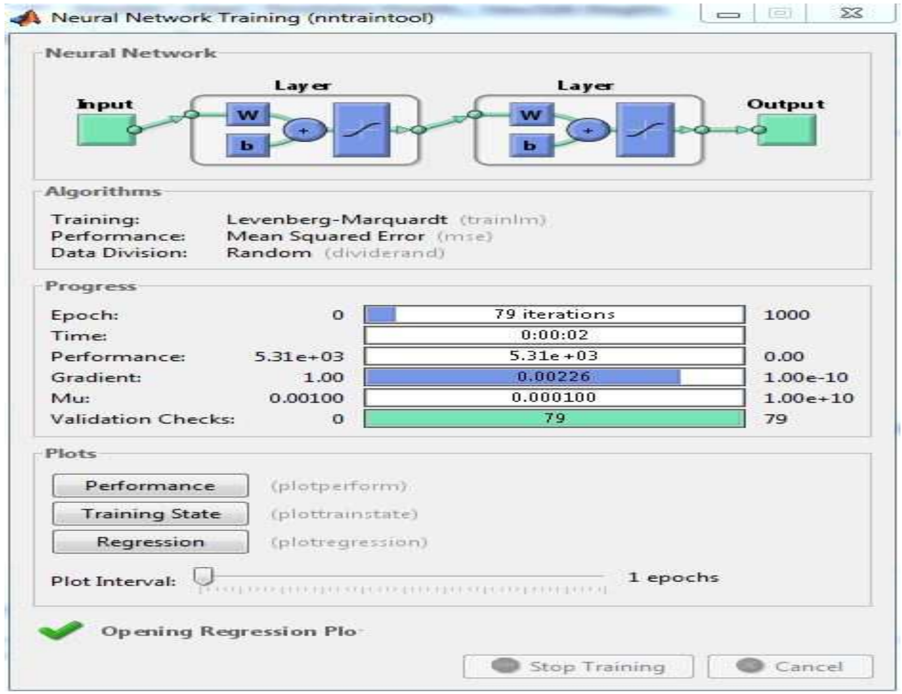
Plots

Plot Interval: 1 epochs

Opening Regression Plo

ANN Output Schedule for MS_H_2SO_4_TC





Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Progress

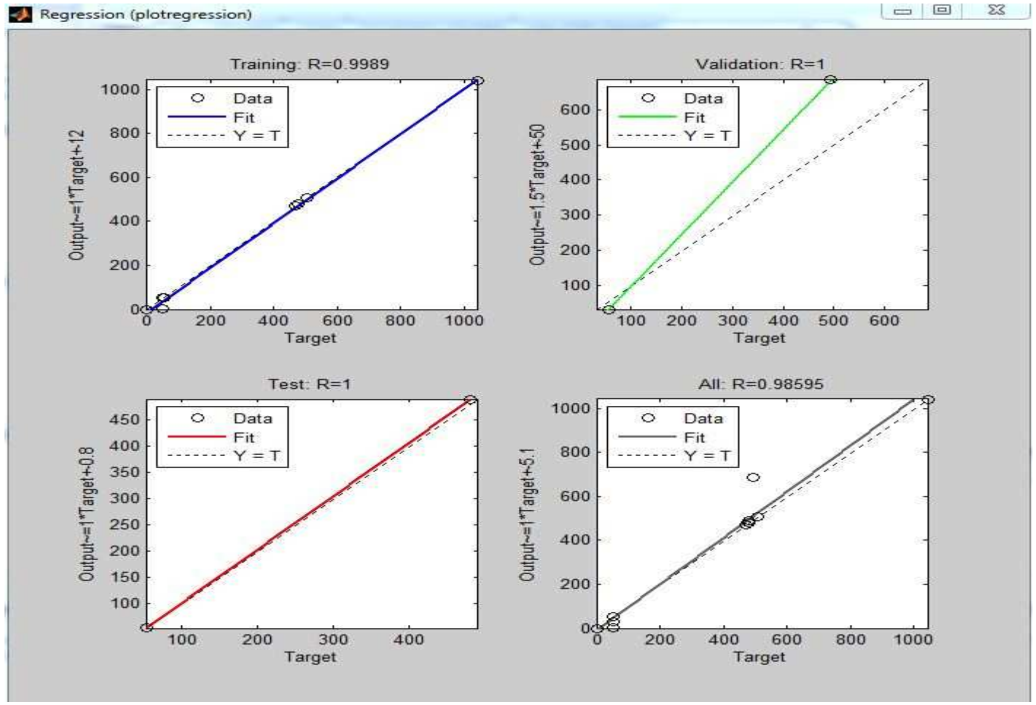
Epoch:	0	79 iterations	1000
Time:		0:00:02	
Performance:	5.31e+03	5.31e+03	0.00
Gradient:	1.00	0.00226	1.00e-10
Mu:	0.00100	0.000100	1.00e+10
Validation Checks:	0	79	79

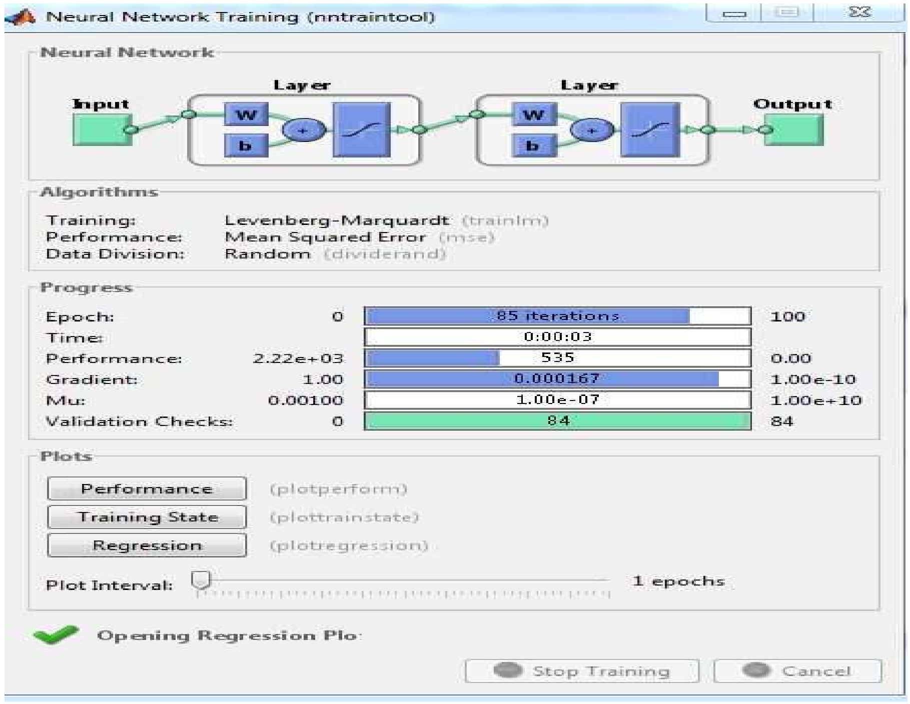
Plots

Plot Interval: 1 epochs

✓ Opening Regression Plo

ANN Output Schedule for Al_HCl_TC





Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

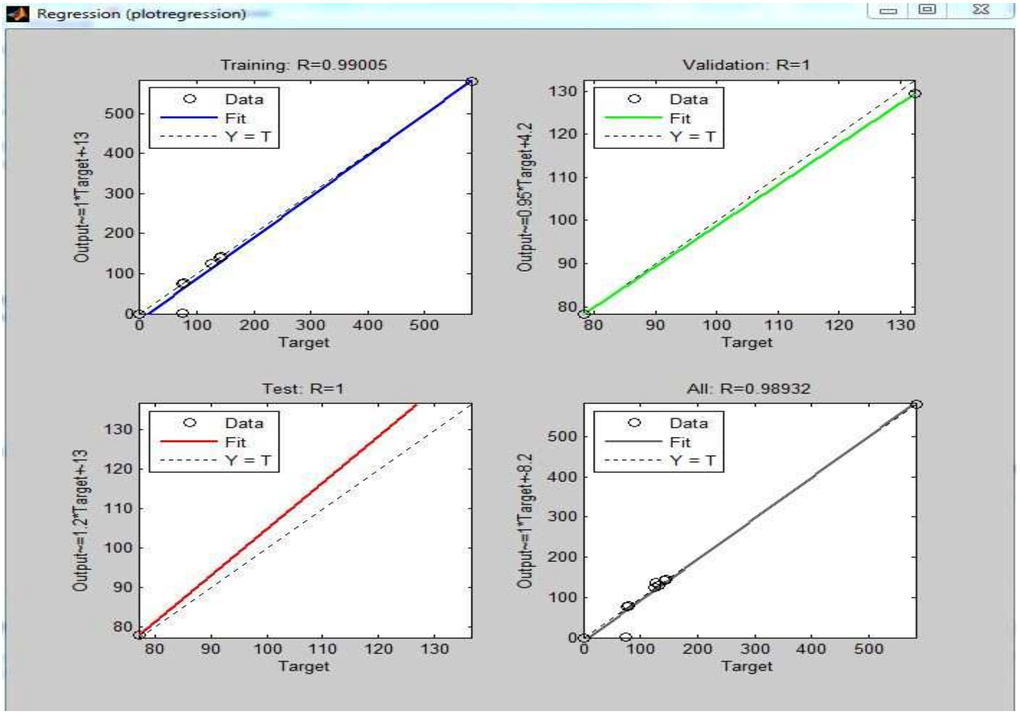
Progress

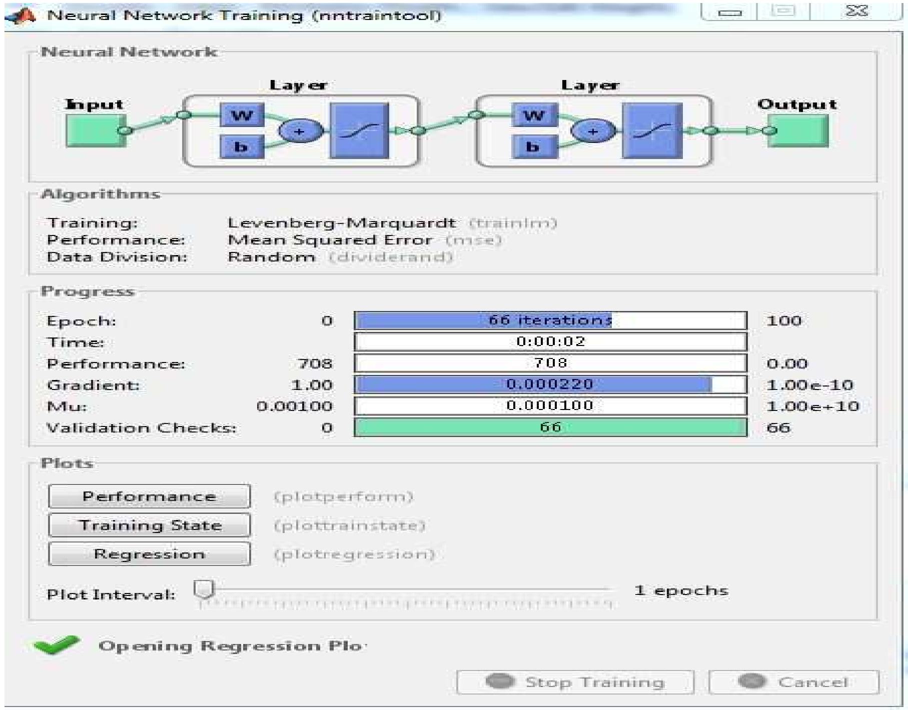
Epoch:	0	85 iterations	100
Time:		0:00:03	
Performance:	2.22e+03	535	0.00
Gradient:	1.00	0.000167	1.00e-10
Mu:	0.00100	1.00e-07	1.00e+10
Validation Checks:	0	84	84

Plot Interval: 1 epochs

✓ Opening Regression Plo

ANN Output Schedule for $Al\_H_2SO_4\_TC$





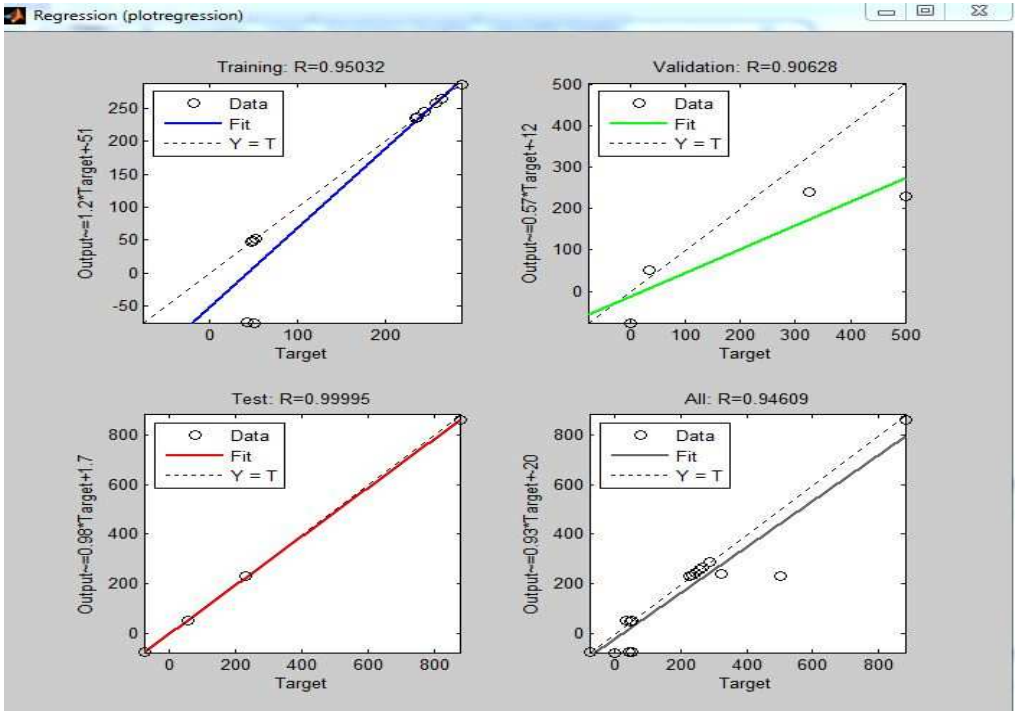
Algorithms

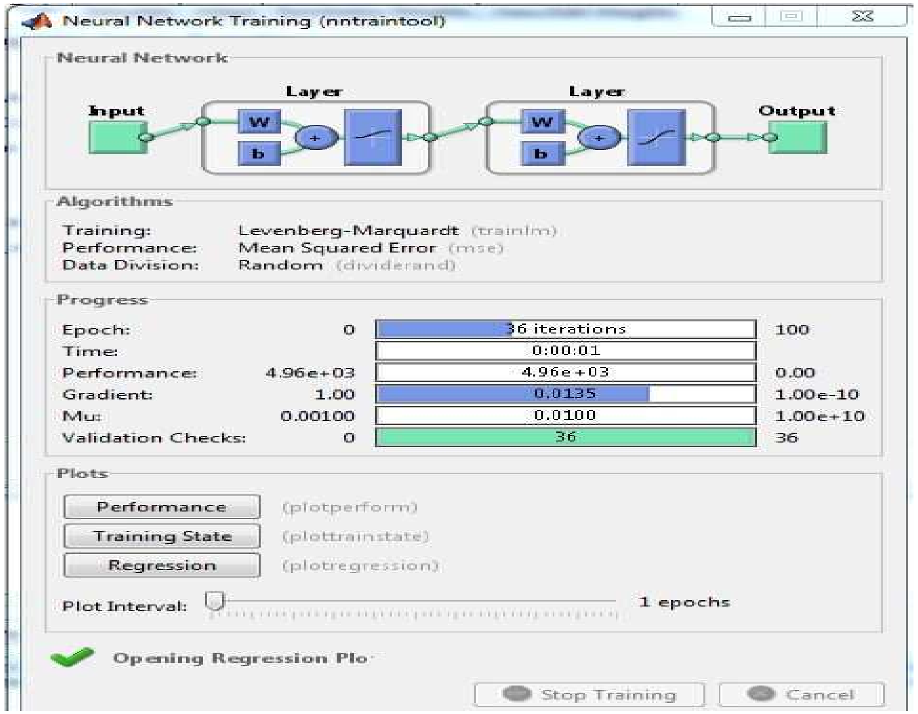
Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Progress

Epoch:	0	66 iterations	100
Time:		0:00:02	
Performance:	708	708	0.00
Gradient:	1.00	0.000220	1.00e-10
Mu:	0.00100	0.000100	1.00e+10
Validation Checks:	0	66	66

ANN Output Schedule for MS_HCl_SA





Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Progress

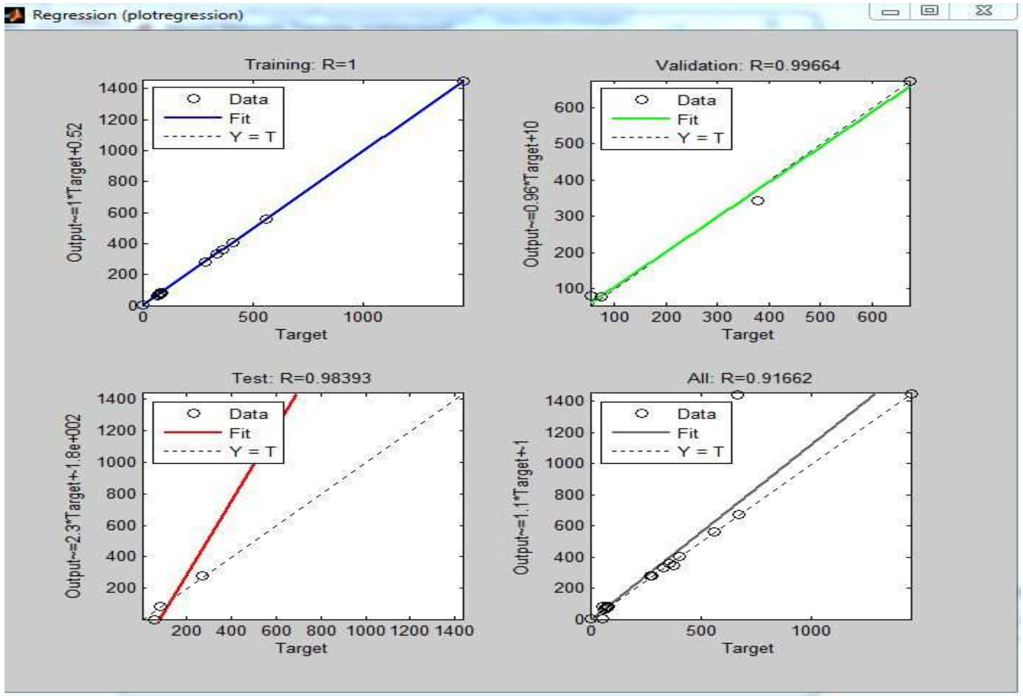
Epoch:	0	36 iterations	100
Time:		0:00:01	
Performance:	4.96e+03	4.96e+03	0.00
Gradient:	1.00	0.0135	1.00e-10
Mu:	0.00100	0.0100	1.00e+10
Validation Checks:	0	36	36

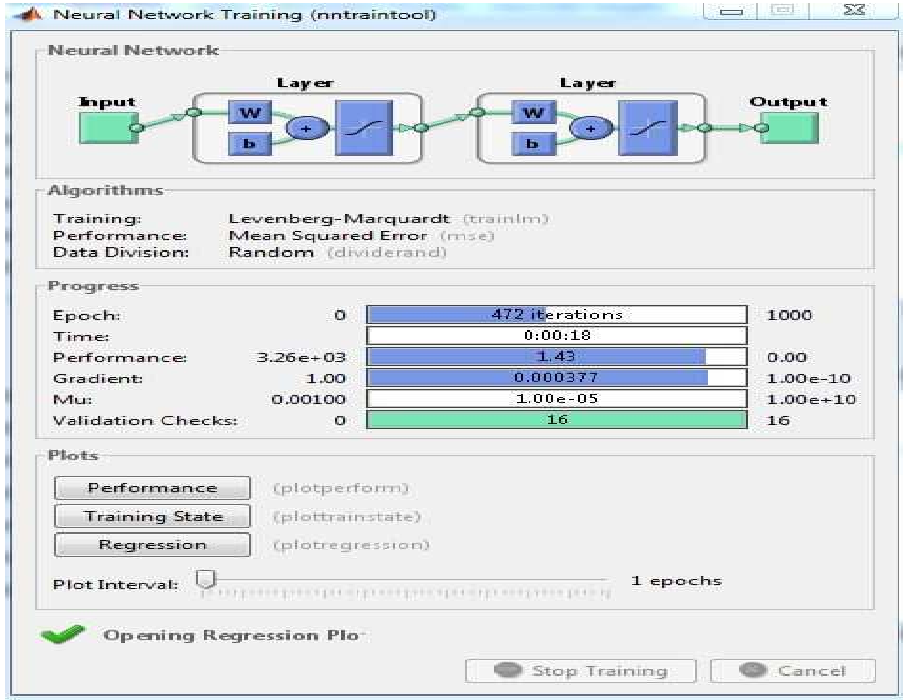
Performance (plotperform)
Training State (plottrainstate)
Regression (plotregression)

Plot Interval: 1 epochs

✓ Opening Regression Plo

ANN Output Schedule for MS_H_2SO_4_SA





Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

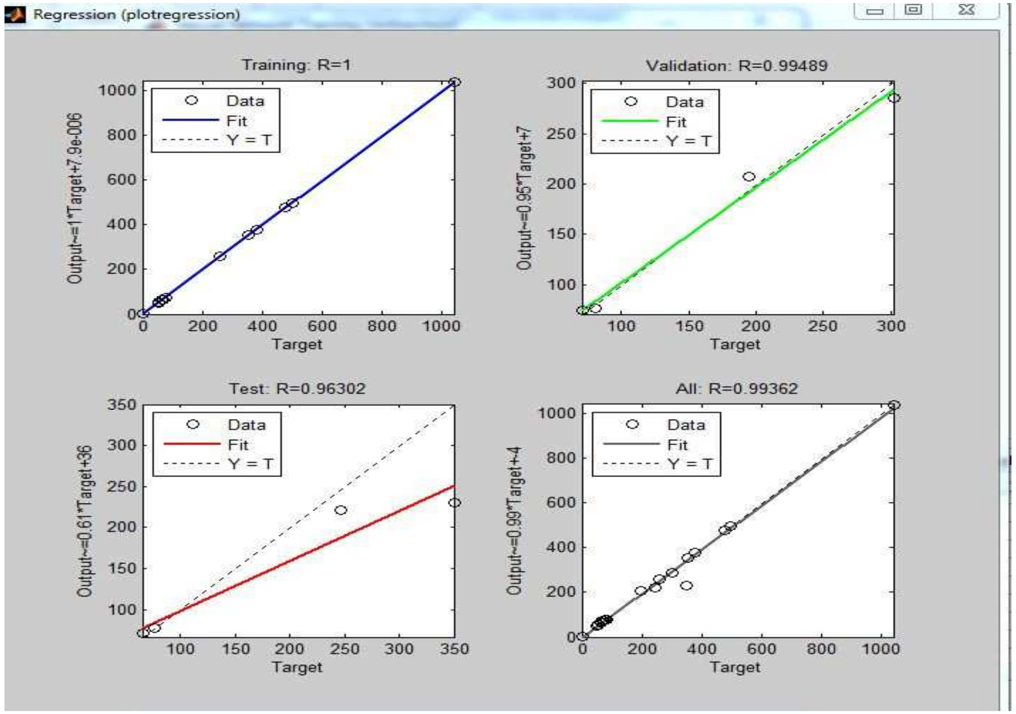
Epoch: 0 | 472 iterations | 1000
Time: 0:00:18
Performance: 3.26e+03 | 1.43 | 0.00
Gradient: 1.00 | 0.000377 | 1.00e-10
Mu: 0.00100 | 1.00e-05 | 1.00e+10
Validation Checks: 0 | 16 | 16

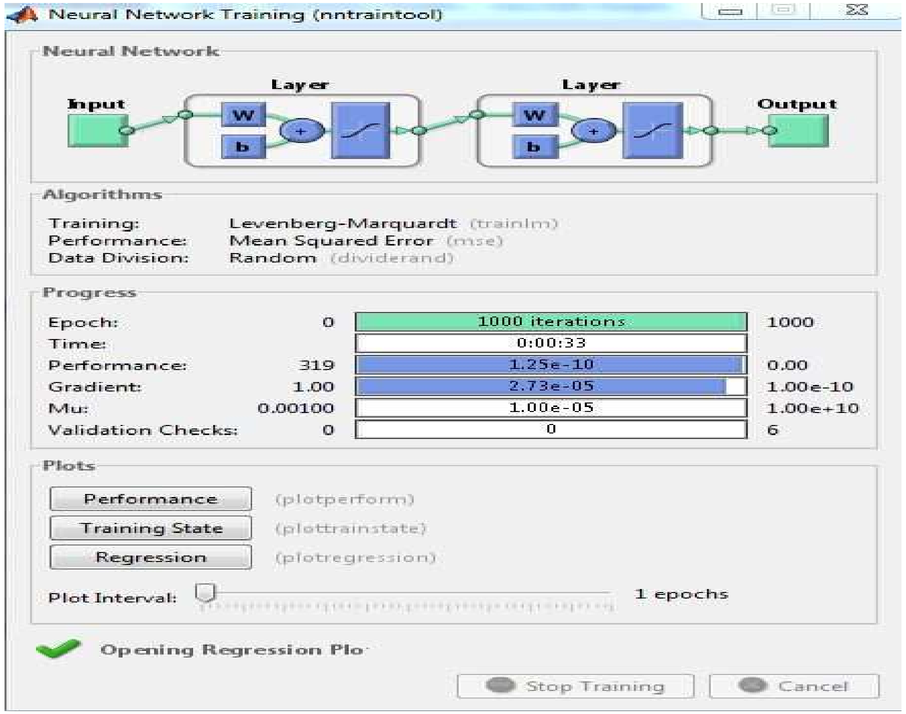
(plotperform)
(plottrainstate)
(plotregression)

Plot Interval: 1 epochs

Opening Regression Plo

ANN Output Schedule for Al_HCl_SA





Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Progress

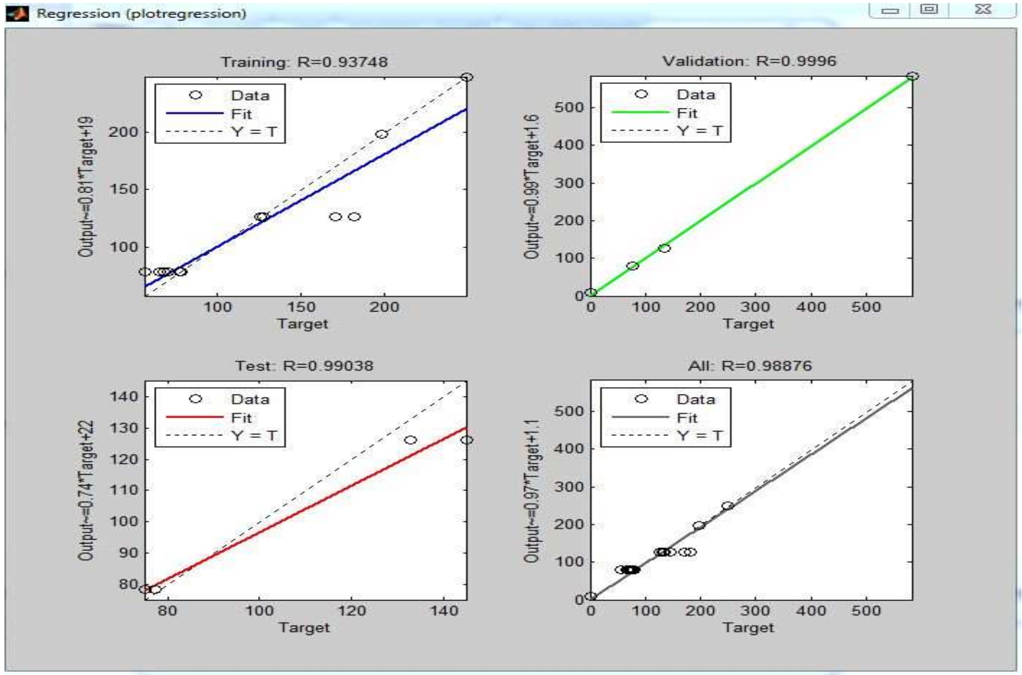
Epoch: 0 1000 iterations 1000
Time: 0:00:33
Performance: 319 1.25e-10 0.00
Gradient: 1.00 2.73e-05 1.00e-10
Mu: 0.00100 1.00e-05 1.00e+10
Validation Checks: 0 0 6

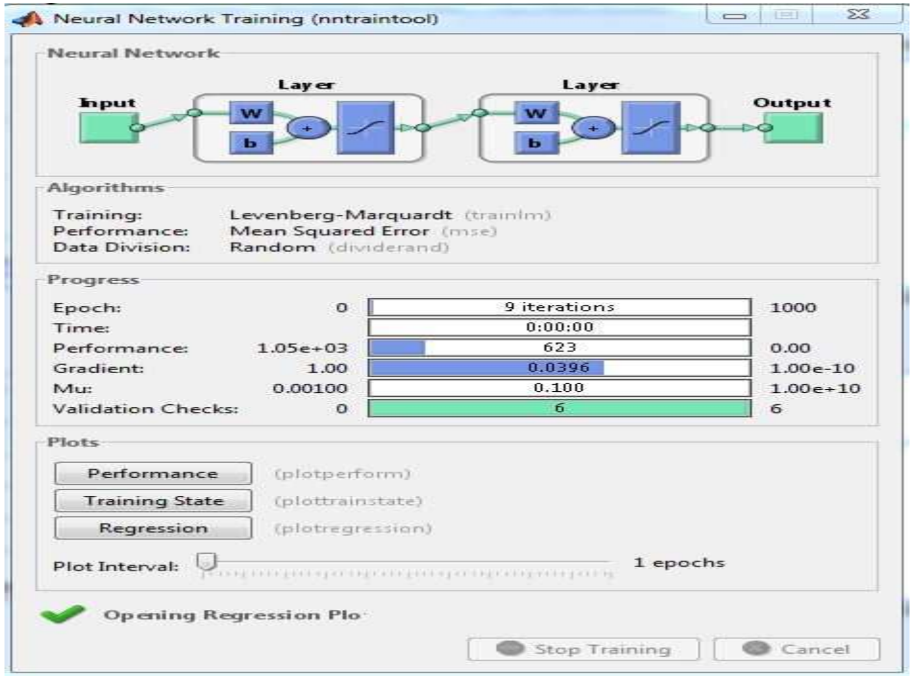
Plots

Plot Interval: 1 epochs

Opening Regression Plo

ANN Output Schedule for $Al\_H_2SO_4\_SA$





Neural Network Training (nntraintool)

Neural Network

Algorithms

Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Data Division: Random (dividerand)

Progress

Epoch:	0	9 iterations	1000
Time:		0:00:00	
Performance:	1.05e+03	623	0.00
Gradient:	1.00	0.0396	1.00e-10
Mu:	0.00100	0.100	1.00e+10
Validation Checks:	0	6	6

Plots

Performance (plotperform)
Training State (plottrainstate)
Regression (plotregression)

Plot Interval: 1 epochs

✓ Opening Regression Plo

Stop Training
Cancel