Adsorption and Corrosion Inhibition of *Clytostoma callistegioides* (leaf & flower extracts) on Mild Steel in 1M HCl solution

By

G.B.Hemalatha

13PCH006

A dissertation submitted to

Avinashilingam Institute for Home Science and Higher

Education for Women, University

(Estd. u/s of UGC Act 1956)

Coimbatore – 641043

In Partial Fulfillment of the Requirements

for the Degree of Master of Science in Chemistry

March, 2015

Adsorption and Corrosion Inhibition of *Clytostoma callistegioides* (leaf & flower extracts) on Mild Steel in 1M HCl solution

By

G.B.Hemalatha

13PCH006

A dissertation submitted to

Avinashilingam Institute for Home Science and Higher

Education for Women, University

(Estd. u/s of UGC Act 1956)

Coimbatore – 641043

In Partial Fulfillment of the Requirements

for the Degree of Master of Science in Chemistry

March, 2015

Certified as Bonafide Research Work

ignature of the
Guide

Signature of the
Head of Department

ACKNOWLEDGEMENT

ACKNOWLEDGEMENT

Many people contribute their best to the successful completion of my work. I wish to graciously acknowledge each one of them for the constant support given to me that made it possible for me to do this work to the extent of my satisfaction. I humbly bow my head before the **Lord Almighty** who blessed me with will power and courage to complete this endeavor successfully.

I am grateful to **Dr.(Thiru) T.S.K.Meenakshi Sundaram,** M.A.,M.Phil.,Ph.D., Chancellor, Avinashilingam Institute for Home Science and Higher education for Women, University Coimbatore**,** for permitting me to carry out my work in this eminent Institution.

I extend my sincere thanks to **Dr.(Tmt) Sheela Ramachandran** M.Sc., P.G.Dip., Ph.D., (Avinashilingam) ,Vice Chancellor, Avinashilingam Institute for Home Science and Higher education for Women, University Coimbatore, for providing all facilities necessary for my thesis work.

With profound respect, I place a deep sense of gratitude **to Dr.(Tmt) Venmathi,** M.Sc., Dip .Ed ., M.Phil., Ph.D. Registrar (Incharge), Avinashilingam Institute for Home Science and Higher education for Women, University Coimbatore, for providing adequate help required to carry out my work.

With heart full of gratitude, I sincerely acknowledge the help and support rendered by **Dr. Saroja Prabhakaran**, M.A., Dip. Ed., Ph.D former Vice Chancellor, for rendering adequate help required to carry out the work.

I owe my special thanks to **Dr**. **(Tmt) A.Parvathi,** M.Sc., Dip .Ed ., M.Phil., Ph.D. Dean, Faculty of Science, Avinashilingam Institute for Home Science and Higher education for Women, University Coimbatore, for her kind help.

With great pleasure I would like to express my affable and cordial thanks to **Dr.(Tmt)R.Shyamala,**M.Sc.,Dip.Ed.,(Madras),M.phil.(Bharathiar)Ph.D.(Avinashilingam),Professor and Head ,Department of Chemistry, Avinashilingam Institute for Home Science and Higher education for Women, University Coimbatore **,** for providing laboratory facilities and for her unflinching encouragement during my thesis work.

My heartful thanks to my preserving guide **Dr. (Tmt) R.Rajalakshmi,** M.Sc., B.Ed., (MaduraiKamaraj),M.Phil.,(Bharathiar),Ph.D.(Avinashilingam), Professor, Department of Chemistry, Avinashilingam Institute for Home Science and Higher education for Women, University Coimbatore, for her meticulous care, innovative ideas, constructive thoughts, motivation, patience, and constant succor throughout my thesis.

I extend my deep sense of gratitude to **Mrs. A. Prithiba,** M.Sc., M.Phil., Assistant Professor, Department of Chemistry, Avinashilingam Institute for Home Science and Higher education for Women, University Coimbatore, for her constant support and tremendous care rendered for carrying out of my thesis successfully.

I wish to thank **all my staff members of Chemistry Department**, Avinashilingam Institute for Home Science and Higher education for Women, University Coimbatore who made a congenial atmosphere to work throughout my thesis.

At length, my love high lights on **my adorable parents, brother, grandmother, friends, relatives and my–well-wishers** for without all there is no glossary for my glory.

Hemalatha.G.B

CONTENTS

Chapter no	List of contents	Page no
	List of tables	
	List of figures	
	List of abbreviations	
1	Introduction	
2	Review of literature	
3	Materials & methods	
4	Results & discussion	
5	Summary & conclusion	
	References	

LIST OF TABLES

Table no	Title of tables	Page no
1	Phytochemical screening of CCL & CCF	
2	FT-IR spectral results for CCL & CCF	
3	Role of concentration of CCL extract on MS in 1M HCl	
4	Role of temperature on corrosion of MS in the presence of various concentration of CCL extract in HCl	
5	Role of concentration of CCF extract on MS in 1M HCl	
6	Role of temperature on corrosion of MS in the presence of various concentration of CCF extract in 1M HCl	
7	Values of correlation coefficient obtained for Langmuir and Temkin adsorption isotherms	
8	Values of Ea , ΔHa and ΔSa of MS in various concentration of CCL in HCl medium	
9	Values of Ea , ΔHa and ΔSa of MS in various	

	concentration of CCF in HCl medium	
10	**Values of -ΔG, ΔH and ΔS of MS in various concentration of CCL 1M HCl medium**	
11	**Values of -ΔG, ΔH and ΔS of MS in various concentration of CCF 1M HCl medium**	
12	**Electrochemical polarization parameters for the corrosion of MS in the presence of CCL extract in 1M HCl**	
13	**Electrochemical polarization parameters for the corrosion of MS in the presence of CCF extract in 1M HCl**	
14	**Linear polarization resistance and impedance parameters for the corrosion of MS in the presence of CCL extract in 1M HCl**	
15	**Linear polarization resistance and impedance parameters for the corrosion of MS in the presence of CCF extract in 1M HCl**	
16	**Impedance parameters for the corrosion of MS in the presence of CCL extract in 1M HCl**	
17	**Impedance parameters for the corrosion of MS in the presence of CCF extract in 1M HCl**	
18a	**FT-IR spectral details of CCL concentrate and corrosion product**	
18b	**FT-IR spectral details of CCF concentrate and corrosion product**	
19	**Chemical constituents in *Clytostoma callistegioides***	

LIST OF FIGURES

FIGURE No	**TITLE OF FIGURE**	**PAGE No**
1a	**FT-IR spectrum of CCL powder**	
1b	**FT-IR spectrum of CCF powder**	
2	**IE as the function of Conc - MS/CCL/1M HCl**	

3	**IE as the function of immersion time - CCL/MS/1M HCl**	
4	**Variation of IE as a function of concentration (CCL extract in 1M HCl)**	
5	**Variation of IE as a function of temperature (CCL extract in 1M HCl)**	
6	**IE as the function of concentration MS/CCF/HCl**	
7	**IE as the function of immersion time - CCF/MS/1M HCl**	
8	**Variation of IE as a function of concentration (CCF extract in 1M HCl)**	
9	**Variation of IE as a function of temperature (CCF extract in 1M HCl)**	
10	**Langmuir Adsorption isotherm - MS/CCL/HCl**	
11	**Temkin Adsorption isotherm - MS/CCL/HCl**	
12	**Langmuir Adsorption isotherm - MS/CCF/HCl**	
13	**Temkin Adsorption isotherm - MS/CCF/HCl**	
14	**Arrhenius plot (MS/HCl/CCL)**	
15	**Transition plot-MS/CCL/HCl**	
16	**Arrhenius plot (MS/HCl/CCF)**	
17	**Transition plot –MS/CCF/HCl**	
18	**- ΔG Vs temp for CCL extracts in HCl**	
19	**- ΔG Vs temp for CCF extracts in HCl**	

LIST OF ABBREVIATIONS

CC	*Clytostoma callistegioides*
CCL	*Clytostoma callistegioides* leaves
CCF	*Clytostoma callistegioides* flowers
HCl	Hydrochloric acid
MS	Mild Steel

IE	Inhibitor Efficiency
CR	Corrosion Rate
ppm	Parts per million
mpy	Mils per year
θ	Surface coverage
I_{corr}	Corrosion current
E_{corr}	Corrosion potential
b_a	Anodic Tafel slope
b_c	Cathodic Tafel slope
C_{dl}	Double layer capacitance
R_{ct}	Change transfer resistance
R_p	Polarization resistance
mV	milli Volt
LPR	Linear polarization resistance
EIS	Electrochemical Impedance Spectroscopy

INTRODUCTION

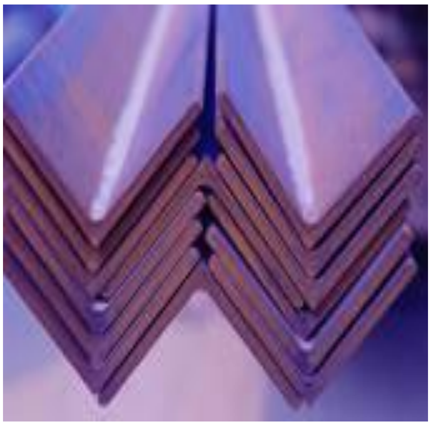
1.INTRODUCTION

Corrosion is a common occurrence, like the rusting and flaking of an old iron yard piece. Energy, often large amounts, is poured into winning the desired metals from their natural ores; manufacturing some metal product very costly. Corrosion causes deterioration of manufactured products, damaging their structure and ultimately rendering the product useless.

Metals and alloys are used as construction and fabrication materials in engineering. If the metal or alloy structure is not properly maintained, they deteriorate slowly by the action of atmospheric gases, moisture and other chemicals. This phenomenon of deterioration of metals and alloy is known as corrosion.

Corrosion is defined as the gradual eating away or deterioration of a metal by chemical or electrochemical reaction with its environment.

The most familiar example of corrosion is the rusting of iron when exposed to atmospheric conditions. During the process, a layer of oxide is formed and the iron becomes weak. It has been roughly assessed that the amount of iron wasted due to corrosion is one-fourth of world production. So it is better to control corrosion. Corrosion damages to materials are pictorially represented below



1.1. IMPORTANCE OF CORROSION STUDIES

It is now a day’s necessary to pay more attention to metallic corrosion than was done earlier due to

- Corrosion can lead to failures in plant infrastructure and machines which are usually costly to repair, costly in terms of cost or contaminated product, in terms of environmental damage, and possibly costly in terms of human safety.
- Increasing use of metals in all fields of technology.
- The conversion of metal resources, the world’s supply of which is limited, and the wastage of which includes corresponding losses of energy and water resources accompanying the reduction and fabrication of metal structure.
- Use of rare and expansive metals whose protection requires special precautions.
- Use of new high strength alloys which are usually more susceptible to certain types of corrosive attacks.
- Increasing pollution of air and water resulting in a more corrosive environment.
- Strict safety standards of operating equipment which may fail in a catastrophic manner due to corrosion.

1.2. FACTOR INFLUENCING CORROSION REACTIONS

Factors associated mainly with the metals

- Effective electrode potential of metals in a solution.
- Over voltage of hydrogen on the metal.
- Chemical and physical homogeneity of the metal surface.
- Inherent ability to form an insoluble protective film.

Factors which vary mainly with the environment

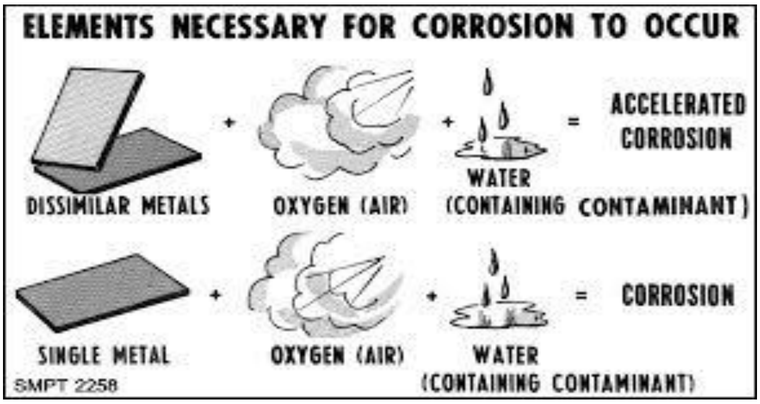
- Hydrogen-ion concentration in the solution
- Influence of oxygen in solution adjacent to the metal
- Specific nature and concentration of other ions in solution
- Rate of flow of the solution in contact with metal
- Temperature
- Cyclic stress(corrosion fatigue)
- Ability of environment to form a protective deposit on the metal

1.3. CAUSES OF CORROSION

Corrosion is a natural process. The primary driving force of corrosion is based upon the transformation of iron from natural state to steel. The refining of iron ore into steel requires the addition of energy. Steel is essentially an unstable state of iron and corrosion is the process of iron returning to its natural state. The energy used in the refining process is driving force of corrosion.

A primary cause of corrosion is due to an effect known as galvanic corrosion. All metals have different natural electrical potentials. Where two metals with different potentials are connected to each other in a common environment, current will flow causing corrosion to occur.

All the metal expect gold, platinum, and silver exist in nature in the form of their oxides, carbonates, sulphides, sulphates, etc. these combined form of metals represent their thermodynamically stable (low energy) state. The metals are extracted from this ores after supplying large amount of energy. Metals in the uncombined condition have higher energy and are in an unstable state. It is their natural tendency to go back to the low energy state i.e. combined state by recombining with the element present in the environment. This is the main reason for corrosion.



Two other unique causes are stress and hydrogen.

- Stress corrosion occurs when even a very small pit form in a metal under stress concentrated stress either deepens and extends the pit, or cracks the protective film which tends to form. Under continued exposure to the corrosive medium and stress, the crack extends by alternate corrosion and stress failure.

- Hydrogen embrittlement and hydrogen attack results when atomic hydrogen penetrates into the gain boundaries of steel producing micro cracks, blistering and loss of ductility. The atomic hydrogen combines into molecule and results in blistering and laminations.

1.4. CONSEQUENCES OF CORROSION

Some important consequences of corrosion are summarized below:

1.4.1. Plant shutdown:

Shutdown of nuclear plants, process plants, power plants and refineries may cause severe problems to industry and consumers.

1.4.2. Loss of products:

Leaking containers, storage tanks, water and oil transportation lines and fuel tanks cause si9gnificant loss of product and may generate severe accidents and hazards and. It is well known that at least 25% of water is lost by leakage.

1.4.3. Loss of efficiency:

Insulation of heat exchanger tubing and pipelines by corrosion products reduces heat transfer and piping capacity.

1.4.4. Contamination:

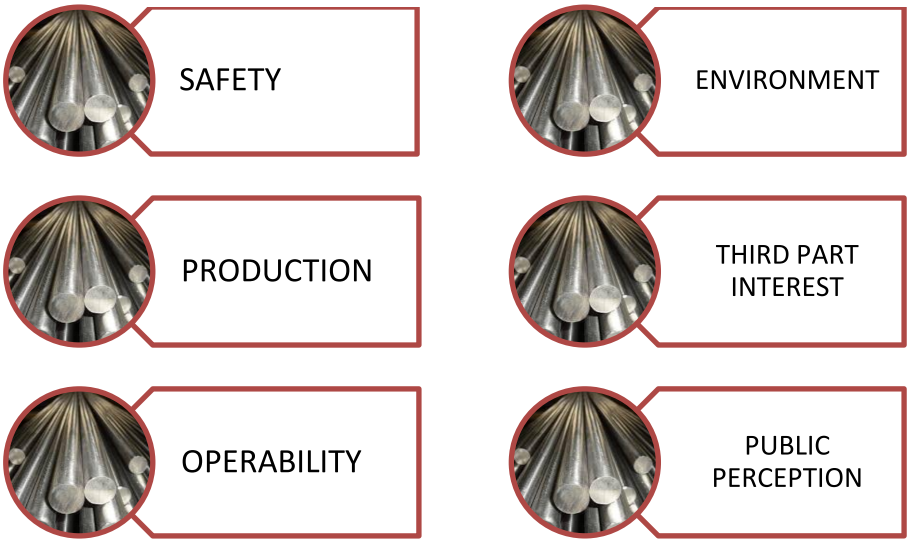
Corrosion products contaminate chemicals, pharmaceuticals, dyes, packaged goods, etc. with dire consequences to consumers.

1.4.5. Nuclear hazards:

The Chernobyl disaster of 1986 is a living example of transport of radioactive corrosion products in water fatal to human, animal and biological life.

1.4.6. CONSEQUENCE FACTORS

The point has been made that the consequence of a corrosion failures are more important than the failure itself. Thus, the consequence that bear on plant operators' minds include:

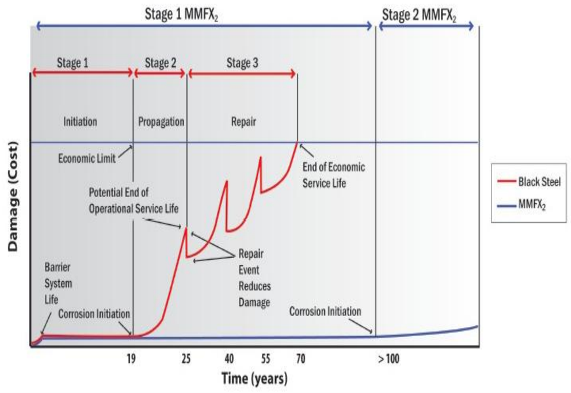


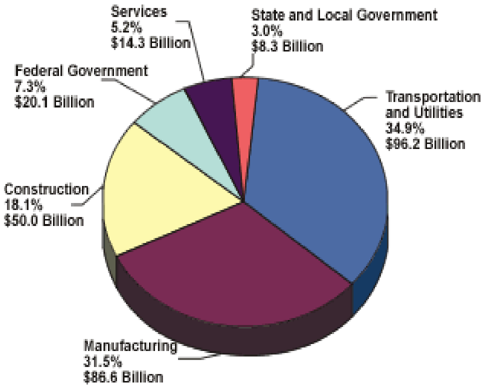
1.5. COST OF CORROSION

Corrosion is recognized as one of the most serious problems in our modern societies and the resulting losses each year are in hundreds of billions of dollars. Cost of corrosion studies have been undertaken by several countries including, the United States, the United Kingdom, Japan, Austria, Kuwait and China.

Our economy would be drastically changed if there were no corrosion. But corrosion touches all inside and outside the home, on the road, on the sea, and in aerospace vehicles. (Fontana Mars G. 1987). NACE international study shows the cost of corrosion in USA is $ 300 billion/year.

A recent report describes the annual direct and indirect costs of metallic corrosion in the United States and preventive strategies for optimum corrosion management. The total direct cost of corrosion is estimated at $276 billion/year, which is 3.1% of the 1998 U.S. gross domestic product (GDP).





DIRECT COSTS	INDIRECT COSTS
❖ Infrastructure $22.6 billion	➢ Cost of labor attributed to corrosion management activities
❖ Utilities $47.9 billion	➢ Cost of the equipment required because of corrosion-related activities
❖ Transportation $29.7 billion	➢ Loss of revenue due to disruption in supply of product
❖ Production and manufacturing $17.6 billion	➢ Cost of loss of reliability
❖ Government $20.1 billion	➢ Grand Total: $275.5 BILLION
❖ Total: $137.9 BILLLION	

1.6.IMPACT OF CORROSION ON INDUSTRY

The impact of corrosion on the industry has been viewed in terms of its effect on both capital and operational expenditures (CAPEX and OPEX) and health, safety and the environment (HSE). To fight against the high cost and the impact of corrosion within the oil industry, an overview of topical research and engineering activities is presented. This covers corrosion and metallurgy issues related to drilling, production, and transportation and refinery activities.

1.6.1. THE NUCLEAR INDUSTRY

The nuclear industry has most of corrosion problems of other industries and some that are all of its own. Right from the start, the potential for disaster was recognized and tackled head-on by adopting high grade materials in many parts of systems. For boiling water reactors and pressurized water reactors average capacity loss 5% -8% in 1982.

1.6.2.THE AEROSPACE & DEFENSE INDUSTRY

The particular demands of the aerospace industry have created a manufacturing environment with a very high and proper regard to optimizing corrosion performance, as a result of which the safety record has been exemplary and the efficiencies of operation have been outstanding. Failure of military systems in action due to materials or corrosion failure is a much feared phenomenon and is dealt with by reliability, a wider topic that arose from the needs of defense industry.

1.6.3. THE FOOD INDUSTRY

The food quality requirements lead most plants to select stainless steel as a material of choice. Assuming that the stainless steel consumption and cost in this industry is entirely attributed to corrosion, a total annual direct cost of corrosion is estimated at $2.1 billion. The importance of cleanliness in food processing plants is extremely high. To eliminate bacteria and viruses from surfaces and equipment, it is imperative to adopt an effective cleaning and sanitization program. Most of these sanitizers can be quite corrosive to metals.

1.6.4. THE OIL INDUSTRIES

The wide-ranging environmental conditions prevailing in the oil and gas industry necessitates the appropriate and cost effective materials choice and corrosion control measures. The implementation of these measures are becoming increasingly important as the impact of corrosion on safety, economy and the environment takes up more challenging roles. Furthermore, production conditions tend to become more corrosive hence requiring a more stringent corrosion management strategy.

1.7. ESTIMATION OF CORROSION LOSS

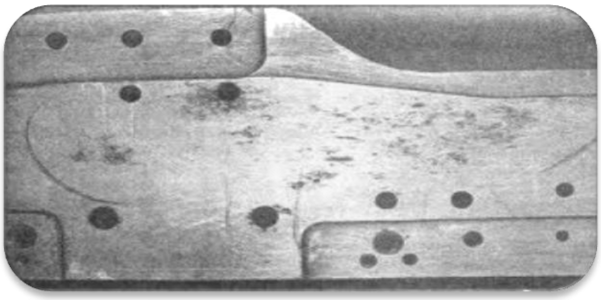
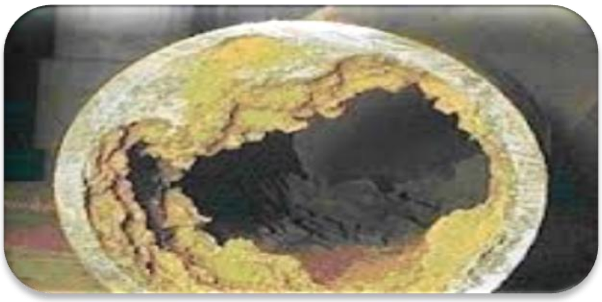
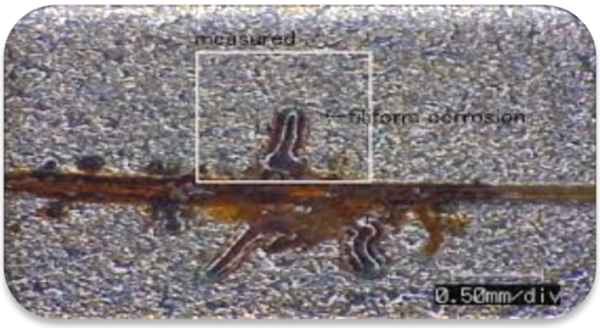
The cost of corrosion exceeded $1 trillion in United States in 2013. With little fanfare, a significant milestone in the effect of corrosion on the U.S. economy occurred in 2013 when **the total cost of corrosion in the US exceeds $1 trillion annually** for the first time. In a widely-cited study (NACE Corrosion Costs Study) by the National Association of Corrosion Engineers, NACE, the direct cost of corrosion in the U.S. was estimated to equal $276 Billion in 1998, approximately 3.1 % of GDP. However, this estimate is incomplete and outdated. (***www.g2mtlabs.com)***

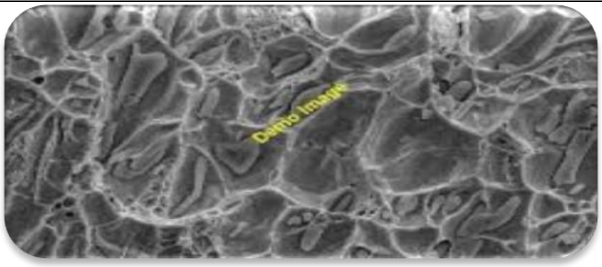
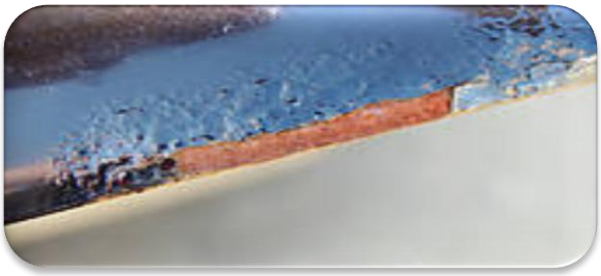
Closer examination of the 1998 NACE corrosion study's own analysis, along with a calculation of inflation since the report was produced, indicates that total corrosion costs in the U.S. now exceed $1 trillion dollars a year, and probably exceeds $5 trillion annually around the world (assuming 6% of the GWP of 84.97 Trillion in 2012) . The indirect cost of corrosion of is estimated to be at least equal to the direct cost. In that case, the total cost of corrosion is $993 B in March 2013 and estimated to exceed $1 trillion June 2013 ***(based on estimates of GDP from http://forecasts.org/gdp.htm)***

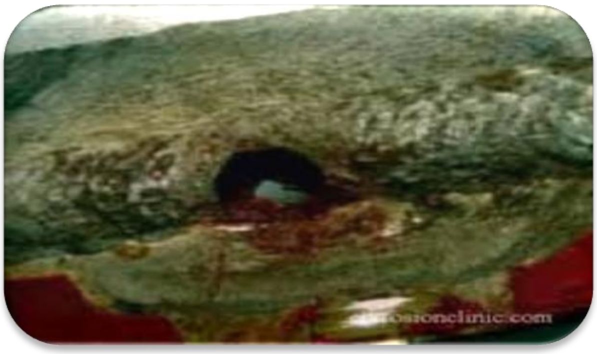
1.8. FORMS OF CORROSION

There are many types and causes of corrosion and depending on a particular scientist's and corrosion engineer's tendencies to look upon the subject more broadly or narrowly there is no clear and exact total for the number of corrosion types. The different forms of corrosion represent corrosion phenomena categorized to their appearance.

Illustration	Form of corrosion
	**Uniform corrosion** This is also called general corrosion. The surface effect produced by most direct chemical attacks (e.g., as by an acid) is a uniform etching of the metal.
	**Galvanic corrosion** Galvanic corrosion is an electrochemical action of two dissimilar metals in the presence of an electrolyte and an electron conductive path. It occurs when

	dissimilar metals are in contact.
	**Concentration cell corrosion** Concentration cell corrosion occurs when two are more areas of a metal surface are in contact with different concentrations of the same solution.
	**Pitting corrosion** Pitting corrosion is localized corrosion that occurs at microscopic defects on a metal surface. The pits are often found underneath surface deposits caused by corrosion product accumulation.
	**Crevice corrosion** Crevice or contact corrosion is the corrosion produced at the region of contact of metals with metal or metals with nonmetals. It may occur at washers, under barnacles.
	**Film form corrosion** This type of corrosion occurs on painted or plated surfaces when moisture permeates the coating. Long branching filaments of corrosion product extend out from the original corrosion pit and cause degradation of the protective coating.
	Intragranular corrosion Intragranular corrosion is an attack

	on or adjacent to the grain boundaries of a metal or alloy.
	**Stress corrosion cracking** Stress corrosion cracking is caused by the simultaneous effects of tensile stress and specific corrosive environment. Stresses may be due to applied loads, residual stresses from the manufacturing process, or a combination of both.
	**Corrosion fatigue** Corrosion fatigue is a special case of stress corrosion caused by the combined effects of cyclic stress and corrosion. No metal is immune from some reduction of its resistance to cyclic stressing if the metal is in a corrosive environment.
	**Fretting corrosion** The rapid corrosion that occurs at the interface between contacting, highly loaded metal surfaces when subjected to slight vibratory motion is known as fretting corrosion.
	**Erosion corrosion** Erosion corrosion is the result of a combination of an aggressive chemical environment and high fluid-surface velocities.
	Dealloying

	Dealloying is a rare form of corrosion found in copper alloys, gray cast iron, and some other alloys. Dealloying occurs when the alloy loses the active component of the metal and retains the more corrosion resistant component in a porous ‘sponge” on the metal surface.
	**Hydrogen damage** Hydrogen embrittlement is a problem with high-strength steels, titanium, and some other metals. Control is by eliminating hydrogen from the environment or by the use of resistance alloys.
	**Corrosion in concrete** Concrete is a widely-used structural material that is frequently reinforced with carbon steel reinforcing rods, post-tensioning cable or prestressing wires. The steel is necessary to maintain the strength of the structure, but it is subject to corrosion.
	**Microbial corrosion** Microbial corrosion (also called microbiologically-influenced corrosion or MIC) is corrosion that is caused by the presence and activities of microbes. This corrosion can take many forms and can be controlled by biocides or by

	conventional corrosion control methods.

1.9.ELECTROCHEMICAL CORROSION THEORY

The special characteristic of most corrosion processes is that the oxidation and reduction steps occur at separate locations on the metal. This is possible because metals are conductive, so the electrons can flow through the metal from the anodic to the cathodic regions. The presence of water is necessary in order to transport ions to and from the metal, but a thin film of adsorbed moisture can be sufficient.

A corrosion system can be regarded as a short-circuited electrochemical cell in which the anodic process is something like

$$\mathbf{Fe(s) \rightarrow Fe^{2+}}\,(aq) + \mathbf{2}\, e^{-}$$

And the cathodic steps can be any of

$$\mathbf{O_2 + 2\ H_2O + 4}e^{-} \mathbf{\rightarrow 4\ OH^{-}}$$

$$\mathbf{H^{+}} + e^{-} \rightarrow \mathbf{½\ H_2}\,(g) \text{ and } \mathbf{M^{2+} + 2}\ e^{-} \rightarrow \mathbf{M}(s)$$

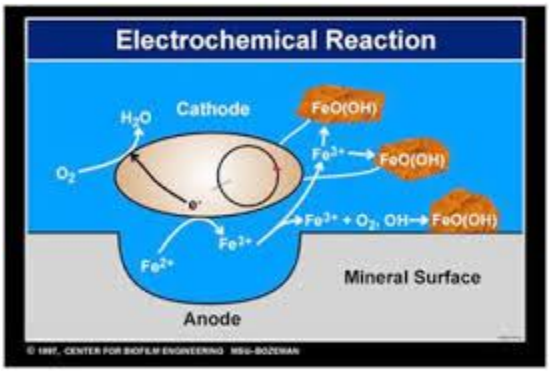
Where M is a metal.

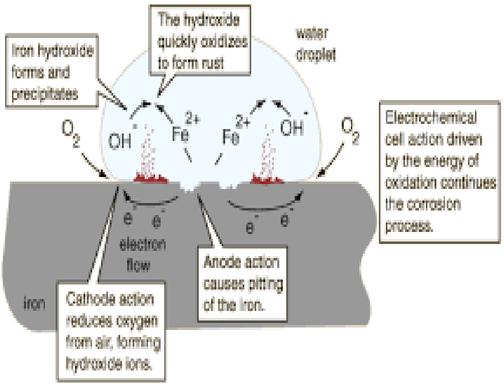
Electrochemical corrosion of iron. Corrosion often being at a location

- Where the metal is under stress (at a bend or weld) or is isolated from the air (where two pieces of metal are joined or under a loosely-adhering paint film). The metal ions dissolved in the moisture film and the electrons migrate to another location.
- Where they are taken up by a depolarizer. Oxygen is the most common depolarizer; the resulting hydroxide ions with Fe^{2+} to form the mixture of hydrous iron oxides known as rust.

Which part of the metal serve as anode and cathode can depend on many factors, as can be4 seen from the irregular corrosion patterns that are commonly observed. Atoms in regions that have undergone stress, as might be produced by forming or machining, often tend to have higher free energies, and tend to become anodic.

If one part of a metallic object is protected from the atmosphere so that there is insufficient O_2 to build or maintain the oxide film, this "protected" will often be the site at which corrosion is most active. The fact that such sites are usually hidden from view accounts for much of the difficulty in detecting and controlling corrosion.





1.10. CORROSION CONTROL METHODS

There are four basic methods for corrosion control & corrosion prevention.

1. Materials resistance to corrosion
2. Protective coatings
3. Cathodic protection
4. Corrosion inhibitors

In most cases, effective corrosion control is obtained by combining two are more of these methods. Corrosion control should be considered at the design stage of a given facility or system. The methods selected must be appropriate for the materials used, for the configurations, and for the types and forms of corrosion which must be controlled.

1.10.1. Materials resistance to corrosion

There are no materials that are immune to corrosion in all environments. Materials must be matched to the environment that they will encounter in service. Corrosion resistance data are used to assess the suitability of a material in an environment.

1.10.2. Protective coatings

Protective coatings are the most widely used corrosion control technique. Essentially, protective coatings are a means for separating the surfaces that are susceptible to corrosion from the factors in the environment which cause corrosion to occur. Remember, however, that protective coatings can never provide 100% protection of the surface. If localized corrosion at a coating defect is likely to cause rapid catastrophic failure, additional corrosion control measures must be taken. Coatings are particularly useful when used in combination with other methods of corrosion control such as cathodic protection or galvanic corrosion.

1.10.3. Cathodic protection

Cathodic protection interferes with the natural action of the electrochemical cells that are responsible for corrosion. Cathodic protection can be effectively applied to control corrosion of surfaces that are immersed in water or exposed to soil.

Cathodic protection on its classical form cannot be used to protect surface exposed to the atmosphere. The use of anodic metallic coatings such as zinc on steel (galvanizing) is, however, a form of cathodic protection, which is effective in the atmosphere.

1.10.4. Corrosion inhibitors

Corrosion inhibitors are a chemical compounds added to the corrosive environment to reduce the rate of its attack on the metal or alloy. The chemicals which can act as corrosion inhibitors may be inorganic or organic. The inorganic compounds such as chromates inhibit the corrosion process via formation of passive oxide film on the metal surface and thus prevent the corrosive medium to attack the bar metal. On the other hand, the organic compounds adsorb on the metal surface forming a barrier between the metal and the corrosive environment.

Some structural features of the organic compounds help them to do so. These include the presence of oxygen, nitrogen or sulfur atoms as well as presence of double bonds. The lone pair of electrons of the mentioned atoms facilitates the adsorption process. Some criteria should be considered when making a choice of chemical compounds for inhibition of corrosion. Inhibition of metallic corrosion is mainly an economical process. Therefore, the first criterion must be fulfilled by the used inhibitors is their prices. The other very important criterion should be considered when dealing with corrosion inhibitor is its effect on the human and environment. Unfortunately, most of the effective corrosion inhibitors are synthetic compounds can cause harm to human and environment. Upon looking around we will find very rich substance with wide varieties of chemical structures.

Most of naturally occurrence substances are safe and can be extracted by simple and cheap procedures. Recent literature full of researches which test different extracts for corrosion inhibition applications. The examples are numerous such as henna, olive, shirshzallouh, vanillin, natural honey, khella, onion, ficus, opuntia, many oils extracted from different parts of different plants and many others. Many of these naturally occurring substances proved their ability to act as corrosion inhibitors of different metals and alloys in different aggressive media.

1.11.IMPORTANCE OF GREEN INHIBITOR

The term “green inhibitor” or “eco-friendly inhibitor” refers to the substances that are biocompatibility in nature, environmentally acceptable, readily available and renewable source. Due to bio-degradability, eco friendliness, low cost and easy availability, the extracts of some common plants based chemicals and their by-products have been tried as inhibitors for metals under different environments (Abdel-Gabeet al.2006, Ebenso and Ekpe 1996, Ebensoet ai.2004, Ekpeet al.2000).

Green corrosion inhibitor can be grouped into two categories, namely organic green inhibitor and inorganic green inhibitors. Molecular structure of inhibitor is the main factor determining its characteristics. Presence of hetero atom (S, N, and O) with free electron pairs, aromatic rings with delocalized π-electrons, high molecular weight alkyl chains; substituent group in general improves inhibition efficiency. It is noticed that organic compounds show higher inhibition efficiency as compared to inorganic.

1.11.1. Selection process of green corrosion inhibitors

In addition to corrosion inhibition, an important aspect to be considered in the selection process is the effects on the use and discharge of chemicals to health, safety and the environment. Literature study shows that green corrosion inhibitor with minimum or no health and environmental hazards which is applicable to wide range of metals and various environmental conditions is to be discovered or invented.

1.12. PLANT DESCRIPTION

This vine is a member of the Bignoniaceae family with such famous relatives as cross vine (***Bignonia capreolata***) and trumpet creeper (*Campsis radicans*). Like its cousins, the violet trumpet vine is a robust and carefree grower with distinctive showy flowers. Also called painted trumpet, it is a woody stemmed evergreen vine that with a habit of clambering over adjacent foliage, fences and structures using tendrils to hang on tight. The bright glossy green leaves are oblong, about 3 in (7.6 cm) long and 1.5 in (3.8 cm) wide. They are arranged opposite in pairs and tendrils arise at the point where the leaves join the stem. In late spring the vine covers itself in color when the spectacular 3 in (7.6 cm) trumpet flowers appear. The trumpets are pale lavender and delicately detailed with dark violet and purple streaks. Flowers are followed by large prickly seed pods. (*www.backyardgardener.com)*

Location

Violet trumpet vine is native to Argentina and the southern part of Brazil.

Culture

It will grow in any well drained soil. Growth is more rampant in moist fertile soil. This vine is slower growing and has a more compact form in light sandy soils.

NATURE OF THE PLANT	
Growth Rate	**Fast**
Hardiness	**Hardy**
Adverse Growth Factors	**None**
Special Features	**Showy Flowers**
Water Use	**Low**
Low	**6.5-7.5 (neutral)**
Exposure	**Full Sun, Partial Shade, Shade**
Soil Type	**Not Particular**
Drainage	**Good Drainage**
Diseases	**No serious diseases or pests**

Usage

Violet trumpet vine is a very enthusiastic grower and will take over small gardens and yards. It is a large plant best used in large spaces and is best used on fences and pergolas where it can stretch out and be beautiful.

1.12.1. SCIENTIFIC CLASSIFICATION

Kingdom : ***Plantae*** ***Subkingdom :*** ***Angiosperms*** ***Division :*** ***Eudicots*** ***Class :*** ***Asterids*** ***Order :*** ***Lamiales*** ***Family :*** ***Bignoniaceae*** ***Genus :*** ***Clytostoma*** ***Species :*** ***C.Callistegioides*** ***Tamil name :*** **PATHIRI MULIGAI**	

1.12.2. OBJECTIVES

- To select an ecofriendly "zero cost" inhibitor for corrosion of MS in 1M HCl medium.
- To utilize CCL & CCF extracts as corrosion inhibitor for MS in 1M HCl medium.
- To carryout phytochemical screening for CCL & CCF extracts.
- To study the effect of concentration of the extract at room temperature on corrosion inhibition of MS in 1M HCl.
- To carryout immersion studies using the selected CCL & CCF extracts.
- To find the stability of CCL & CCF extracts at higher temperatures.
- To calculate Kinetic and Thermodynamic parameters.
- To fit the mass loss results into various adsorption isotherms.
- To evaluate the IE of CCL & CCF extracts using electrochemical measurements.
- To suggest a suitable mechanism of inhibition.
- To compare the efficiency of the CCL & CCF by mass loss and electrochemical methods.

REVIEW OF LITERATURE

2. REVIEW OF LITERATURE

This research led to investigate the effectively and environmentally safe inhibitor for mild steel in an acid media. The present study on “**Adsorption and Corrosion Inhibition of *Clytostoma callistegioides* (leaf & flower extracts) on Mild Steel in 1M HCl solution**” is reviewed under the following topics.

Natural products as inhibitors

○ Effect of natural product as inhibitors on mild steel.Corrosion behavior of mild steel with varying parameters

○ Effect of temperature, concentration and influence of exposure time.

Natural Products as Inhibitors

Due to toxic nature and high cost of some chemicals currently used as inhibitors, it is necessary to develop environmentally acceptable and less expensive inhibitors. Natural products from animal waste exhibit high inhibition activity. Due to the bio degradability, eco-friendliness, cost-effectiveness, less toxic and easy availability, the trend of using them has become increasingly important in the recent years. Greater research efforts have been directed towards formulating environmentally acceptable inhibitor.

- ***Gopal Ji et al., (2015)*** tested the inhibition and adsorption effects of the aqueous extracts of ***Musa paradisica*** (Banana) peels on mild steel corrosion in 1 M HCl as well as change in inhibition efficiency with ripening of the peels are investigated by weight loss measurement, electrochemical impedance spectroscopy (EIS), Tafel polarization and atomic force microscopy (AFM) techniques. Inhibition ability of the extracts decreases with the maturity stages. Furthermore, the extracts are characterized by FTIR spectroscopy, UV–visible spectroscopy and high performance liquid chromatography (HPLC) techniques. Adsorption behavior of the extracts is also studied, which suggest Langmuir isotherm model as a most suitable adsorption mechanism.
- ***Bammou et al., (2014)*** carried out the influence of natural occurring extract of ***Chenopodium Ambrosioides*** (CAE) on the corrosion inhibition of carbon steel in sulfuric acid solution is studied by the weight loss method, potentiodynamic polarization and impedance spectroscopy (EIS) measurements. The experimental results reveal that extract has a good inhibiting effect on the metal

tested in 0.5 M H_2SO_4 solution. The adsorption of ***Chenopodium Ambrosioides*** extract is found to obey the Langmuir adsorption isotherm.

- ***Maxime Chevalier et al., (2014)*** reported on the inhibiting effect of the ***Aniba rosaeodora*** alkaloidic extract on the corrosion of C38 steel in 1 M hydrochloric acid. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques were applied to study the metal corrosion behavior in the absence and presence of inhibitor. Polarization studies showed that the ***Aniba rosaeodora*** alkaloidic extract was a mixed-type inhibitor and its inhibition efficiency increased with the inhibitor concentration. Studies on the phytochemical constituents of the total alkaloids extract shows that it contains the anibine as the major alkaloid. The results obtained from the electrochemical study have clearly showed that the inhibition efficiency of the total extract was due to the presence of anibine. The XPS studies showed the formation of inhibitor layer containing the ***Aniba rosaeodora*** alkaloidic extract and the anibine molecules.
- ***Punita Mourya et al., (2014)*** evaluated the corrosion behavior of the extract of ***Tagetes erecta*** (Marigold flower) [TEF] has been evaluated as a corrosion inhibitor for mild steel in 0.5 M H_2SO_4 solution by means of gravimetric, potentiodynamic polarization and electrochemical impedance spectroscopic measurements. Tafel polarization studies reveal that TEF acts as an efficient mixed inhibitor. The adsorption of the inhibitor on the mild steel (MS) surface follows the Langmuir adsorption isotherm, indicating monolayer adsorption. The activation parameters governing adsorption show that the inhibitor is physically adsorbed. The results of quantum chemical calculation indicate high feasibility of adsorption of molecular and protonated Lutein, a major component of TEF.
- ***Uwah et al., (2013)*** studied the inhibitive effect of the ethyl acetate extract of ***Uncaria gambir*** on the corrosion of mild steel in 1 M HCl solution has been investigated by weight loss measurement as well as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The presence of this catechin-containing extract reduces remarkably the corrosion rate of mild steel in acidic solution. The effect of temperature on the corrosion behavior of mild steel was studied in the range of 303–333 K. The results from this corrosion test clearly reveal that the extract behaves as a mixed type

corrosion inhibitor with the highest inhibition at 1000 ppm. Surface analyses via scanning electron microscope (SEM) shows a significant improvement on the surface morphology of the mild steel plate. Linearity of Langmuir isotherm adsorptions indicated the monolayer formation of inhibitor on mild steel surface.

- **Loganayagi** ***et al.,(2014)*** investigated the anticorrosion ability of ***Opuntia elatior*** fruit extract was tested on mild steel (MS) in 1 M HCl and H_2SO_4 media by a weight loss method at various temperatures, electrochemical experiments such as potentiodynamic polarization (PDS) and electrochemical impedance spectroscopy (EIS), and surface characterization techniques using scanning electron microscope (SEM) and X-ray diffraction (XRD) studies. The major phytoconsituent, opuntiol, was isolated chromatographically and characterized by infra-red (IR) and nuclear magnetic resonance (NMR) spectroscopic studies. The results of the weight loss studies indicated that inhibition efficiencies were enhanced with an increase in concentration of extract and decreased with a rise in temperature. Adsorption of the extract on a mild steel surface obeyed the Temkin isotherm. Results of PDS revealed the mixed mode inhibitive action, and results of EIS studies confirmed the adsorption of the extract at the metal–solution interface. Further, SEM and XRD studies clearly revealed the film-forming ability of opuntiol on the surface of mild steel. Thus, the anticorrosion activity of *O. elatior* can be related to the presence of opuntiol.
- ***Mehdipour et al., (2014)*** evaluated the inhibition action of ***Aloe Vera leaf*** extract as environmentally friendly inhibitor for the corrosion protection of stainless steel in 1 M H_2SO_4 solution was studied by electrochemical techniques as well as scanning electron microscope. The results of linear polarization and electrochemical impedance spectroscopy proved the effectiveness of Aloe Vera extract as concentration increased. Corrosion inhibition of Aloe extract was also studied by electrochemical noise (EN). Employing EN, different aspects like transient analysis, noise resistant and characteristic charge were characterized. Moreover, a literature review of Aloe Vera characterization using high-performance liquid chromatography and GC-MS was carried out.
- ***Gopal Ji et al.,(2013)*** studied the Inhibition effect of ***Chlorophytum borivilianum*** root extract (CBRE) on mild steel corrosion in 1 M HCl and 0.5

M $_{H2}S_{O4}$ media has been studied using various techniques, viz., weight loss, electrochemical impedance spectroscopy, Tafel polarization, and scanning electron microscopy. Characterization of CBRE is carried out using Fourier transform infrared spectroscopy, UV–visible spectroscopy, and preliminary phytochemical screening tests. Results of the techniques used are in good agreement and reflect the potential of the extract for corrosion inhibition of mild steel in acidic environments.

- ***Umoren et al., (2013)*** investigated the corrosion inhibition effect of date palm **(*Phoenix dactylifera)*** seed extracts for mild steel in 1 M HCl and 0.5 M H_2SO_4 solutions was investigated by weight loss and electrochemical methods. Polarization curves indicate that the extract functions as a mixed inhibitor, affecting both the anodic and cathodic partial reactions of the corrosion process. The date palm seed extract is a better corrosion inhibitor for mild steel in HCl than in a H_2SO_4 solution.
- Alkaloid extracts of leaves (OOL) and bark (OOB) of ***Ochrosia oppositifolia,*** as well as isoreserpiline (ISR), the major alkaloid isolated from OOL and OOB, were carried out by ***Pandian Bothi Raja et al., (2013)*** as potential corrosion inhibitors for mild steel (MS) in 1 M HCl medium. The inhibition properties of these phytoconstituents were studied using electrochemical techniques (potentiodynamic polarization measurements and electrochemical impedance spectroscopy, EIS) and scanning electron microscopy (SEM). The results indicated that these green inhibitors effectively reduced the corrosion rate.
- ***Ramananda Singh (2013)*** analysed the inhibition effect of extract of ***Adhatoda vasica*** in aqueous 0.5 M H_2SO_4 on corrosion of mild steel and its mechanism of the inhibition by weight loss method, potentiodynamic polarisation technique and electrochemical impedance spectroscopy (EIS). The inhibition efficiency of *Adhatoda vasica* on corrosion of mild steel in 0.5 M H_2SO_4 solution increases on increasing in its concentration and decreases with rise in temperature. The results of the Potentiodynamic Polarization measurement reveals that the extract acts as mixed type inhibitor. The adsorption of the on mild steel surface was found to follow Langmuir isotherm. Scanning electron microscopy (SEM) study confirmed the adsorption of the extract molecules on surface of metal.
- The effectiveness of leaves extract of ***Emilia sonchifolia*** and ***Vitex doniana*** as corrosion inhibitors of mild steel in 2.5M HCl medium using gasometric

method at 30°C and 60°C ***(Ilomaekeet al, 2013).*** Adsorption of *Emilia sonchifolia* leaves extract on the surface of the mild steel follows Langmuir, Temkin and Freunlich adsorption isotherm while adsorption of *Vitex donania* leaves extract on the surface of the mild steel obeyed Langmuir and Temkin adsorption isotherm. The adsorption of the inhibitor was through physical means.

- ***Nwosu et al.,(2013)*** investigated the effectiveness of leaf extract of ***Achyranthes aspera* L**. on the corrosion inhibition of mild steel in 0.5 M H2SO4 medium at room temperature using gravimetric technique .The results revealed that the extract can afford a maximum efficiency of 92.3%. *A. aspera* L. extract was adsorbed on the mild steel surface in accordance with Langmuir, Frumkim, and Flory-Huggins adsorption isotherm models. The thermodynamic data inferred that the adsorption of the inhibitor onto the surface of mild steel was spontaneous in nature.
- ***Shivakumar and Mohana (2013)*** obseraved the inhibitive performance of leaf extracts of ***Cinnamoum zeylanicum*** (*CZ*) was tested as natural corrosion inhibitor for mild steel in 0.5 M HCl and 0.5 M H2SO4, respectively by gravimetric and electrochemical techniques. The results indicate that leaf extracts of *CZ* act as an efficient natural corrosion inhibitor in both the acid solutions. The inhibition efficiency was found to increase with increase in *CZ* extracts concentration and decrease with increase in temperature. Polarization measurements showed that the studied inhibitor acts as mixed inhibitor in both the acids with significant reduction of cathodic and anodic current densities. The adsorption characteristics of *CZ* extracts of on mild steel surface was found to obey Langmuir isotherm. The adsorption was through physical means. The electrochemical impedance studies further confirm the formation of an adsorbed film on the mild steel**...**
- ***Mundulea sericea*** leaves (MSLE) as a corrosion inhibitor for mild steel in acidic solution was investigated by mass loss, LPR potentiodynamic polarization 1M HCl and EIS method. The adsorption of MSLE on mild steel surfaces in 1MHCl and 0.5M H2SO4 was found to obey Langmuir and Temkin adsorption isotherms ***(S.Leelavathi, R.Rajalakshmi, NACE CORROSION 2013).***

- ***Benali et al., (2013)*** tested the corrosion and inhibition behaviour of mild steel in sulfuric acid + 5% EtOH in the presence of tannin extract of ***Chamaerops humilis*** plant (LF-Ch) and potassium iodide (KI) using electrochemical methods. It was found that the inhibition efficiency increased with LF-Ch extract concentration. A synergistic effect was observed between KI and extract with optimum of concentration of 100 mg /L LF-Ch extract + 0.025% potassium iodide. Adsorption of extract alone or in combination with potassium iodide on the metal surface obeyed the Langmuir adsorption isotherm and thermodynamic calculations revealed that the adsorption of inhibitor were of chemical nature. According to the authors, the adsorption of LF-Ch extract on the mild steel in aggressive medium leads to the formation of a protective film which grows in thickness and effectiveness with increasing exposure time.
- ***Onuegbu et al., (2013)*** investigated that ***Eupatorium odoratum*** **(E.O)** was utilised as a corrosion inhibitor for mild steel in 1.0M H_2SO_4 acid medium. The weight losses of the mild steel were taken for complete four days, for two temperatures namely 30°C and 60°C. The rates of corrosion of the mild steel was found to increase with increase in concentration of the acid and also decrease with increase in concentration of the *Eupatorium odoratum extract.* The extract afforded a maximum efficiency of 71% at the concentration of 0.5g/l. The activation energy values showed that the *Eupatorium odoratum* extract is physically adsorbed on the mild steel coupons.
- According to ***Raja et al., (2013)***, ***Neolamarckia cadamba*** crude extract (bark, leaves) and its pure alkaloid (3b-isodihydrocadambine) investigated for mild steel corrosion in 1 M HCl medium exhibited excellent inhibition properties at all studied concentration of the inhibitors. Potentiodynamic polarization, electrochemical impedance, scanning electron microscopy, FTIR spectroscopy and molecular modelling were employed for this study. Polarization measurements indicated that these green inhibitors acted through mixed type inhibition. SEM studies evidenced the formation of a protective film over metal surface .According to the authors, FTIR, supported by molecular modelling proved that this shielding effect was caused by alkaloids, particularly 3b isodihydrocadambine.
- ***Hui et al ., (2013)*** reported the corrosion inhibition of mild steel in 1.0 M HCl by the ***Aloes*** **leaves** extract .The investigation was carried out using weight loss,

potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The results show that the inhibition efficiency increases with the increase of the extract concentration. The adsorption of the extract molecules on the steel surface was found to obey Langmuir adsorption isotherm. From the activation energy and other thermodynamic parameters calculated for the inhibition process, strong interaction between inhibitor and mild steel surface was noted.

- ***Olasehinde (2013)*** studied on the effectiveness of acid extract of ***Nicotiana tabacum*** **l**eaves on mild steel in 1M HCl was carried out using weight loss method**.** Experiments were performed for varying immersion period, concentration of the inhibitor and temperature. The inhibition efficiency was found to increase with increase in concentration of *Nicotiana tabacum* leaves extract but decreased with rise in temperature and exposure time. Thermodynamic studies revealed that corrosion inhibition may be due to the spontaneous physical adsorption of the plant constituents on the surface of mild steel. Experimental data was approximated by Langmuir and Temkin adsorption isotherms. Kinetic treatment of the data followed a first order reaction.
- Corrosion inhibition efficiency of dry ***Polyalthia longifolia*** (Asoka tree) leaves in 1N HCl medium was investigated by weight loss method. Inhibition was found to increase with increase in concentration of the extract. Adsorption of extract molecules on mild steel surface obeyed the Langmuir, Temkin, Freundlich adsorption isotherms. The results obtained prove that the leaves of Polyalthia Longifolia act as a good corrosion inhibitor having efficiency of 87% at 1.5% inhibitor concentration ***(Vasudha and Shanmuga priya,2013).***
- Extract of various plants ***(Wrightia tinctoria, Clerodendrum phlomidis, and Ipomoea triloba)*** leaves was investigated by **Patel et al.,(2013)** as corrosion inhibitor for mild steel in 0.5M H_2SO_4 using conventional weight loss, electrochemical polarization, electrochemical impedance spectroscopy and scanning electron microscopic studies. The weight loss results showed that all the plant extracts act as excellent corrosion inhibitors. Electrochemical polarization data revealed the mixed nature of the inhibitors. Scanning electron microscopic studies validated the results obtained from other investigated techniques.

- Inhibition of mild steel corrosion using aqueous extract of **C*ocos nucifera L.*** peduncle in acidic solutions was analysed by mass loss method and electrochemical measurements.The inhibition efficiency was found to increase with increase in concentration, time of immersion and temperature. The adsorption of the inhibitor molecule onto the metal surface was found to obey El-Awady kinetic thermodynamic and Frumkin adsorption isotherm ***(Vijayalakshmi, Rajalakshmi, NACE CORROSION 2013).***
- ***Akalezi et al.,(2013)*** suggested the inhibitive action of ***Petersianthus macrocarpus*** leave extract on corrosion of mild steel in 1M HCl and 0.5M H2SO4 solutions was done using gravimetric, electrochemical impedance and potentiodynamic methods. The inhibition efficiency of the inhibitor increased with increasing extract concentration. Results indicated that the extracts functioned as a good inhibitor in both corrodent solutions. Temperature studies in the range 313-333K reveal increase in inhibition efficiency of the extract with rise in temperature. The authors proposed a mechanism of chemical adsorption. The adsorption characteristics of the inhibitor were found to obey Langmuir adsorption isotherm.**).**
- ***Maduabuchi et al.,(2012)*** observed the adsorption and corrosion inhibiting effect of aqueous extracts of ***Punica granatum*** (PNG) on mild steel in 1 M HCl and 0.5 M H_2SO_4 at 30 ± 1 °C was investigated using gravimetric, electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization techniques. Impedance results indicate that the extract organic matter was adsorbed on the metal/solution interface, while polarization data show that the extract behaved mostly as a mixed-type inhibitor. A theoretical study of the adsorption behavior of some of the components of the crude extracts was carried out in the framework of the density functional theory (DFT).
- ***Oguzie et al., (2012)*** studied the adsorption and corrosion inhibiting effect of acid extracts of ***Piper guineense*** (PG) leaves on mild steel corrosion in 1 M HCl and 0.5 M H_2SO_4 was evaluated using gravimetric, potentiodynamic polarization and electrochemical impedance spectroscopy techniques as well as scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The polarization and impedance results revealed that PG inhibited the cathodic and anodic partial reactions of the corrosion process via

adsorption of the extract organic matter on the metal/solution interface. Density functional theory calculations were performed to model the electronic structures of some extract constituents, including chemisorptive interactions with the Fe surface.

- ***Al-Otaibi et al., (2012)*** analysed the alcoholic extracts of eight plants namely ***Lycium shawii***, ***Teucrium oliverianum***, ***Ochradenus baccatus***, ***Anvillea garcinii***, ***Cassia italica***, ***Artemisia sieberi***, ***Carthamus tinctorius***, and ***Tripleurospermum auriculatum*** grown in Saudi Arabia were studied for their corrosion inhibitive effect on mild steel in 0.5 M HCl media using the open circuit potential (OCP), Tafel plots and A.C. impedance methods. All the plant extracts inhibited the corrosion of mild steel in acidic media through adsorption and act as mixed-type inhibitors.
- ***Loto et al.,(2012)*** reported the corrosion inhibition effect of extracts of ***kola plant (Cola acuminata) and green tea (camellia sinensis)*** in mixed form on the protection of mild steel specimens immersed in sulphuric acid solution was studied at ambient temperature by gravimetric and potential monitoring methods. Extracts of kola plant and green tea in different concentrations and combinations were used as green inhibitors. There was significant reduction in the weight loss and in the corrosion rate of the test samples, particularly at the added extracts concentration of 100% and also at the concentrations of 50 and 25%. The best corrosion inhibition performance for mild steel was obtained using the combined extracts of kola leaf and green tea at100% concentration.
- ***Hui Cang et al.,(2012)*** suggested the inhibition for the corrosion of mild steel in sulphuric acid solution by the extract of ***Stevia rebaudiana*** leaves using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. Inhibition was found to increase with increasing concentration of the leaves extract. The effect of temperature on the corrosion behavior of mild steel in 0.5M H_2SO_4 with addition of extract was also studied.
- The influence of ***Cassia alata (CALE)*** leaves extract on the corrosion inhibition of mild steel in 1M HCl acid solution was studied by ***(Leelavathi & Rajalakshmi 2012)*** using loss electrochemical measurements and surface analytical techniques. Cassia alata leaves adsorbed on the mild steel surface following Langmuir and Temkin isotherms. Electrochemical measurements

confirmed the mixed mode of inhibition. SEM documented the formation of protective layer on the mild steel surface.

- ***Rajalakshmi et al.,(2012)*** analysed the inhibitive properties of Leaf Sheath extract of ***Cocos Nucifera*** for the corrosion of MS were studied using conventional weight loss and electrochemical measures of monitoring corrosion.The results revealed that the Leaf Sheath extract of Cocos Nucifera inhibited the corrosion of Mild steel. The inhibitor was found to function by being adsorbed on the surface of Mild steel. The adsorption of the inhibitor followed the Langmuir and Temkin type adsorption isotherm. The leaf sheath extract of Cocos Nucifera in HCl medium proved to be zero cost inhibitor, eco-friendly,Non-toxic and highly economical.
- ***Hui Cang et al.,(2012)*** *reported the* inhibition for the corrosion of mild steel in sulphuric acid solution by the extract of ***Stevia rebaudiana*** leaves using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. Inhibition was found to increase with increasing concentration of the leaves extract. The effect of temperature on the corrosion behavior of mild steel in 0.5M H_2SO_4 with addition of extract was also studied.
- Several naturally occurring substances were treated as corrosion inhibitors for mild steel in acidic media. An overview of emerging scenario in the frontiers of ecofriendly corrosion inhibitors of plant origin for mild steel was highlighted by ***Rajalakshmi et al.,(2012)***. This review listed the corrosion inhibiting properties of natural products for mild steel in aggressive media.
- The Corrosion inhibition of mild steel in 1 M H_2SO_4 by leaves and stem extracts of ***Sida acuta*** was evaluated by***, Umoren et al.,(2011)*** using chemical (weight loss and hydrogen evolution) and spectroscopic (AAS, FTIR and UV-V) techniques at 30–60ºC. It was found that the leaves and stem extracts of S. acuta inhibited the acid induced corrosion of mild steel.
- ***Vijayalakshmi et al.,(2011)*** reported the inhibitive effect and adsorption properties of petiole extract obtained from destructive distillation of ***cocos nucifera*** for the corrosion of mild steel in 0.5M H_2SO_4 and 1M HCl were evaluated using mass loss, polarization and electrochemical impedance techniques of monitoring corrosion. The results obtained indicate that petiole extract of *cocos nucifera* behaves as good inhibitor for the corrosion of mild

steel in 0.5 M H_2SO_4 and 1M HCl. The electrochemical measurements reveal that the petiole extract behaved like mixed type inhibitor.

- ***Umoren et al.,(2011)*** the Corrosion inhibition of mild steel in MH_2SO_4 by leaves and stem extracts of ***Sida acuta*** using chemical (weight loss and hydrogen evolution) and spectroscopic (AAS, FTIR and UV-V) techniques at 30–60°C. It was found that the leaves and stem extracts of S. acuta inhibited the acid induced corrosion of mild steel.
- The corrosion inhibition of low carbon steel in 1MHCl solution with different concentrations of ***Schinopsis lorentzii*** extract was suggested by ***Husnu Gerengiet et al.,(2011)*** using Tafel extrapolation, linear polarization, and electrochemical impedance spectroscopy (EIS).
- The effect of plant extract of Papaveraceae family ***Argemone mexicana*** is studied for use as a low cost and efficient corrosion inhibitor for mild steel in acidic environment. ***Gobal et al., (2011).*** Weight loss and electrochemical methods are used to study the corrosion. Nearly 80% corrosion inhibition is observed at around 200 mg L^{-1} inhibitor concentration and maximum (92.5%) for 500 mg L^{-1} extract concentration in 1 M HCl. Inhibition mechanism is studied using UV–vis, electrochemical, and surface imaging techniques. This plant extract is the rich source of organic inhibiting molecules as proteins, amino acids, tannins, phenolic compounds, saponins, and flavonoids and nonalkaloids organic compounds such as fused benzene rings, hetero N atom rings, $-OCH_3$, and −OH groups.
- ***Al-Turkustani et al., (2011)*** analysed the inhibitive effect of water and alcoholic extracts of ***Medicago Sative*** (***MS***) on the corrosion of steel in 2.0 M H_2SO_4 containing 10% EtOH has been studied using chemical (weight-loss(ML), hydrogen evolution(HE)), electrochemical (potentiodynamic polarization (PDP) and impedance spectroscopy (EIS)) techniques. Also, scanning electron microscopy (SEM) is used to support the obtained results. The results showed that the inhibition efficiency increases with the increase of ***M. Sative*** (***MS***) concentration. The water and alcholic extracts of ***MS*** plant act as mixed type inhibitors with nearly the same efficiency. The inhibition action of ***M. Sative*** (***MS***) extracts was discussed in terms of their horizontal adsorption on the metal surface. The adsorption follows Langmuir adsorption isotherm.

- The effect of extract of ***Musa paradisiacal*** on corrosion inhibition of mild steel in aqueous 0.5 M sulphuric acid was investigated by ***Ramananda Mayanglambam et al., (2011)*** using weight loss method, potentiodynamics polarisation technique and electrochemical impedance spectroscopy (EIS). The inhibition efficiency is found to increase with increase in concentration of the extract. Polarization measurement indicates that *Musa paradisica* act as mixed type inhibitor.

- ***Ambrish Singh et al.,(2010)*** observed the inhibition of the corrosion of mild steel in hydrochloric acid solution by the seed extract of ***Karanj (Pongamia pinnata)*** using weight loss, electrochemical impedance spectroscopy, potentiodynamic polarization, and linear polarization techniques. Inhibition was found to increase with increasing concentration of the extract.
- ***Kamal, Sethuraman et al.,(2010)*** carried out the inhibition of the corrosion of mild steel in 1M HCl and 1M H_2SO_4 by ***Spirulina platensis*** at different temperatures using by weight loss method, potentiodynamic polarization method, electrochemical impedance spectroscopy measurements and SEM analysis. The results of weight loss studies correlated well with those of impedance and polarization studies.
- ***Vijayalakshmi et al., (2010)*** studied the inhibitory effect of extract obtained from destructive distillation of ***Palmyra palm(Borassus flabellifer Linn.)*** shell on the corrosion of mild steel in 0.5M H_2SO_4 and 1M HCl was investigated using weight loss and electrochemical measurement techniques. The results show that the inhibition efficiency increases with increase of palmyra palm shell extract concentration.
- The efficacy of ***Bakery waste – egg shell*** extract on corrosion mitigation of MS in 0.5M H_2SO_4 solution by weight loss and electrochemical methods evaluated by ***Rajalakshmi et al., (2010)***. The extract was found to exhibit good inhibiting properties offering a maximum of 97.8% efficiency. Electrochemical results reveal the mixed mode of inhibition of to egg shell extract.
- ***Oguzie et al.,(2010)*** evaluated the inhibition of low-carbon-steel corrosion in 1 M HCl and 0.5M H_2SO_4 by extracts of ***Dacryodis edulis (DE)*** using gravimetric and electrochemical techniques. DE extract was found to inhibit the

uniform and localized corrosion of carbon steel in the acidic media, affecting both the cathodic and anodic partial reactions.

- The effectiveness of essential oil of aerial parts of ***Salvia aucheri Boiss. var. mesatlantica*** on the corrosion of steel in 0.5 M H_2SO_4 using electrochemical polarization and weight loss measurements studied by ***Znini* et al.,(2010)**. The adsorption of oil on the steel surface was found to obey Langmuir adsorption isotherm.
- ***El Ouariachi et al.,(2010)*** suggested that ***Rosmarinus officinalis*** essential oil obtained by hydro distillation can be used as a corrosion inhibitor of steel in 0.5 M H_2SO_4. The inhibitive nature was studied using weight loss measurements and electrochemical polarisation methods. Results obtained indicate that the corrosion rate is reduced and *R. officinalis* oil adsorbs on the metal surface and then inhibits corrosion process.
- ***Eddy et al.,(2009)*** evaluated the Inhibitive and adsorption properties of ethanol extract of ***Phyllanthus amarus*** for the corrosion of mild steel in H_2SO_4 using gravimetric, thermometric and gasometric methods. Ethanol extract of *Phyllanthus amarus* leaves is a good adsorption inhibitor for the corrosion of mild steel in H_2SO_4. Thermodynamic consideration indicates that the adsorption of the extract is exothermic and spontaneous.
- ***Badiea et al,(2009)*** observed the effects of ***radish leaves and black cumin*** extracts on the corrosion behaviour of low carbon steel in industrial water in the temperature range of 30-80°c using weight loss technique, potentiodynamic polarization methods and EIS. The inhibition efficiency increases with increase in concentration of inhibitor decrease in efficiency with rise in temperature.Both extracts acted as anodic inhibitors.SEM indicated that the film formed on the metal surface was smooth.The adsorption behaviour obeyed Flory-Huggins isotherm. A better improvement in protection was odtained by black cumin that of radish leaves.
- The inhibitive and adsorption properties of ethanol extract of ***Colocasia esculenta*** for the corrosion of mild steel in H_2SO_4 weight loss, hydrogen evaluation and IR methods of monitoring corrosion was investigated by ***Nnabuk Okon Eddy et al,(2009)***.The results obtained indicated that extract is a good inhibitor. Calculated values of activation energy and inhibition efficiency at 303 and 333k revealed that the mechanism of adsorption extract on the mild

steel surface is physical adsorption. Also the adsorption of the inhibitor on mild steel surface was found to be spontaneous, endothermic and consistent with the assumption of Langmuir adsorption isotherm.

- In this investigation **Karthikaiselvi et al.,(2009)** evaluated the inhibitive effect of acid extract of ***Myristica Frangans*** on mild steel in 1M HCl by weight loss, DC Polarization method and AC impedance spectroscopy. Results indicated that the inhibition efficiency of extract increased with increase in inhibitor concentration and with temperature. The adsorption of extract followed Langmuir adsorption isotherm. Thermodynamic functions have been evaluated from temperature studies. Electrochemical measurements revealed that extract acts as a mixed type inhibitor.
- ***Okafor et al (2008)*** tested The inhibitive action of leaves (LV), seeds (SD) and a combination of leaves and seeds (LVSD) extracts of ***Phyllanthus amarus*** on mild steel corrosion in HCl and H_2SO_4 solutions was studied using weight loss and gasometric techniques. The results indicate that the extracts functioned as a good inhibitor in both environments and inhibition efficiency increased with extracts concentration. Temperature studies revealed an increase in inhibition efficiency with rise in temperature and activation energies decreased in the presence of the extract. A mechanism of chemical adsorption of the plants components on the surface of the metal is proposed for the inhibition behaviour. The adsorption characteristics of the inhibitor were approximated by Temkin isotherm.
- The inhibition of the corrosion of mild steel by ethanol extract of ***Musa sapientum peels*** in H_2SO_4 was investigated by gasometric and thermometric methods. The results of the study reveals that the different concentrations of ethanol extract of *M. sapientum* peels inhibit mild steel corrosion. ***Eddy et al.,(2008).***
- ***Emeka E. Oguzie*** **,(2008)** studied the inhibitive behaviour on mild steel in 2M HCl and 1M H_2SO_4 by leaf extracts of ***Occimum viridis , Telferia occidentalis, Azadirachta indica*** **and** ***Hibiscus sabdariffa*** and extract from the seeds of *Garcinia kola* by gasometric technique at 300 and 60 °C. Inhibition efficiency was found to increase with increase in extracts concentration. Synergistic effects increased the inhibition efficiency in the presence of halide additives.

- Estimation of the effective performance of acid extracts of ***Poultry waste*** (Hen feather) on the corrosion inhibition of mild steel in 0.5M H_2SO_4 at ambient temperature was observed by ***Subhashini et al, (2008).*** Conventional weight loss and electrochemical measurement techniques were used for evaluation. The maximum efficiency was found to be 95.5% for a period of 6 hours with 0.5% concentration of the hen feather extract. Experimental results were fitted to Langmuir adsorption isotherm. Electrochemical studies confirm the inhibitive nature of the hen feather extract and also the mixed nature of the inhibitor.
- The inhibitive action of leaf extracts of ***Sansevieria trifasciata*** on aluminium corrosion in 2 M HCl and 2 M KOH solutions was studied using gasometric technique. Synergistic effects increased the inhibition efficiency in the presence of halide additives. The results indicated that the inhibition efficiency increased with concentration and decreased with increasing temperature. The results were approximated by Freundlich isotherm. ***Oguzie (2007).***
- The inhibitive effect of ethanol extracts of ***Garcinia kola*** for the corrosion of mild steel in 1MH_2SO_4 solutions was studied by hydrogen evolution technique at 30-60°C. It was found that the inhibition efficiency was increased with increasing extract concentration and decreased with temperature. The inhibition efficiency increased on addition of potassium iodide to extract indicating synergism. The experimental data obeyed the Langmuir adsorption isotherm. ***Osabor et al, (2007).***
- ***Subha et al, (2006)*** have evaluated the influence of ***Calendula officinalis*** towards the corrosion of mild steel in 1M HCl by weight loss method and polarization technique. The results showed that the inhibition efficiency of the compound was found to vary with the concentration of the inhibitor, immersion time and temperature. The maximum efficiency 94.67% was found at 0.5% concentration of the inhibitor after 2hours.
- The inhibitive effect of the extract of Khillah **(*Ammi visnaga*)** seeds, on the corrosion of SX 316 steel in 1M HCl solution was determined using weight loss measurements as well as potentiostatic technique by ***El-Etre (2006)***.The studies proved that the inhibition efficiency increases as the extract concentration is increased. The researcher has reported that the negative values for the energy of adsorption indicated the spontaneity of the adsorption process.

- ***Sethuraman et al, (2005)*** investigated the inhibition efficiency of the extract of ***Strychnos nux-vomica*** for the corrosion of mild steel in 1 M sulfuric acid using weight loss test at 303-323 K, electrochemical measurements, and scanning electron microscope. It was found that the inhibition efficiency was increased with increasing extract concentration and decreased with temperature. The possible active ingredient responsible for the anticorrosion effect is identified as brucine which is isolated and screened for the anticorrosion effect using electrochemical studies and quantum chemical studies.
- ***Sethuraman et al, (2005)*** reported the corrosion inhibition effect of ***Datura metel*** extract in acidic solution for mild steel by weight loss and electrochemical techniques. Datura metel showed significant corrosion inhibitive effect in acid medium on mild steel. The adsorption of the inhibitor on the metal surface obeyed the Langmuir and Tempkin adsorption isotherm.The results of A.C. impedence and polarization studies were well correlated with the weight loss method.
- ***Sheyreese M. Vincent et al,(2005)*** analysed the effective environmentally safe inhibitors such as ***green tea .***Green tea extracts contain significant amount of water soluble electrochemically active compounds as well as high concentration of alkaloids,fatty acids and N and O containing compounds.The studies were carried out rapid and convenient zero resistance ammeter(ZRA) technique.They found that both the leaf as well as plant wastes are excellent sources of corrosion inhibitors and can replace a wide variety of current toxix and polluting industrial inhibitors includind tobacco.
- ***Parikh & Joshik et al, (2004)*** were chemically extracted dry leaves of 'Mehndi' (Heena;***Lawsonia intermis***) and 'Babul' (***Acacia Arabica***) with 5% HCl for mild steel. Variable experimental parameters like effect of inhibitor concentration, temperature, immersion period and stirring rate were studied, 1% inhibitor concentration in 5% HCl environment gave 83% and 85% inhibition efficiency respectively.
- The influence of ***jojoba oil*** on the corrosion of iron in 1M HCl had been studied using weight loss and electrochemical polarization method by ***Chetouani et al., (2004).*** It was found that the corrosion inhibition efficiency increased with the concentration of the Jojoba oil to attain 100% inhibition. The effect of temperature on the corrosion behavior of iron indicated that the inhibition

efficiency decreased with the rise of temperature. It was found that the adsorption follows Frumkin isotherm.

- ***Maheswari et al.,*****(2003)** observed the performance of ***Cajanus cajan*** seed extract on the corrosion inhibition of mild steel in 1M HCl. A maximum efficiency of 95.59% was observed at 0.7concentration at 65°C and the efficiency of 92.84% at 0.7 concentration of 5% extract.
- ***Guy D. Davis and Anthony Von Fraunhofer (2003)*** tested the extracts of ***tobacco*** plants as effective corrosion inhibitor in salt water for steel and aluminium and to galvanic couples of these metals with themselves or with Cu. The results indicated that corrosion inhibition efficacy is 96% for steel/Al, 90% for steel/Cu and 79% for Al/Cu. Other measurements such as polarization resistance and visual inspection of immersed specimens individually show similar results.
- ***Rajalakshmi et al., (2002)*** investigated of the performance of acid extract of ***Ficus banghalensis*** bark on the corrosion inhibition of mild steel in 1M HCl and 0.5 M H2SO4 at room temperature. Mass loss, electrochemical polarization and impedence measurements were used. It was found that the inhibitor increased with increase in concentration.
- ***Prithiba et al., (2002)*** reported the corrosion inhibition effect of ***Ervatamia Coronaira*** leaves extract in 1M HCl and 0.5M H_2SO_4 for mild steel by weight loss and electrochemical techniques .The effectiveness of the plant extracts could be attributed to the presence of indole alkaloid.
- ***Manohari and Rajalakshmi et al*****.,(2001)** determined the effective performance of extracts of ***Psidium gujava*** (bark) and ***Callistemon*** (leaves) for mild steel in 1M HCl. The extracts were effective at high concentration and at room temperature. The polarization curves showed as of mixed type inhibitor.
- **Sethuraman *et al,*(2001)** observed the effect of ***Solanum trilobatum*** extract on the corrosion of mild steel in 5% HCl by weight loss measurement. It was found that inhibition efficiency increased with increase in concentration.
- The effect of ***cashew*** juice extract on corrosion inhibition of mild steel in HCl was investigated by ***Loto and Mohammed et al.,*****(2000).** Weight loss and potential measurement techniques were used. The extracts from bark provided no inhibition while nut-juice extract accelerate corrosion. Apple juice extracts

at a concentration of 2ml/100ml of 0.1M HCl gave good results of corrosion inhibition.

- Aqueous extracts of Henna ***(Lawsonia inermis)*** leaves powder were evaluated as corrosion inhibitors for steel and commercial aluminum in saline, acidic and alkaline waters by ***Al-Sehaibani (2000).*** Weight loss measurements showed that the extracts can inhibit efficiently the corrosion of steel for 37days in HCl with 96% efficiency & for aluminum in NaOH up to 99.8% while no inhibition occurred for steel or aluminum in NaCl solutions.
- ***Minhaj et al.,*****(1999)** investigated the inhibitive effects of aqueous extracts of ***Eucalyptus***(leaves), ***Hibiscus*** (flowers), ***Agarius*** on the corrosion of mild steel for cooling systems using tap water by weight loss and polarization methods. The results showed that all the plant extract inhibit corrosion of mild steel and their inhibitive efficiencies were in the order: Agaricus (85%) > Hibiscus > Eucalyptus (74%).
- Corrosion inhibition of mild steel by the extracts of ***Pongamia glabra and Annona squamosa*** in HCl and H_2SO_4 media was studied by ***Sakthivel et al., (1999).*** Weight loss, polarization, hydrogen permeation and impedance studies were carried out at various temperatures. Weight loss measurement showed that the maximum inhibition efficiency was found to be 97% at 1% concentration. Polarization studies inferred that, Pongamia glabra and Annona squamosa were mixed and cathodic inhibitor respectively.
- ***Smita and Mehta et al.,*****(1998)** suggested that the acid extracts of ***Calotropis giganta*** latex inhibited the acid corrosion of mild steel effectively at 0.08% and the inhibition decreased with decrease in concentration. Electrochemical studies showed that inhibitor was mixed type and effective one.
- ***Farooqi et al.,*** **(1997)** investigated the inhibitive effects of aqueous extracts of ***Jasminum auriculatum*** (leaves), ***Monocardia charantia*** (fruits) & ***Hibiscus*** **(**flower) on the corrosion of mild steel for cooling water system, using 3% NaCl water. The inhibition efficiencies of the extracts were compared with that of HEDP. All the extracts were found to inhibit corrosion and their inhibition efficiencies were HEDP(93%), *Jasminum auriculatum*(80%), *Monocardica charantia*(79%) and Hibiscus(76%).Polarization measurements shows that extract of jasmine was anodic while *Monocardia charantia* and Hibiscus were

found to be cathodic. Impedance measurements show that the complex formation tendency of the extracts.

- ***Farooqi et al., (1997)*** reported the corrosion inhibitive nature of ***Cordia latifolia* and *Curcumin*** for mild steel in cooling systems. Their inhibition efficiencies were compared with that of hydroxy ethylidene 1-1 diphosphonic acid. The blow down of the cooling system is also analysed for environmental 18 factors.

MATERIALS & METHODS

3.MATERIALS AND METHODS

In any research work the materials and methods adopted are the aspects, which decide and determine qualitatively and quantitatively the outcome of the research. In the present investigation, efforts have been taken to study the inhibitive action of the ***Clytostoma callistegioides*** *(flower and leaves)* extract as corrosion inhibitor for mild steel (MS) in 1M HCl. The design of the present investigation consisted of the following steps.

3.1.SELECTION OF SAMPLE

Mild steel is one of the most important widely used engineering materials particularly for the structure and automobile applications due to low cost and easy availability. MS suffers from severe corrosion in aggressive environment, which needs to be protected. Hence the study of corrosion inhibitor of MS in aqueous aggressive media is the subject of pronounced technological significance. Thus the investigation was carried out using mild steel.

3.2.PREPARATION OF SAMPLE

Regular sample of area 1x5 cm^2 have been cut from a large sheet of mild steel. A hole was drilled in the specimen, mechanically polished, degreased, washed with de ionized water then thoroughly dried and kept in desiccators for weight loss tests. The mild steel specimens used in the following percentage elemental of composition as shown in table.

C- 0.089%	S-0.019%	Mo-0.021%
Mn-0.215%	Fe-99.58%	P-0.017%

3.3.TEST MEDIUM

Acid solutions are widely used in chemical laboratories and in several industrial processes such as pickling, acid cleaning, acid de-scaling and oil wet cleaning etc. among the commercially available acids hydrochloric acid and sulphuric acid are used in nearly all industries and is vital commodity in our national economy. Experiments were performed in 1m HCl. The acid used was LR grade.

3.4.SELECTION OF INHIBITOR

The choice of the inhibitor is based on the following consideration,

- ✓ Less expensive
- ✓ Possess no threat to the environment
- ✓ Non-toxic
- ✓ Easily available
- ✓ Bio-degradable
- ✓ Low cost
- ✓ Eco-friendly

3.5.PREPARATION OF THE INHIBITOR

In the present investigation we have selected eco-friendly plant extract of ***Clytostoma callistegioides*** *(flower and leaves)* studies were done separately. The extract was prepared by refluxing 25g of leaves and flowers in 500ml of HCl for three hours and kept overnight for cooling. The cooled extract was filtered and made up to 500ml with 1M HCl to get 5% extract of inhibitor.

3.6.PHYTOCHEMICAL SCREENING

Phytochemical examinations were carried out for all the extracts as per the standard methods.

1. Detection of alkaloids: Extracts were dissolved individually in dilute Hydrochloric acid and filtered.

a) Mayer's Test: Filtrates were treated with Mayer's reagent (Potassium Mercuric Iodide). Formation of a yellow coloured precipitate indicates the presence of alkaloids.

b) Wagner's Test: Filtrates were treated with Wagner's reagent (Iodine in Potassium Iodide). Formation of brown/reddish precipitate indicates the presence of alkaloids.

c) Dragendroff's Test: Filtrates were treated with Dragendroff's reagent (solution of Potassium Bismuth Iodide). Formation of red precipitate indicates the presence of alkaloids.

d) Hager's Test: Filtrates were treated with Hager's reagent (saturated picric acid solution). Presence of alkaloids confirmed by the formation of yellow coloured precipitate.

2. Detection of carbohydrates: Extracts were dissolved individually in 5 ml distilled water and filtered. The filtrates were used to test for the presence of carbohydrates.

a) Molisch's Test: Filtrates were treated with 2 drops of alcoholic α-naphthol solution in a test tube. Formation of the violet ring at the junction indicates the presence of Carbohydrates.

b) Benedict's Test: Filtrates were treated with Benedict's reagent and heated gently. Orange red precipitate indicates the presence of reducing sugars.

c) Fehling's Test: Filtrates were hydrolysed with dil. HCl, neutralized with alkali and heated with Fehling's A & B solutions.Formation of red precipitate indicates the presence of reducing sugars.

3. Detection of glycosides: Extracts were hydrolysed with dil. HCl, and then subjected to test for glycosides.

a) Modified Borntrager's Test: Extracts were treated with Ferric Chloride solution and immersed in boiling water for about 5 minutes. The mixture was cooled and extracted with equal volumes of benzene. The benzene layer was separated and treated with ammonia solution. Formation of rose-pink colour in the ammonical layer indicates the presence of anthranol glycosides.

4. Legal's Test: Extracts were treated with sodium nitropruside in pyridine and sodium hydroxide. Formation of pink to blood red colour indicates the presence of cardiac glycosides.

5. Detection of saponins

a) Froth Test: Extracts were diluted with distilled water to 20ml and this was shaken in a graduated cylinder for 15 minutes. Formation of 1 cm layer of foam indicates the presence of saponins.

b) Foam Test: 0.5 gm of extract was shaken with 2 ml of water. If foam produced persists for ten minutes it indicates the presence of saponins.

6. Detection of phytosterols:

a) Salkowski's Test: Extracts were treated with chloroform and filtered. The filtrates were treated with few drops of Conc. Sulphuric acid, shaken and allowed to stand. Appearance of golden yellow colour indicates the presence of triterpenes.

b) Libermann Burchard's test: Extracts were treated with chloroform and filtered. The filtrates were treated with few drops of acetic anhydride, boiled and cooled. Conc. Sulphuric acid was added. Formation of brown ring at the junction indicates the presence of phytosterols.

7. Detection of phenols

Ferric Chloride Test: Extracts were treated with 3-4 drops of ferric chloride solution. Formation of bluish black colour indicates the presence of phenols.

8. Detection of tannins

Gelatin Test: To the extract, 1% gelatin solution containing sodium chloride was added. Formation of white precipitate indicates the presence of tannins.

9. Detection of flavonoids

a) Alkaline Reagent Test: Extracts were treated with few drops of sodium hydroxide solution. Formation of intense yellow colour, which becomes colourless on addition of dilute acid, indicates the presence of flavonoids.

b) Lead acetate Test: Extracts were treated with few drops of lead acetate solution. Formation of yellow colour precipitate indicates the presence of flavonoids.

10. Detection of proteins and aminoacids

a) Xanthoproteic Test: The extracts were treated with few drops of conc. Nitric acid. Formation of yellow colour indicates the presence of proteins.

b) Ninhydrin Test: To the extract, 0.25% w/v ninhydrin reagent was added and boiled for few minutes. Formation of blue colour indicates the presence of amino acid. **(Prashant Tiwari ,et al, Jan-March 2011)**

3.7.TECHNIQUES EMPLOYED

- Mass loss methods
- Electrochemical measurement

3.8.Mass loss methods

It is one of the oldest techniques of monitoring corrosion rate and is carried out by exposing the weighed metal coupons in the test media for a period of time. It is then removed and weighed. The weight loss obtained for the coupons are then measured.

In the current study per weighed coupons were immersed in triplicate with the help of glass hook into a beaker containing 100ml of 1 M HCl acid with and without inhibitor for a particular period of time. The coupons are then washed, dried and reweighed. The average weight loss of coupons was recorded. Varying the parameters such as concentration, time of immersion and temperature the experiments were conducted

- Concentration (0.1% - 0.7%)
- Time of immersion (1/2 h, 1h, 3h, 6h, 12h & 24h)
- Temperature (313K-353K)

3.8.1.Determination of corrosion rate

Many expressions are available to express the corrosion rate. The widely used expression is measured in milli inches per year using formula,

$$\mathbf{C.R\ (mpy) = 543 \times W / D \times A \times T}$$

Where,

W-Weight loss in g

D-Density of mild steel in g/cm^2

A-Area of the sample in cm^2

T-Exposure time in hours

3.8.2.Determination of percentage of inhibition and surface coverage

The percentage of inhibition efficiency and surface coverage were calculated by using the following equation,

$$\mathbf{I.E\ (\%) = w_o - w/w_o \times 100}$$

$$\boldsymbol{\theta} = \mathbf{w_o - w/w_o \times 100}$$

Where,

w_o - corrosion rate without inhibitor in g

w – Corrosion rate with inhibitor in g

Determination of thermodynamic parameters,

The change in free energy (ΔG) of adsorption of the inhibitors can be calculated by using the following equation (Abdel.A and Saied.A., 1981)

$$\mathbf{Log\ C = [\log \theta / (1-\theta)] - \log B}$$

Where,

$\text{Log } B = - 1.74 - (\Delta G / 2.303\ RT)$

θ is the surface coverage, C is the concentration of inhibitor, and R is the gas constant 8.314 J/mol, T is the temperature in K

The value of enthalpy of adsorption ΔH and entropy of adsorption ΔS were obtained from the basic thermodynamic equation (I.E) Gibbs Helmholtz equation

$$\Delta G = \Delta H - T\Delta S$$

A plot of ΔG versus T will be a straight line with intercept ΔH and slope ΔS.

3.8.3.Adsorption isotherm

Corrosion inhibition is a surface process with specific adsorption of inhibitor on the metal surface. In recent years, attempts have been made to understand the nature of interaction between the inhibitor and metal surface in term of adsorption isotherm. The knowledge of the adsorption behavior of the inhibitor is important for definition of its active mechanism. The dependence of surface coverage on concentration is through the following adsorption isotherms.

Langmuir [log (θ / 1-θ) Vs log C]

Temkin (θ Vs log C)

3.8.4.Activation energy (E_a)

The activation energy at different concentration of the inhibitor at various temperatures was determined by plotting log CR Vs 1/T. (Arrhenius plot). From the slope of the plot activation energy (E_a) was calculated using the following formula.

E_a = -2.303 x R x slope of the Arrhenius plot

Where,

R is the gas constant 8.314 J/mole

3.8.5. Activation Parameters

An alternative formulation of Arrhenius equation is

$$CR = (RT/ Nh)\exp(\Delta Sa/ R)\exp(\Delta Ha/ R)$$

Where,

h is Planck's constant

N is Avagadro number

ΔSa is entropy of activation

ΔHa is enthalpy of activation

A plot of log (CR/T) Vs 1/T gave a straight line with a slope of - ΔHa /2.303R and an intercept of log(R/Nh + ΔSa/2.303R) from which the values of ΔHa and ΔSa were calculated.

3.10.ELECTROCHEMICAL METHOD

3.10.1.Polarization techniques

Electrochemical studies were carried out using conventional three electrode cell with large area of platinum foil as counter electrode saturated calomel electrode (SCE) as reference electrode and sample was as working electrode. Electrochemical measurements was done by using electrochemical analyser solatron.

Before starting the measurements the electrode potential was allowed to stabilize for 30 minutes. Polarization studies were conducted at a scan rate of 2mV/sec from -0.1 to -1mV with respect to the corrosion potential in the presence and absence of the inhibitor. 1 sq.cm.of polished mild steel surface was exposed and the electrochemical studies are carried out at 303K.

3.10.2.Tafel plot

In the Tafel plot technique, a controlled scan can be applied, extending in both the anodic and the cathodic directions of corrosion potentials for a few hundred milli volts. The linear region of the plot (applied potential Vs log current) is projected to intersect. This defines corrosion current (I_{corr}) and the corrosion potential (E_{corr}) and the slope of the linear region is the Tafel slopes (ba and bc).

The inhibitor efficiency was calculated using the following equation,

$$\mathbf{I.E\ (\%) = \frac{I_{corr}\ (blank) - I_{corr}\ (inhibited)}{I_{corr}\ (blank)} *100}$$

I.E from LPR technique

$$\textbf{I.E (\%)} = \frac{\mathbf{R_p(inhibited) - R_p(blank)}}{\mathbf{R_p(inhibited)}} \mathbf{*100}$$

Where,

R_p (inhibited) and R_p (blank) are linear polarization resistance in the presence and absence of the inhibitor respectively.

3.10.3.Impedance spectroscopy

In this method an AC signal of 5-10mV of frequency 10KHz to 10MHz is applied to the system. Impedance date can be presented in the form of Nyquist or Bode plot. From the data, the R_{ct} and Cdl are obtained. The I.E can be calculated using the equation,

$$\textbf{I.E (\%)} = \frac{\mathbf{R_{ct}(inhibited) - R_{ct}(blank)}}{\mathbf{R_{ct}(inhibited)}} \mathbf{*100}$$

R_{ct} (inhibited) and R_{ct} (blanck) are charge transfer resistance in the presence and absence of the inhibitor respectively. With the help of the double layer capacitance $Cdl_,$ θ can be calculated using the equation,

$$\boldsymbol{\theta} = \mathbf{1} - \frac{\mathbf{C_{dl}\ (inhibited)}}{\mathbf{C_{dl}\ (blank)}}$$

Where,

C_{dl} (inhibited) and C_{dl} (blank) are the double layer capacitance in the presence and absence of the inhibitor respectively.

3.11.SURFACE ANALYTICAL TECHNIQUES

3.11.1.FTIR technique

The qualitative aspects of infrared spectroscopy are one of the most important powerful attributes of this diverse and versatile analytical technique. In order to indentify the presence of plant constituents in the extract and that absorbed on the metal surface, FTIR technique was followed. The metal specimens were immersed in

100ml of the test solution with optimum 0.45% concentration of the both inhibitors for 24hrs. it was then dried with acetone and absorbed materials were carefully scratched and the power was taken for FTIR analysis. The powder obtained by evaporating the extract on a water bath was also subjected to FTIR analysis.

FT-IR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample and is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular finger prints of the sample. Like a finger print no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. FTIR studies are carried out to characterize the functional group present on the mild steel.

3.11.2.OPTICAL ELECTRON MICROSCOPE

Surface morphology of the specimens with and without inhibitors was studied using an optical electron microscopic method. The specimens were immersed in 100ml of test solution containing 0.45% concentration of the inhibitor and blank solution for 3 hours. Then they were removed and quickly rinsed with water, well dried and finally analyzed through Carl Zeiss optical electron microscope.

Optical electron microscope deals with the examination of materials by optical microscopy are essential in order to understand the relationship between properties and microstructure. Metallography is the study of metals by optical examination. This is most commonly done using a conventional light microscope. Structures which are coarse enough to be discernible be the naked eye is termed macrostructures. Those which require magnification to be visible are termed microstructures.

RESULTS & DISCUSSION

4.RESULTS AND DISCUSSION

The quantitative data obtained from the thesis entitled “**Adsorption and Corrosion Inhibition of *Clytostoma callistegioides* (leaf & flower extracts) on Mild Steel in 1M HCl solution** ” are presented and discussed in the light of the objectives set forth.

A concise summary of literature show that in acid solution the prime features of the corrosion of mild steel are rapid corrosion without the formation of a passive layer of corrosion products and cathodic reaction comprising mainly of hydrogen evolution. To control corrosion process on the mild steel, many methods are available. Among this, one of the most appropriate methods is to use of inhibitors. In this direction the present study has been conducted to explore the inhibition efficiency that can be afforded by ***Clytostom callistegioides* (leaf & flower)** extract in acid medium. The inhibitive actions of inhibitors are well demonstrated from the overall results.

The aim of the proposed investigation was to study the dissolution behaviour of steel so as to explore the optimum concentration of the inhibitor for maximum inhibition efficiency using weight loss measurements and electrochemical measurements such as

- ❖ Mass loss measurements
- ❖ Electrochemical measurements
    - Tafel intercept method
    - Linear polarization method
    - Electrochemical impedance spectroscopy

This study was conducted to evaluate the efficacy of acid extracts of ***Clytostom callistegioides* (leaf & flower)** on MS corrosion in acid medium by weight loss method .The results pertaining to this attempt is also listed and discussed.

Efforts were also made to analyze the surface of MS with absence and presence of the investigated inhibitors by **optical electron microscope**. To confirm, the adsorptive behaviour of the current inhibitors, studies were done to analyze the constituents present on MS surface after exposure to the inhibitor by **FTIR technique**.

4.1CHARACTERIZATION OF CCL & CCF EXTRACTS

4.1.1.PHYTOCHEMICAL SCREENING TEST

Phytochemical screening test were conducted as per the mentioned in Material & Methods. Result of phytochemical screening is presented in the table1. The data presented in the table 1 reveal the presence of phytochemicals such as,

TABLE 1 PHYTOCHEMICAL SCREENING OF CCL & CCF

PHYTOCONCONSTITUENTS	CCL	CCF
Phenol	+	+
Saponin	+	+
Tannin	+	+
Glycosides	-	-
Fatty acids	+	+
Flavanones	+	+
Carbohydrate	-	-

+ Present , - Absent

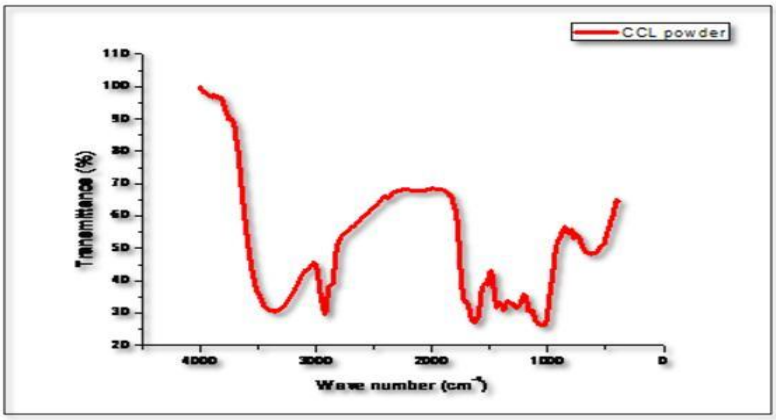
4.1.2. FT-IR SPECTRAL ANALYSIS

FT-IR spectral data of the powdered plant extract are presented in the figure1 (a&b). And the values of frequencies are listed in the table for CCL & CCF

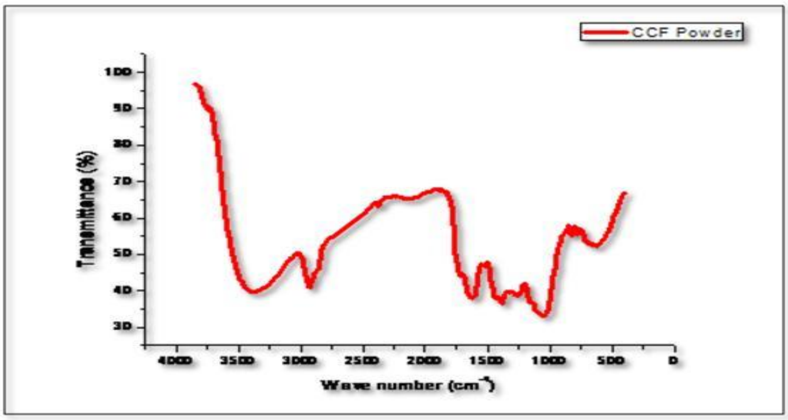
TABLE 2: FT-IR SRECTRAL RESULTS FOR CCL & CCF

POWDERED PLANT MATERIAL CCL			**POWDERED PLANT MATERIAL CCF**		
Frequency cm^{-1}	**Assignment**	**Functional group**	**Frequency cm^{-1}**	**Assignment**	**Functional group**
3356	OH stretch	Alcohol	3371	OH stretch	Alcohol
2924	C-H stretch	Alkenes	2924	C-H stretch	Alkenes
1627	C=C Stretch	Alkenes	1627	C=C Stretch	Alkenes
1527	C–C stretch (in–ring)	Aromatic	1442	C-C in ring	Aromatic
1033	C–H rock	Aliphatic amines	1257	C-N Stretch	Aliphatic
601	≡C-H bending	Alkynes	825	γ -Fe_2O_3	-

FIGURE 1



1a:FT-IR spectrum of CCL powder



1b: FT-IR spectrum of CCF powder

4.3. MASS LOSS METHOD

Mass loss measurements were carried out for mild steel both in the absence and presence of acid extracts of leaf & flower of ***Clytostom callistegioides***. The experimental results have been evaluated on the following parameter,

- Effect of concentration of inhibitor
- Impact of period of immersion
- Role of temperature

4.3.1. MASS LOSS METHOD OF MS CORROS ION IN THE PRESENCE CCL EXTRACT IN 1M HCl

4.3.1.1 EFFECT OF CONCENTRATION OF CCL ON MS/HCl

The mass loss method of monitoring corrosion rate and IE is useful owing to its simple applications and good reliability**. Figure 2** and **Table 3** show the corrosion rate values of MS in both 1 M HCl solutions without and with different concentrations of CCL extract at 298K.Analysing the data presented in **Table 3** it is noted that inhibition efficiency increases with the increase of concentration of the extract. Maximum I.E 96.24% for CCL extract was achieved at 0.7%.A further increase in concentration of CCL does not cause any appreciable change in performance of CCL. This may be due to the reason that the total surface coverage is accomplished by the said concentration and beyond that, any further addition will not yield any increase in the I.E. At constant temperature the I.E increases with increase in concentration of the extract, explained on the basis of increased adsorption of the compound on the metal surface.

The increase in inhibitive action with the increase in concentration of the inhibitor can be ascribed to the blocking of active sites on metal surface. The active polar sites form a monolayer on the surface of mild steel. At any instant a fraction of θ of the metal surface is covered by the inhibitor molecules and uncovered fraction (1- θ) reacts with acid as it does in the absence of the inhibitor. At all test durations 0.7% extract showed maximum efficiency. This behaviour may be attributed to the increase of the surface coverage (θ) by the adsorption of the extract on the mild steel surface.

4.3.1.2. IMPACT OF PERIOD OF IMMERSION OF MS/HCl/CCL

Analysing the data presented in **Table 3**, as the concentration of CCL extract increases, the corrosion rate decreases for all periods of immersion. Maximum I.E was found to be 96.24% at 6 hours immersion time. However the I.E is stabilized at 12 hours furnishing around 90.45%. This result indicates that the studied extract functioned well at longer period of immersion. These finding also highlighted the stability of the extract at longer period of immersion in 1M HCl medium. The corrosion inhibition can be attributed to the adsorption of the inhibitor at the steel/HCl solution interface. A value of I.E with respect to time of immersion is graphically represented in the **Figure 3**.

4.3.1.3. ROLE OF TEMPERATURE ON CORROSION OF MS/CCL/HCl

Temperature can influence the interaction between the mild steel and the acid in the presence and absence of CCL extract. To evaluate the stability of adsorbed layer /film of inhibitor on MS surface ,as well as activation parameters of corrosion process of steel in 1M HCl acid medium the mass loss measurements were carried out from

303K-353Kin the presence and absence of CCL extract at optimum concentration during the ½ hour immersion time . The aim was to evaluate the thermodynamic stability of the adsorbed film of inhibitor on mild steel. Taking a critical look on the table 2 the result indicates that the I.E increases with the increase in temperature upto 323K (91.22%).After 323K there is a slight decline in the I.E. However I.E is stabilized at 323K (92.52%) and then decreased around 85.52% at 363K.This practically shows that the rise in temperature increases the inhibitive process upto 313K (93.95%) and then at higher temperature I.E is slightly declined and stabilized. This may be ascribed due to the following reasons: The adsorption and desorption of inhibitive molecules continuously occur at the metal surface and equilibrium exists between these two molecules processed at particular temperature. With the increase in temperature the equilibrium between the adsorption and desorption processes are shifted, leading to higher desorption rate than adsorption. The desorption at elevated temperature thus exposes the metal surface to further attack.

TABLE 3-ROLE OF CONCENTRATION OF CCL EXTACT ON MS IN 1M HCl

S.No	Conc (%)	Corrosion rate and inhibition efficiency											
		½ h		1 h		3 h		6 h		12 h		24 h	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	0.1	247	45.28	132	77.53	231	77.56	180	81.9	58	68.32	58	58.76
2.	0.2	238	47.17	123	79.08	213	79.35	101	89.9	41	77.86	31	61.43
3.	0.3	230	49.05	106	82	113	88.99	99	90.1	29	84.35	24	69.93
4.	0.4	221	51.04	89	84.78	99	90.36	50	95.01	26	85.88	23	71.67
5.	0.5	204	55.01	59	89.85	90	91.19	49	95.03	20	88.74	19	75.82
6.	0.6	119	73.58	55	90.02	79	92.29	47	95.29	19	89.31	19	76.26
7.	0.7	110	75.47	46	90.57	55	94.63	37	96.24	17	90.45	18	77.34

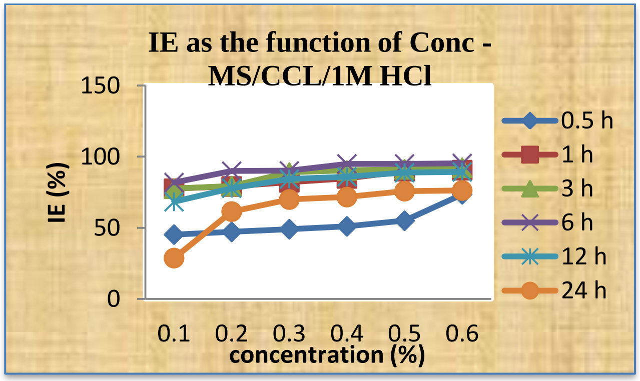


FIGURE 2

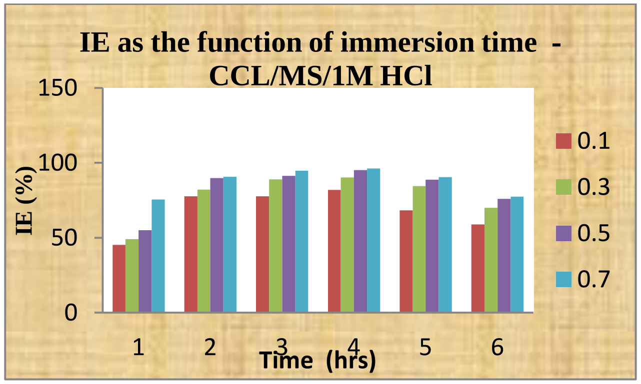


FIGURE 3

TABLE 4 -ROLE OF TEMPERATURE ON CORROSION OF MS IN THE PRESENCE OF VARIOUS CONCENTRATION OF CCL EXTRACT IN 1M HCl

S.No	Conc (%)	Corrosion rate and inhibition efficiency											
		303K		313K		323K		333K		353K		363K	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	0.1	247.35	45	1287.95	54	1953	48.07	887	48	9203	53.61	100098	76.18
2.	0.2	238.82	47	870.00	69	1543	58.96	852	50	8111	59.11	9032	78.70
3.	0.3	230.29	49	511.77	81	8444	77.55	673	60.50	6294	68.27	8367	80.27
4.	0.4	221.76	51	426.47	84	639	82.99	648	62	5706	71.24	7778	81.65
5.	0.5	204.70	55	324.12	88	588	84.36	631	63	4631	76.66	7215	82.98
6.	0.6	119.41	73	213.23	92	460	87.76	622	63.5	3787	80.91	6311	85.11
7.	0.7	110.88	75	170.59	93	281	92.52	614	64	3062	84.57	6141	85.52

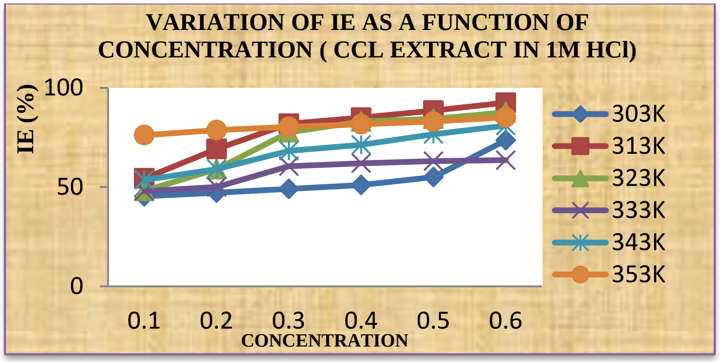


FIGURE 4

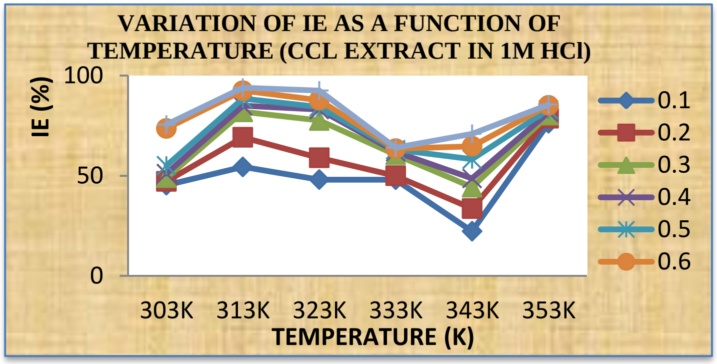


FIGURE 5

4.3.2MASS LOSS METHOD OF MS CORROSION IN THE PRESENCE OF CCF EXTRACT IN 1M HCl

4.3.2.1.EFFECT OF CONCENTRATION OF CCF ON MS/HCl

The weight loss method of monitoring corrosion rate and IE is useful owing to its simple applications and good reliability**.** **Figure 6** and **Table 5** show the corrosion rate values of MS in both 1 M HCl solutions without and with different concentrations of CCF extract at 298K.Analysing the data presented in **Table 5** it is noted that inhibition efficiency increases with the increase of concentration of the extract. Maximum I.E 96.24% for CCF extract was achieved at 0.7%.A further increase in concentration of CCF does not cause any appreciable change in performance of CCF. This may be due to the reason that the total surface coverage is accomplished by the said concentration and beyond that, any further addition will not yield any increase in the I.E. At constant temperature the I.E increases with increase in concentration of the extract, explained on the basis of increased adsorption of the compound on the metal surface.

The increase in inhibitive action with the increase in concentration of the inhibitor can be ascribed to the blocking of active sites on metal surface. The active polar sites form a monolayer on the surface of mild steel. At any instant a fraction of θ of the metal surface is covered by the inhibitor molecules and uncovered fraction (1- θ) reacts with acid as it does in the absence of the inhibitor. At all test durations 0.7% extract showed maximum efficiency. This behaviour may be attributed to the increase of the surface coverage (θ) by the adsorption of the extract on the mild steel surface.

4.3.2.2. IMPACT OF PERIOD OF IMMERSION OF MS/HCl/CCF

Analysing the data presented in **Table 5**, as the concentration of EH extract increases, the corrosion rate decreases for all periods of immersion. Maximum I.E was found to be 96.24% at 6 hours immersion time. However the I.E is stabilized at 12 hours furnishing around 90.45%. This result indicates that the studied extract functioned well at longer period of immersion. These finding also highlighted the stability of the extract at longer period of immersion in 1M HCl medium. The corrosion inhibition can be attributed to the adsorption of the inhibitor at the steel/HCl solution interface. A value of I.E with respect to time of immersion is graphically represented in the **Figure 6**.

4.3.2.3.ROLE OF TEMPERATURE

Temperature can influence the interaction between the mild steel and the acid in the presence and absence of CCF extract. To evaluate the stability of adsorbed layer /film of inhibitor on MS surface ,as well as activation parameters of corrosion process of steel in 1M HCl acid medium the weight loss measurements were carried out from 303K-353Kin the presence and absence of CCF extract at optimum concentration during the ½ hour immersion time . The aim was to evaluate the thermodynamic stability of the adsorbed film of inhibitor on mild steel. Taking a critical look on the table 2 the result indicates that the I.E increases with the increase in temperature upto 323K (91.22%).After 313K there is a slight decline in the I.E. However I.E is stabilized at 333K & 343K (84%) and then increased around 90% at 363K.This practically shows that the rise in temperature increases the inhibitive process upto 313K(91.22%) and then at higher temperature I.E is slightly declined and stabilized. This may be ascribed due to the following reasons: The adsorption and desorption of inhibitive molecules continuously occur at the metal surface and equilibrium exists between these two molecules processed at particular temperature. With the increase in temperature the equilibrium between the adsorption and desorption processes are shifted, leading to higher desorption rate than adsorption. The desorption at elevated temperature thus exposes the metal surface to further attack.

TABLE 5 :ROLE OF CONCENTRATION OF CCF EXTACT ON MS IN 1M HCl

S.No	Conc (%)	Corrosion rate and inhibition efficiency											
		½ h		1 h		3 h		6 h		12 h		24 h	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	0.1	392	22.03	213	21.87	240	62	63	47.95	39	75.38	133	8.49
2.	0.2	332	33.89	183	32.81	119	81	53	56.14	33	79.65	108	26.21
3.	0.3	230	54.23	115	57.81	113	82	49	59.07	25	84.25	86	41.14
4.	0.4	170	66.10	110	59.37	103	84	48	60.24	23	85.67	72	50.60
5.	0.5	153	69.49	106	60.94	92	85	44	63.75	20	87.42	70	52.06
6.	0.6	93	81.35	102	62.50	78	87	27	77.19	19	88.30	43	70.18
7.	0.7	85	83.05	101	62.86	68	89	18	84.80	15	90.27	32	78.03

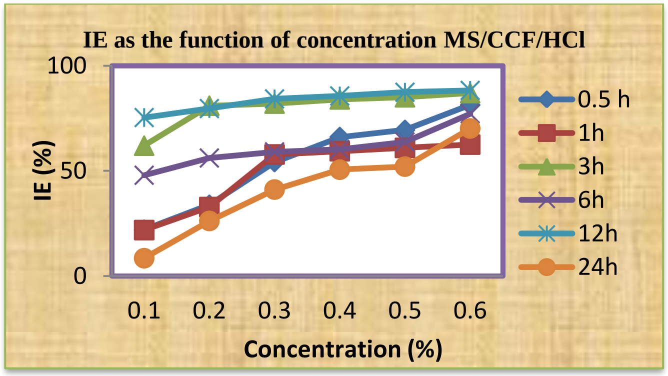


FIGURE 6

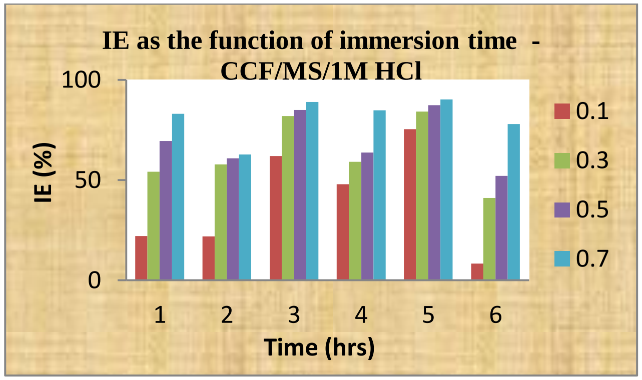


FIGURE 7

TABLE 6 :ROLE OF TEMPERATURE ON CORROSION OF MS IN THE PRESENCE OF VARIOUS CONCENTRATION OF CCF EXTRACT IN 1M HCl

S.No	Conc (%)	Corrosion rate and inhibition efficiency											
		303K		313K		323K		333K		353K		363K	
		CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
1.	0.1	392	22.03	409	14	1526	57	1927	48.89	9203	53.61	12726	60.06
2.	0.2	332	33.89	247	48	810	77	1467	61.08	8111	59.11	6576	79.36
3.	0.3	230	54.23	196	59	725	80	1262	66.52	6294	68.27	5245	83.54
4.	0.4	170	66.10	145	70	639	82	1160	69.23	5706	71.24	5126	84.1
5.	0.5	153	69.49	127	73	503	86	989	73.37	4631	76.66	3974	87.53
6.	0.6	93	81.35	119	75	452	87	614	83.71	3787	80.91	3309	89.61
7.	0.7	85	83.05	110	77	375	91.22	588	84.39	3062	84.57	2797	90

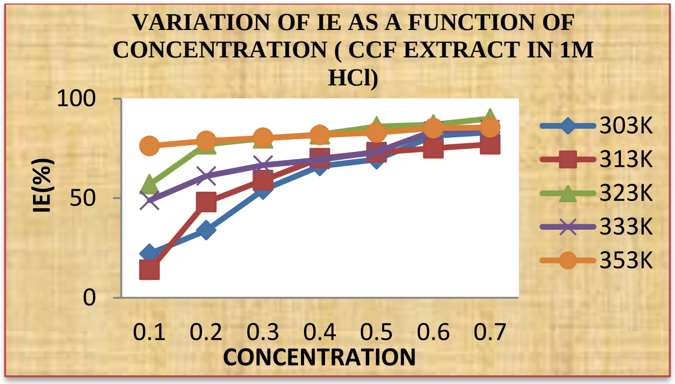


FIGURE 8

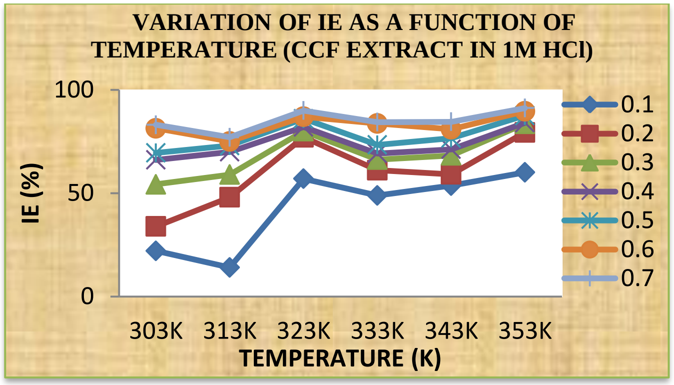


FIGURE 9

4.4.ADSORPTION ISOTHERMS

Adsorption isotherm has been generally studied since organic molecules inhibit corrosion by adsorption at the metal solution interface. Adsorption provides information about the interaction among the adsorbed molecules themselves as well as their interaction with electrode surface. A useful method that assists in the understanding of the mechanism of organo chemical reactions in the adsorption process is the adsorption isotherms (**Bockris J.O.M., 1993**). The adsorption of organic substance (surfactant) at the metal solution interface may be written according to the following displacement reaction:

Organic (solution) + nH_2O(ads) $\longrightarrow$ Organic(ads) + nH_2O(solution)

When n is the number of water molecules removed from the metal surface for each molecule of inhibitor adsorbed. Clearly the value of n depends on how the molecule arrange on the surface due to surface roughness and the interaction among the molecules. Basic θ information on the interaction between the inhibitor molecules and the surface of mild steel can be provided by adsorption isotherm. A correlation between surface coverage **(θ)** and concentration of inhibitor **(1-θ)** in electrolyte can be represented by the Langmuir adsorption isotherm.

$$\frac{C_{INHIBITOR}}{\theta} = I/K + C_{INHIBITOR}$$ **[where K is the adsorption constant]**

Surface coverage values (θ) for the inhibitor were obtained from the mass loss measurements for various concentrations at 303K as shown in **Table 3.**

4.4.1.LANGMUIR ADSORPTION ISOTHERM

A plot of **log (θ /1- θ) Vs log C** gave a straight line which obviously shows that the adsorption of the CCL & CCF extracts can be well fitted to Langmuir adsorption isotherm **(Figure 10, 12)**. These results demonstrated that the inhibitions of MS by CCL and CCF in acidic solution were attributed to adsorption of the compounds on the MS surface. It also confirms the mono layers adsorption.

4.4.2. TEMKIN ISOTHERM

Efforts are also carried out to plot θ Vs log C and the results indicate that the MS/acidic solution interface furnishes a straight line suggesting that the adsorption of CCL & CCF extracts at the MS/acidic solution interface obey Temkin isotherm **(Figure 11,13).**

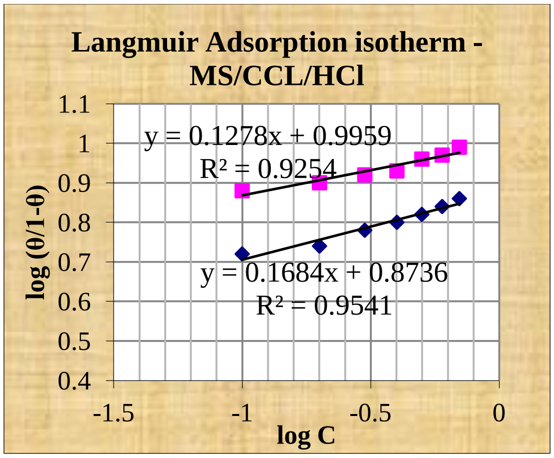


FIGURE 10

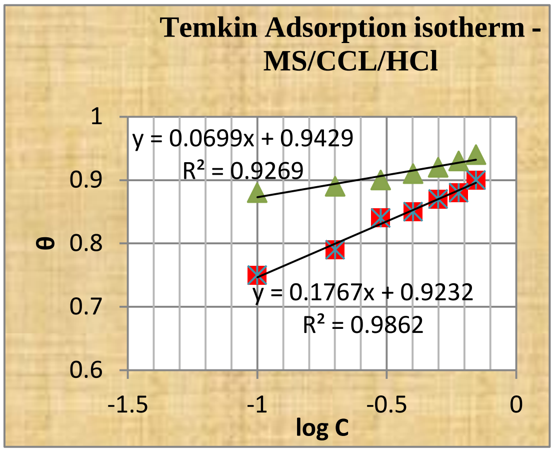


FIGURE 11

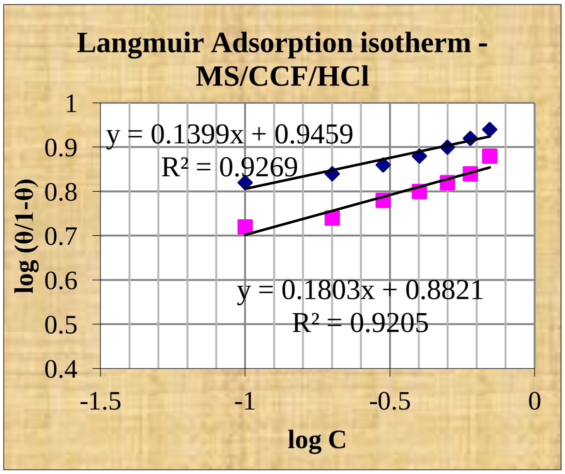


FIGURE 12

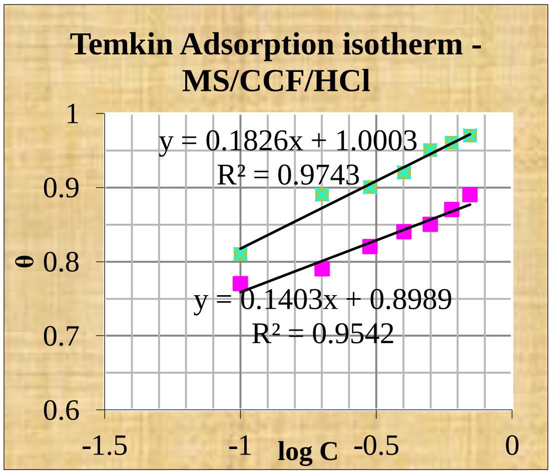


FIGURE 13

4.4.3.STATISTICAL ANALYSIS OF ADSORPTION ISOTHERM

Comparing the linearity of Langmuir and Temkin adsorption isotherm, the correlation co-efficient values were calculated. The correlation co-efficient obtained for the fitness of the data to adsorption models were furnished in the **Table 7**. From these findings, it can be inferred that CCL & CCF were adsorbed on MS surface obeying Langmuir and Temkin isotherms. This confirms that adsorption behavior of the inhibitor is strongly influenced by temperature. The correlation values are significant at 1% level. Hence Langmuir and Temkin adsorption isotherm are both appreciable at all temperatures in the presence of investigated inhibitor in acid media.

TABLE 7:VALUES OF CORRELATION COEFFICIENT OBTAINED FOR LANGMUIR AND TEMKIN ADSORPTION ISOTHERMS

Temperature(K)	Correlation coefficient (R^2)			
	CCL extract in 1M HCl		CCF extract in 1M HCl	
	Langmuir	Temkin	Langmuir	Temkin
303	0.6421	0.6551	0.9694	0.9688
313	0.9827	0.9858	0.9407	0.9505
323	0.9630	0.9636	0.9460	0.9281
333	0.8988	0.9022	0.7693	0.9589
343	0.8850	0.9706	0.9404	0.9706
353	0.9753	0.9206	0.9694	0.9206

4.5.ACTIVATION ENERGY

Activation energy of corrosion reaction was calculated from Arrhenius equation,

$$\text{Log C.R.} = \frac{-Ea}{2.303\ RT}\ \text{Constant}$$

Where **Ea** is the apparent effective energy, R the gas constant and A the Arrehenius preexponential factor. A plot of logarithm of the corrosion rate (C.R) Vs 1/T gave a straight line as shown in **Figure 14 and 16** with slope of -Ea / 2.303 R and the values of activation parameters are listed in the table 8 & 9 for MS/CCL/HCl & MS/CCF/HCl respectively. The average value of activation energies for the corrosion process in 1M HCl was found to lie around 41 & 52KJ/mol. Analysing the table the Ea decreases in the presence of CCL & CCF extract. This means that the extract is more effective at intermediate temperature and this indicates the physical adsorption of CCL & CCF extracts on MS surface. However the variation of IE with temperature could conclude the possibility of chemisorptions also. These extracts functions by physical adsorption at low temperature and chemisorptions at higher temperature. Literature studies reveals unchanged or lowered activation energies in inhibited solution may be interpreted as being indicative of chemisorptions, while the opposite is the case with physical adsorption. Analysing the **Table 8 and 9** the activation energy increases with increase in inhibitor concentration. This behaviour is the indication for the formation of the adsorption film of physical electrostatic nature.

It is noticeable that the lowest values of Ea were obtained with highest inhibition efficiency. This interesting outcome has earlier been observed and discussed in literature with different approaches. **Machu, (1938)** in his studies, on the influence of temperature on inhibitor action concluded that with powerful inhibitors, the Ea was lower for the inhibited solution than that of uninhibited solutions. This type of behaviour means that an inhibitor becomes more effective as the temperature increases. According to by **Putilova, (1960)** as there is an increase in surface area of the metal covered by the inhibitor molecules as the temperature rises. **Riggs, (1967)** reported that in the presence of adsorbed inhibitor, the dissolution of the metal proceeds with two distinct processes (corresponding to the covered area and the bare metal surface). At high degree of coverage the dissolution process is not only determined by the reaction of the metal from the bare surface but also involves the adsorbed inhibitor and consequently the Ea can assume values greater or smaller than those calculated in the absence of the inhibitor. In the current investigation the values were found to be lower than the uninhibited solution in the presence of CCL & CCF in the acidic solution. Experiments conducted by **Bag *et al*, (1996)** also reflected lower Ea values for the inhibited systems. Studies carried out by **Taha *et al*, (1995)** revealed that the presence of inhibitors decreased the Ea of the reaction to an extent depending on the nature of inhibitor. Values of activation energy infer the strong adsorption of inhibitor molecules on MS surface in the present study.

4.5.1.ACTIVATION PARAMETERS OF MS IN THE PRESENCE OF CCL & CCF EXTRACTS IN ACID MEDIUM

An alternative formulation of Arrhenius equation is

$$\mathbf{CR} = (\mathbf{RT/\ Nh})\,\mathbf{exp}\,(\Delta S\mathbf{a/\ R})\ \mathbf{exp}\,(\Delta \mathbf{Ha/\ R})$$

Where,

h is Planck's constant

N is Avagadro number

ΔSa is entropy of activation

ΔHa is enthalpy of activation

A plot of log(CR/T) Vs 1/T gave a straight line with a slope of - ΔHa /2.303R and an intercept of log(R/Nh + ΔSa/2.303R) from which the values of ΔHa and ΔSa were calculated and listed in **Table 8 and 9.** The values of ΔHa & Ea are nearly the same and are higher in the presence of the inhibitor. This indicates that the energy barrier of the corrosion reaction increased in the presence of the inhibitor without changing the mechanism of dissolution. The positive values of ΔHa for both corrosion processes with and without the inhibitor and reveal the endothermic nature of the steel dissolution process and indicate that the dissolution of steel is difficult. The large negative value of ΔSa for mild steel in acid medium implies that the activated complex is the rate determining step, rather than the dissolution step. In the presence of the inhibitor, the value of ΔSa increased and is generally interpreted as an increase in disorder as the reactants are converted to the activated complexes. The positive values of ΔSa reflect the fact that the adsorption process is accompanied by an increase in entropy, which is the driving force for the adsorption of the inhibitor onto the steel surface.

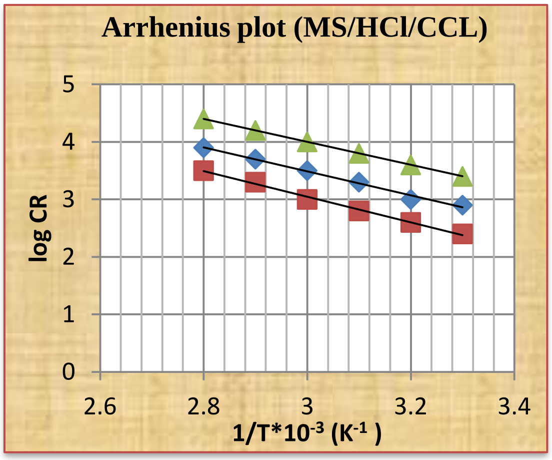


FIGURE14

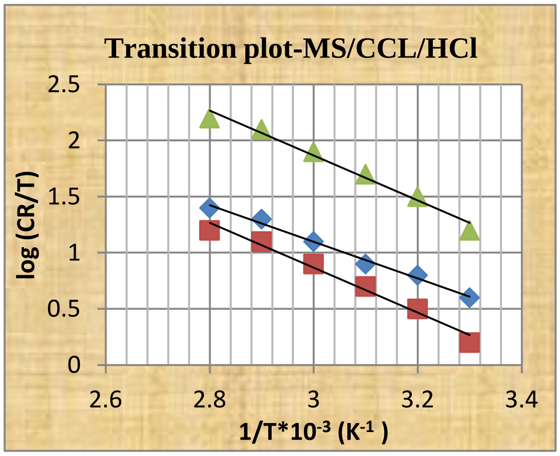


FIGURE 15

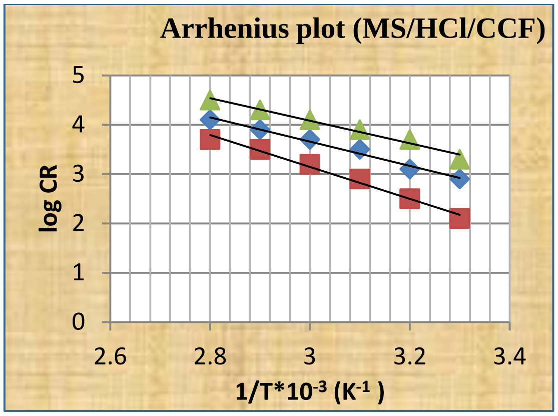


FIGURE 16

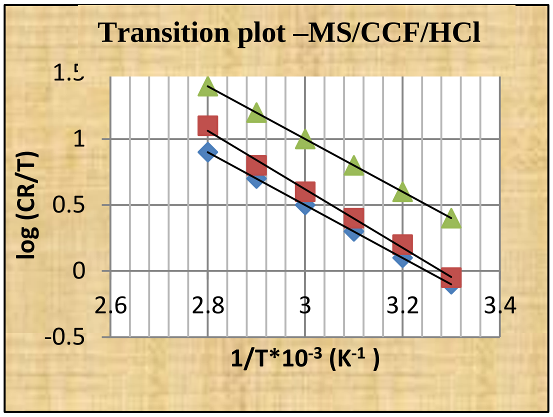


FIGURE 17

TABLE8:VALUES OF E_a , ΔH_a AND ΔS_a OF MS IN VARIOUS CONCENTRATION OF CCL IM HCl MEDIUM

S.No	Conc -V/V (%)	Activation Energy -Ea KJ/mol	ΔHa KJ/mol	ΔSa KJ/mol
1	BLANK	38.51	36.12	-48.01
2	0.1	37.40	35.56	-52.14
3	0.2	39.23	39.11	-53.11
4	0.3	42.52	42.17	-57.26
5	0.4	42.67	42.06	-59.65
6	0.5	43.10	43.07	-60.45
7	0.6	43.25	43.00	-60.55
8	0.7	44.31	44.11	-61.89

TABLE 9:VALUES OF E_a , ΔH_a AND ΔS_a OF MS IN VARIOUS CONCENTRATION OF CCF 1M HCl MEDIUM

S.No	Conc -V/V (%)	Activation energy-Ea KJ/mol	ΔHa KJ/mol	ΔSa KJ/mol
1	BLANK	43.75	43.69	-20.52
2	0.1	44.52	44.34	-35.28
3	0.2	47.04	46.45	-30.21
4	0.3	52.21	51.96	-34.58
5	0.4	61.81	61.43	-45.21
6	0.5	55.22	55.14	-56.34
7	0.6	56.48	56.02	-57.89
8	0.7	59.14	59.11	-56.88

4.6.FREE ENERGY OF ADSORPTION

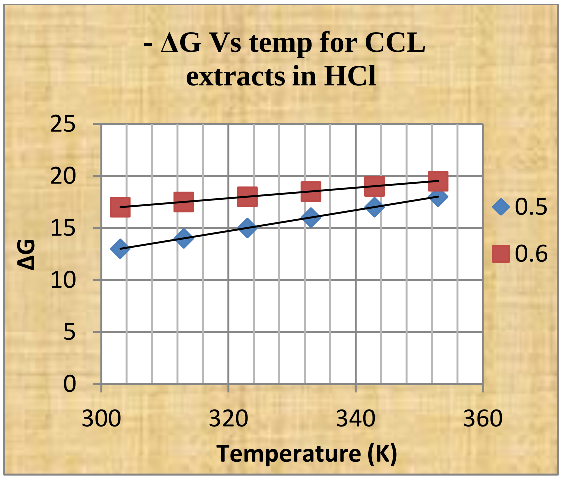
Thermodynamic parameters are useful tool to find out the strength of adsorption of the inhibitor on the electrode surface. In the current study the values of heats of adsorption suggested that in the system there exists a favourable condition for adsorption of inhibitors on the metal surface. Results of temperature study helps in the calculation of thermodynamic parameters viz. change in free energy, entropy and enthalpy. The results of thermodynamic parameters studied in the present systems, is reported in the **Table 10 & 11** and represented in **Figure 18 & 19**. From **Table 10 ,** it is inferred that the $\Delta G_{\mathbf{ads}}$ values range from -11 KJ/mol to – 22 KJ/mol from 306K to 356K. For the present system studied in 1M HCl media the value of ΔG increases with increase in concentration and increased with increase in temperature. **Moretti *et al,* (2002), Abdulaziz *et al,* (1989, 1990), Gomel *et al,* (1995), Rudresh *et al,* (1982)** reported that the negative values of $\Delta G_{\mathbf{ads}}$ adsorption which are characteristic of strong interaction between the inhibitor and the electrode, forming a adsorbed layer on the metallic surface and spontaneity of adsorption.

The negative value of $\Delta G_{\mathbf{ads}}$ ensures that the spontaneity of the adsorption process and stability of the adsorption layer on the steel surface. Generally values of $\Delta G_{\mathbf{ads}}$ upto -22 KJ/mol is consistent with electrostatic interaction between the charged metal (physisoption) while those more negative than -40 KJ/mol are associated with chemisorption as a result of sharing or transfer of unshared electron pairs or π electrons of organig molecules to the metal surface to form a coordinate type of bond . The plot $\Delta G_{\mathbf{ads}}$ Vs 1/T gives a straight line with slope that equals to $\Delta H_{\mathbf{ads}}$. The calculated values are depicted in table 3 which shows that the $\Delta G_{\mathbf{ads}}$ values are negative which indicate the stability of the adsorbed layer on the steel surface and spontaneity of adsorption process. Also the values increase (become less negative)with the increase in temperature which indicates the occurrence of exothermic process.

4.6.1.HEAT OF ADSORPTION (ΔH) AND CHANGE IN ENTROPY (ΔS)

Thermodynamic parameters ΔH and ΔS could be arrived at, from the temperature studies and using a plot of -ΔG Vs T. The values of thermodynamic parameters are listed in the **Tables 10 & 11.**The positive sign of enthalpies reflect the endothermic nature of dissolution process. The negative values of ΔS mean that the process of adsorption is accompanied by an decrease in entropy. It might be explained as follows: Before the adsorption of CCL & CCF onto steel surface the chaotic degree of steel surface was high but when inhibitor molecules was orderly adsorbed on to the steel surface, as a result a decrease in entropy. The negative values of ΔS indicates that activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disorder take place during the course of transition from reactant to the activated complex**. (Saliyan and Adhikari, 2007)**

The positive sign of enthalpies reflect the endothermic nature of dissolution process. **(A.K.Singh et al., 2009.)**



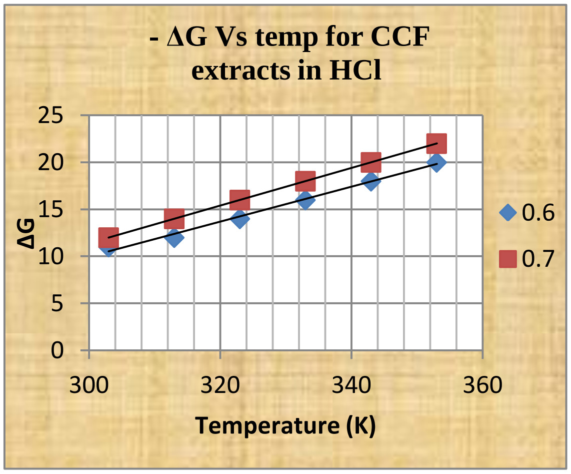


FIGURE 18

FIGURE 19

TABLE 10:VALUES OF -ΔG, ΔH AND ΔS OF MS IN VARIOUS CONCENTRATION OF CCL 1M HCl MEDIUM

S.NO	Concentration of inhibitor V/V(%)	Free energy of adsorption -ΔG (kJ/mol)						Free energy of adsorption ΔS (kJ/mol)	Free energy of adsorption ΔH (kJ/mol)
		303K	313K	323K	333K	343K	353K		
1.	0.1	15.31	16.82	16.73	17.24	14.04	21.90	-0.212	16.66
2.	0.2	13.82	16.69	15.95	15.55	13.60	20.55	-0.158	15.59
3.	0.3	13.01	17.30	16.27	15.56	13.70	19.36	-0.036	15.27
4.	0.4	11.94	17.12	17.29	14.98	13.81	18.70	0.16	14.54
5.	0.5	12.34	17.41	17.07	14.48	14.32	18.24	0.103	14.81
6.	0.6	13.88	18.11	17.23	13.96	14.52	18.35	-0.287	16.40
7.	0.7	13.65	18.08	18.27	13.67	14.86	18.13	0.114	14.89

TABLE 11: VALUES OF -ΔG, ΔH AND ΔS OF MS IN VARIOUS CONCENTRATION OF CCF IM HCl MEDIUM

S.NO	Concentratin of inhibitor V/V(%)	Free energy of adsorption -ΔG (kJ/mol)						Free energy of adsorption ΔS (kJ/mol)	Free energy of adsorption ΔH (kJ/mol)
		303K	313K	323K	333K	343K	353K		
1.	0.1	12.70	11.69	17.35	17.24	18.33	19.70	1.56	10.68
2.	0.2	12.36	14.40	18.32	16.78	17.05	20.37	1.32	11.90
3.	0.3	13.53	14.50	17.71	16.26	17.01	19.95	1.09	12.67
4.	0.4	14.07	15.01	17.29	15.84	21.83	19.31	1.29	12.70
5.	0.5	13.85	14.81	18.04	15.76	16.69	19.37	0.88	13.32
6.	0.6	15.03	14.61	17.77	16.89	16.83	19.39	0.78	13.99
7.	0.7	14.98	14.50	18.16	16.67	17.17	19.89	0.88	13.78

4.7.ELECTROCHEMICAL MEASUREMENTS

Electrochemical measurements was done by using electrochemical analyser solatron. Electrochemical measurements like Linear polarization measurements, Tafel intercept method and electrochemical impedance measurement carried out for mild steel acid corrosion in the presence of (CCL & CCF) extracts. Electrochemical studies were used to predict the nature of inhibitor- anodic, cathodic, or mixed type inhibitors and to predict a suitable mechanism for inhibition process. The values of corrosion kinetic parameters-corrosion current (E_{corr}), corrosion current density (I_{corr}), Tafel slopes (b_a and b_c), linear polarization resistance (R_p) are recorded in the **Table 12 & 13.**

4.7.1.POTENTIODYNAMIC POLARIZATION STUDIES

The kinetics of anodic and cathodic reactions occurring on mild steel electrodes in 1M HCl solutions with different (CCL & CCF) extracts concentrations were studied through the polarization measurements. The complete Potentiodynamic polarization curves are shown in **Figure 20 & 21**. The change in b_a and b_c values indicates the adsorption of (CCL & CCF) extract modify the mechanism of anodic dissolution as well as the cathodic H_2 evolution. There was no definite trend in shift of E_{corr} values in the presence of extract. So they can be classified as mixed type of inhibitor in 1M HCl.

The examination of **Figure-20 & 21 and Table-12 & 13** indicate that addition of the (CCL & CCF) Extracts decreases corrosion current density. The decrease is more pronounced with the inhibitor concentration. The inhibitor present in the corrosive solution hinders the attack of th e corrodant on the steel surface, there by reduces the I_{corr}. Maximum IE of 91.84% & 86.60 was obtained for 0.6% concentration of CCL & CCF extract respectively.

TABLE 12: ELECTROCHEMICAL POLARIZATION PARAMETERS FOR THE CORROSION OF MS IN THE PRESENCE OF CCL EXTRACT IN 1M HCl

S.No	Conc v/v(%)	$-E_{corr}$ mV/SCE	I_{corr} μA/cm^2	b_a mV/dec	b_c mV/dec	IE (%)
1	Blank	-544	5174	217	187	-
2	0.2	-494	777	148	94	84
3	0.4	-493	719	143	91	86
4	0.6	-495	422	153	80	91

TABLE 13:ELECTROCHEMICAL POLARIZATION PARAMETERS FOR THE CORROSION OF MS IN THE PRESENCE OF CCF EXTRACT IN 1M HCl

S.No	Conc v/v(%)	$-E_{corr}$ mV/SCE	I_{corr} μA/cm^2	b_a mV/dec	b_c mV/dec	IE (%)
1	Blank	-544	5174	217	187	-
2	0.2	-511	609	117	86	88
3	0.4	-506	777	142	96	84
4	0.6	-505	693	142	92	86

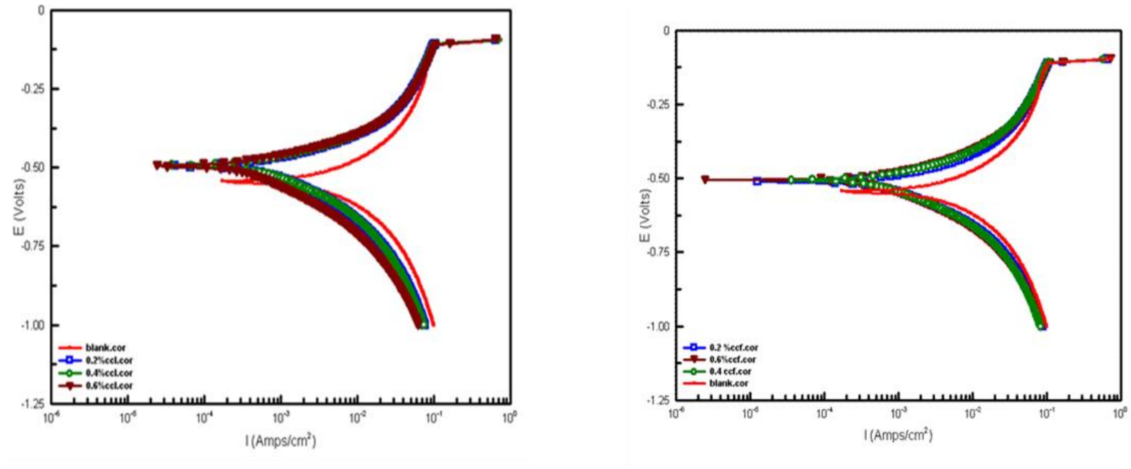


FIGURE 20a)Polarization curve for CCL/MS in 1M HCl 20b) Polarization curve for CCF/MS in 1M HCl

4.7.2.LINEAR POLARIZATION RESISTANCE (LPR) METHOD

The R_P values obtained from LPR method of free acid solution and inhibited acid solution containing highest concentrations of (CCL & CCF) have shown an increase in values from 73.78% to 83.30% in 1M HCl solutions(CCL) and from 66.53% to 74.01% in 1M HCl solutions (CCF). Increase in R_P values with increasing inhibitor concentration confirmed the process of adsorption of (CCL & CCF) in mild steel surface.

TABLE 14: LINEAR POLARIZATION RESISTANCE AND IMPEDANCE PARAMETERS FOR THE CORROSION OF MS IN THE PRESENCE OF CCL EXTRACT IN 1M HCl

S.No	Concentration(v/v)%	Rp (Ω/cm^2)	IE (%)
1	Blank	8	-
2	0.2	32	73
3	0.4	34	75
4	0.6	51	83

TABLE 15: LINEAR POLARIZATION RESISTANCE AND IMPEDANCE PARAMETERS FOR THE CORROSION OF MS IN THE PRESENCE OF CCF EXTRACT IN 1M HCl

S.No	Concentration(v/v)%	R_P (Ω/cm^2)	IE (%)
1	Blank	8	-
2	0.2	25	66
3	0.4	31	72
4	0.6	33	74

4.7.3.ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

EIS is one of the most successful techniques used to evaluate the effectiveness of an inhibitor. The corrosion behaviour of mild steel in acidic solution in the presence of CCL & CCF was investigated by EIS method at 303K after 30 minutes. Various impedance parameters such as charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and the corresponding IE calculated are given in **Tables 16 and 17**. **R_{Ct} and C_{dl}**

The impedance parameters derived from these investigations are mentioned in table- 8.It is worth noting that the presence of inhibitor does not alter the profile of impedance diagrams which are almost semi- circular indicating a charge transfer process mainly controls the corrosion of steel. The increase of charge transfer resistance in the presence of CCL & CCF extract may be due to the gradual replacement of water molecules of the extract on the metal surface. The charge transfer reactions are known to take place at the metal solution surface. Consequently the high Rct values of inhibited electrodes can be explained by the buildup of protective layers and the effective barrier on MS surface. The double layer capacitance is due to the charge separation at metal / electrolyte interface.

The value of C_{dl} decreases with increase in inhibitor concentration thus the thickness of protective layer increases. This can be attributed to the decrease in local dielectric constant and an increase in the thickness of the electrical double layer suggesting that CCL & CCF inhibit the mild steel corrosion by adsorption at the metal/acid interface. The successive coverage of MS surface and growth of layer would have provided an effective corrosion inhibition. It can be found that the charge transfer resistance values increased and the capacitance value decreased with increasing inhibitor concentration. The large charge transfer resistance could be due to a decrease in the active surface necessary for the corrosion reaction. The decrease of C_{dl} shows that the adsorption of inhibitors on the surface of MS changes the double layer. Thus the change in C_{dl} which can result from a decrease in local dielectric constant and due to gradual displacement of H_2O Molecules by adsorption of original molecules present in the CCL & CCF Extract.

TABLE 16 IMPEDANCE PARAMETERS FOR THE CORROSION OF MS IN THE PRESENCE OF CCL EXTRACT IN 1M HCl

S.No	Concentration(v/v)%	R_{ct} (Ω/cm^2)	IE (%)	Cdl (µ F cm^{-2})	Θ
1	Blank	11	-	14	-
2	0.2	51	77	12	0.1428
3	0.4	50	76	11	0.2142
4	0.6	130	91	6	0.5714

TABLE 17: IMPEDANCE PARAMETERS FOR THE CORROSION OF MS IN THE PRESENCE OF CCF EXTRACT IN 1M HCl

S.No	Concentration(v/v)%	Rct (Ω/cm^2)	IE (%)	Cdl (μ F cm^{-2})	Θ
1	Blank	11	-	14.	-
2	0.2	60	80	13	0.0714
3	0.4	54	78	12	0.1428
4	0.6	62	81	10.75	0.9464

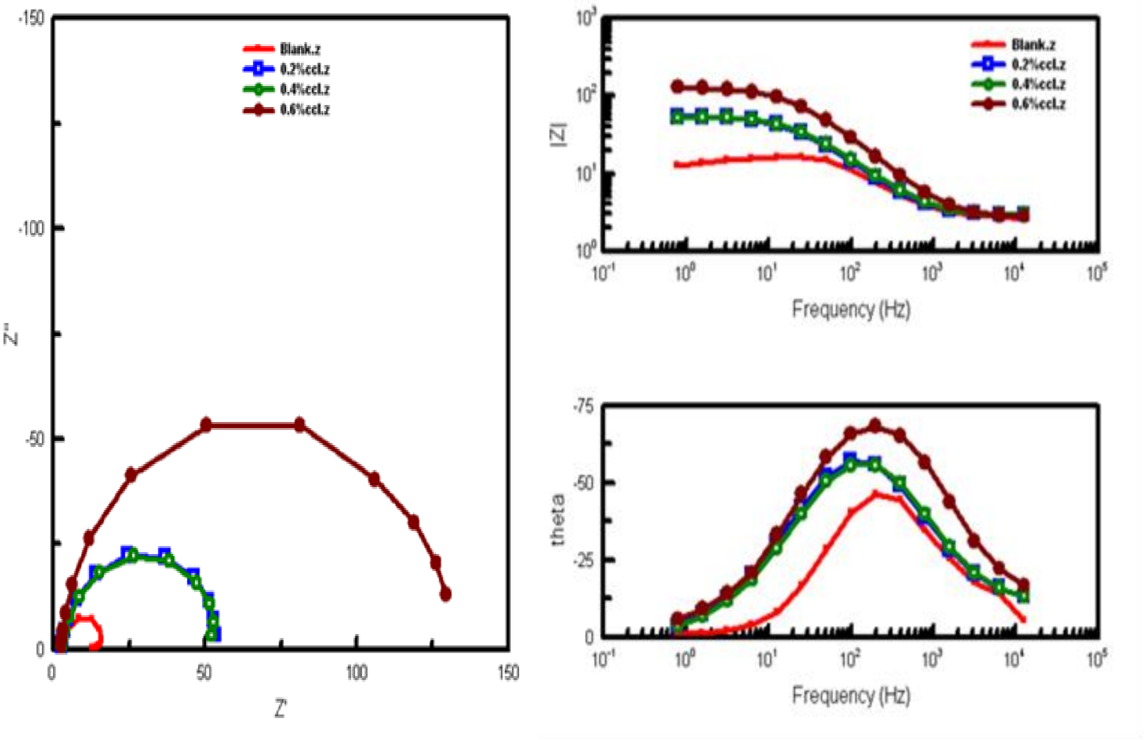


FIGURE 21a) Impedance curve and bode plot of mild steel in the presence of CCL extract in 1M HCl

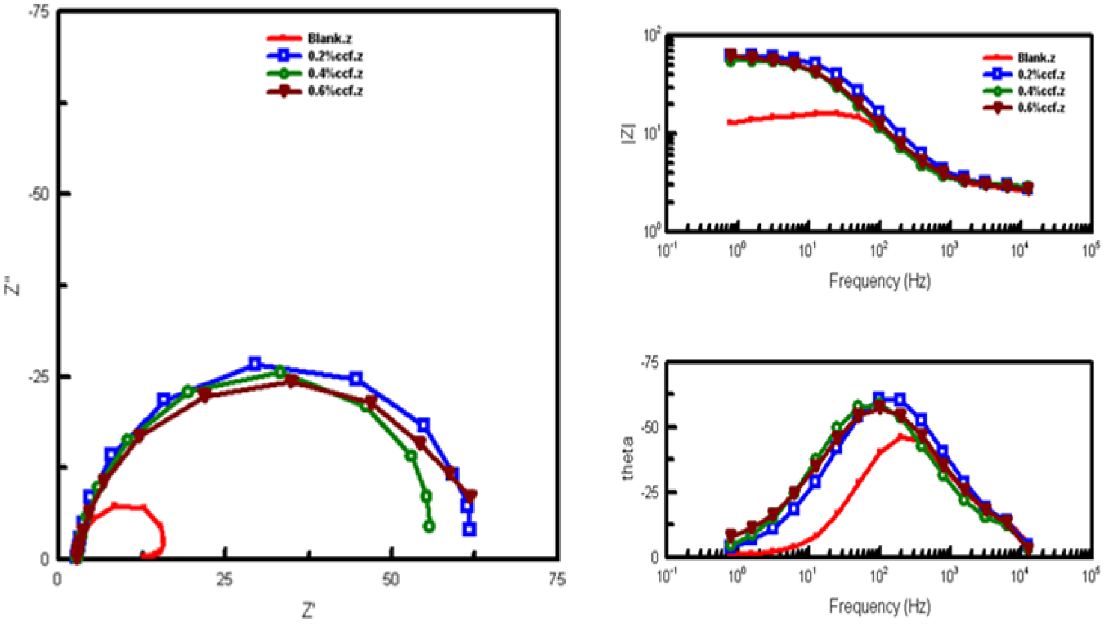


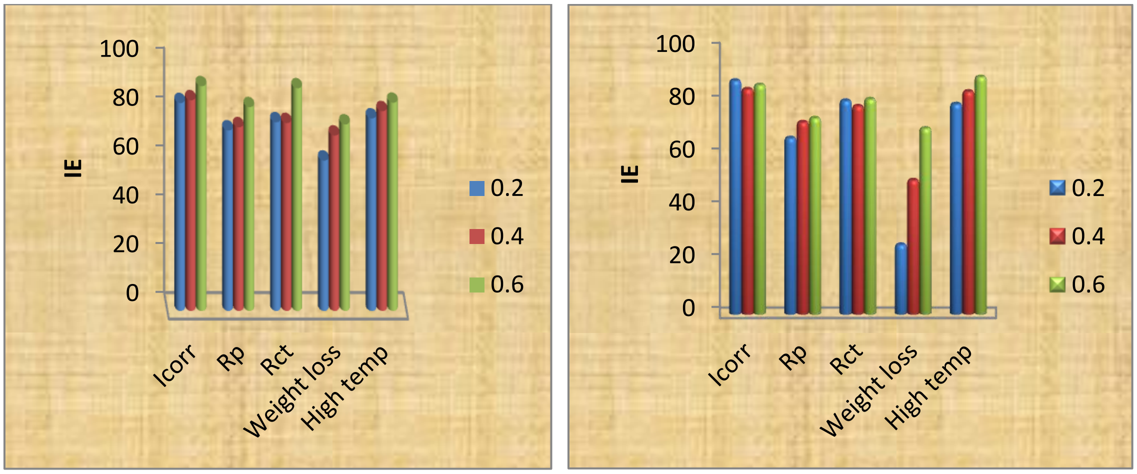
FIGURE 21b) Impedance curve and bode plot of mild steel in the presence of CCF extract in 1M HCl

4.8.PERFORMANCE EVALUATION OF TDL USING CONVENTIONAL MASS LOSS AND ELECTROCHEMICAL MEASUREMENTS:

The values of inhibition efficiency calculated from electrochemical measurements are lower than those obtained from mass loss data. Nevertheless in general the polarization data confirms the result, of steel dissolution measurements. The difference in inhibition efficiency by different techniques can be attributed to the fact that mass loss method gives average corrosion rates while electrochemical measurements give instantaneous corrosion rates. The difference may be expected to arise because the mass loss measurements are experiments of long duration, which helps in the formation of a thick, inherent and adsorbed layer on the metal surface. This leads to the complete shielding of the metal surface from the corrosive environment whereas polarization studies are experiments of short duration and the time will not be enough for the formation of a thick and adsorbed layer. This leads to low value of inhibitor efficiency in some cases. **(Quraishi *et al*, 1996).**

Performance evaluation of CCL & CCF using weight loss and electrochemical measurements in HCl is given in F**igure-22.**

FIGURE 22



22a) PERFORMANCE EVALUATION GRAPH FOR CCL/MS/HCl

22b) PERFORMANCE EVALUATION GRAPH FOR CCF/MS/HCl

4.9.SURFACE ANALYSIS

4.9.1.FT-IR SPECTRAL ANALYSIS

FT-IR spectral studies were carried out for powdered CCL & CCF and for CCL & CCF in mild steel surface immersed in 1M HCl and with 0.7% plant extract for 3 hours and their respective FT-IR peaks are given in **Table 18a** and **b**. **Figure 23sa, b** shows the IR spectra of the CCL & CCF extract in 1MHCl media

4.9.1.1.FT-IR spectra of CCL extract

The FTIR spectra of corrosion product formed on mild steel surface after 3 h immersion in 1 M HCl containing 0.7 % CCL shown in **Figures. 23a**, revealed that the –OH stretching at 3356 cm-1 and C=C stretch at 1627 cm-1 vanished for CCL/1MHCl. The C-N 1249 cm-1 shifted to 1265 cm-1 for CCL/HCl. These progressive shifts and disappearance in the wavelength of absorption are indicative of the interactions between the extract of CCL and the surface of mild steel.

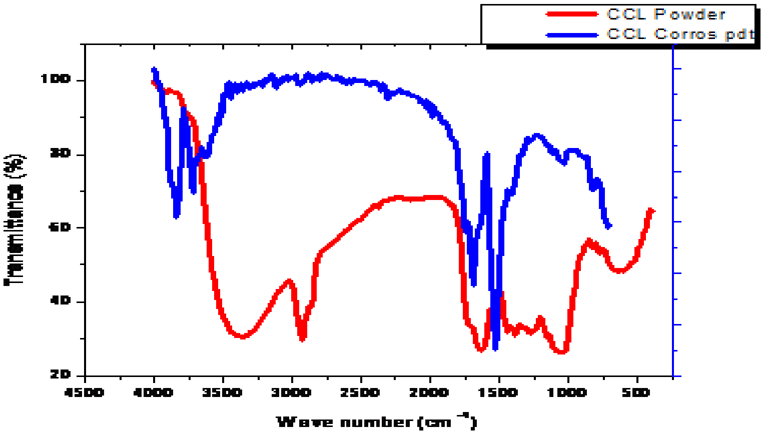
4.9.1.2.FT-IR spectra of CCF extract

From the results of analysis of the FTIR spectra of CCF and that of the corrosion product (**Table 18b**), it can be seen that the O-H stretch at 3371 cm-1 in pure CCF shifted to 3394 cm-1 in the corrosion product of CCF/HCl and which is depicted in **figure 23b**. The shifts in frequencies indicate that there is interaction between CCF and the surface of the metal **(Eddy *et al*, 2010)**.

However, the C-O stretch at 1064 cm-1 were missing in the spectrum of the corrosion products in both acid media indicating that adsorption of CCF on mild steel surface might have proceeded through these functional groups **(Eddy *et al*, 2010)**. Also, some new bonds were found in the spectrum of the corrosion product. This included the C=C aromatic stretch at 1527cm-1, the C=O stretch at 1689cm-1, the ≡C-H bending at 825cm- 1 and 833cm-1. This also indicates that some new bonds were also formed through these functional groups.

TABLE 18a: FTIR SPECTRAL DETAILS OF CCL CONCENTRATE AND CORROSION PRODUCT

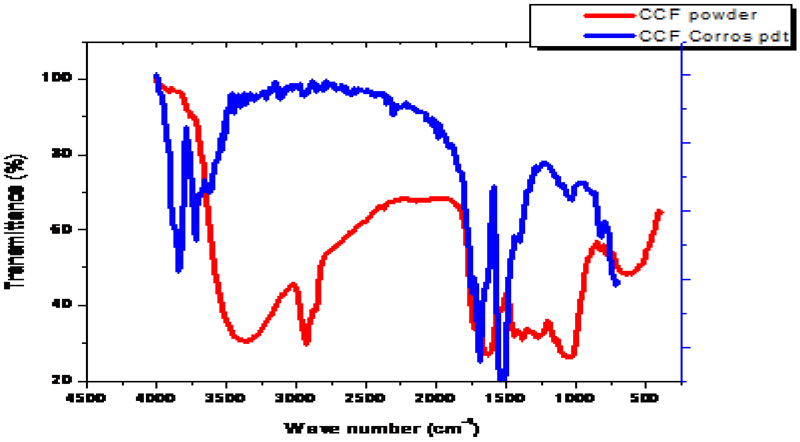
POWDERED PLANT MATERIAL			**CORROSION PRODUCT MS/HCl/CCL**		
Frequency cm^{-1}	**Assignment**	**Functional group**	**Frequency cm^{-1}**	**Assignment**	**Functional group**
3356	OH stretch	Alcohol	3356	OH stretch	Alcohol
2924	C-H stretch	Alkenes	2924	C-H stretch	Alkenes
1627	C=C Stretch	Alkenes	1689	C=O Stretch	Carboxylic acid, ester, ether
1527	C-C in ring	Aromatic	1527	C-C in ring	Arsomatic
1033	C-N Stretch	Aliphatic	1033	C-N Stretch	Aliphatic
601	γ -Fe_2O_3	-	601	-	-



23a)FT-IR spectrum of powdered CCL & CCL/HCl

TABLE 18b: FTIR SPECTRAL DETAILS OF CCF CONCENTRATE AND CORROSION PRODUCT

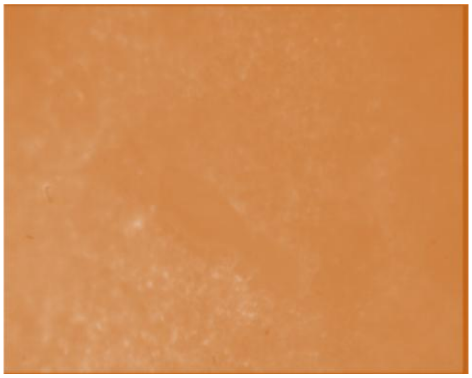
POWDERED PLANT MATERIAL			CORROSION PRODUCT MS/HCl/CCF		
Frequency cm^{-1}	**Assignment**	**Functional group**	**Frequency cm^{-1}**	**Assignment**	**Functional group**
3371	OH stretch	Alcohol	3371	OH stretch	Alcohol
2924	C-H stretch	Alkenes	2924	C-H stretch	Alkenes
1627	C=C Stretch	Alkenes	1689	C=O Stretch	Alkenes
1442	C–C stretch (in–ring)	Aromatic	1527	C-C in ring	Aromatic
1257	C–H rock	Aliphatic amines	1257	-	-
825	≡C-H bending	Alkynes	825	≡C-H bending	Alkynes



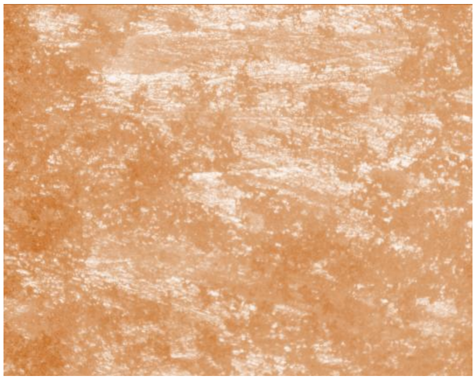
23b) FT-IR spectrum of powdered CCF & CCF/HCl

4.9.2.OPTICAL ELECTRON MICROSCOPY

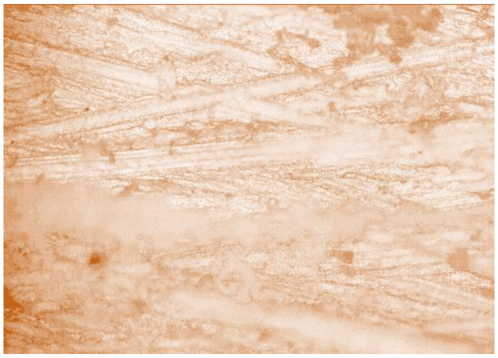
An optical electron microscope was used to determine the change in surface caused by contact with the acid solutions and to watch the effect of adding the inhibitor. The optical electron micrographs of the mild steel in the initial state after pickling with HCl and in the presence of CCL & CCF inhibitors in HCl are shown in **Figure 24b** and **Figure 24b**. Initial MS micrograph was smooth with grains**.** Due to the exposure of mild steel to the HCl acid, (**Figure 24a)** pits were formed on the surface. In the micrographs **25c**, the pits disappeared. This is due to the presence of adsorbed layer of inhibitor molecules. Therefore it can be concluded that corrosion is reduced to a maximum extent in the presence of inhibitor and hence corrosion was inhibited strongly when the inhibitor is present in acid media (**Keera, 2003**).



24a) PHOTO MICRO GRAPH OF MS IN PRESENCE OF HCl



24b) PHOTO MICRO GRAPH OF MS IN CCL/ HCl



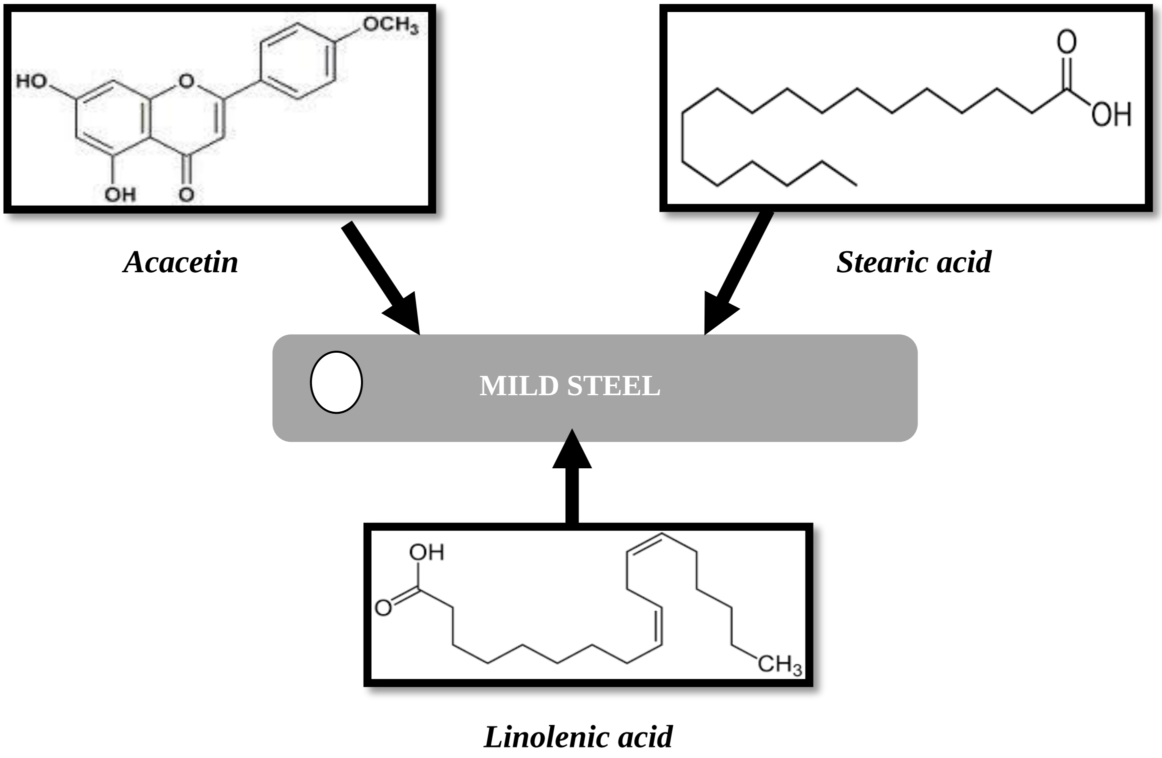
24c) PHOTO MICRO GRAPH OF MS
IN CCF/ HCl

4.4.INHIBITION MECHANISM

Most organic inhibitors contain at least one polar group with an atom of nitrogen, sulphur or in some cases selenium and phosphorus. According to **Hackermann (1965)** the inhibiting properties of the many compounds are determined by the electron density at the reaction centre, with increase in electron density in the center, the chemisorption between the inhibitor and the metal are strengthened. **Hackermann (1951 and 1957)** have studied the adsorption of the organic substances with a long chain. These studies indicates that the longer the substance is adsorbed, the more effectively it protects surface. In the present studies CCL & CCF works out to be a good inhibitor for mild steel corrosion. The inhibitors adsorbed on MS surface which was confirmed by Langmuir and Temkin isotherm.The list of phytochemical constituents present in CCL & CCF is listed in **Table 19**.

TABLE19:CHEMICAL CONSTITUENTS IN *CLYTOSTOMA CALLISTEGIOIDES*

Chemical constituents in CC		
Flavanones	4′-Hydroxywogonin, Acacetin and Galangustin	**Reference (*www.bioportfolio.com)***
Secondary metabolites	Polyphenols, Terpenes, Tannin	
Fatty acids	palmitic, stearic, linoleic and linolenic acids	


Acacetin
Stearic acid
MILD STEEL
Linolenic acid

SUMMARY & CONCLUSION

5. SUMMARY AND CONCLUSION

Industries are mainly depends on the metals and alloys. Corrosion control in industries is very difficult process and also it's very expansive that's why nowadays corrosion research was rapidly changed over the year. Mainly on use of green inhibitor for corrosion control method. These are low cost as well as low risk of environmental pollutions. In this way to arrive at low cost, non toxic and eco-friendly inhibitor formulation, the present study aims to the use of leaves and flower extract of ***Clystoma callistegioides*** **(leaf & flower)** in 1M HCl. FT-IR was used for characterization of the investigated inhibitor. This study was carried out by classical weight loss measurement and electrochemical measurement. The temperature study was helps to find out the mechanism of inhibitor and to calculate the thermodynamic parameters of corrosion process. Effort has been taken to fit the adsorption isotherms like Langmuir and Temkin.

Polarization techniques such as Tafel, Linear polarization resistance and electrochemical impedance spectroscopy have been conducted to find out the inhibitor efficiencies of the acid extracts and nature of the inhibitor. Surface analytical techniques **Optical Electron Microscope & FTIR** results were taken to investigate the adsorption of inhibitors on the MS Surface.

Salient features of the present study:

- The acid extracts of CCL furnished a maximum of 94.63% (1M HCl) and inhibition efficiency and CCF provided a maximum of 90.27%.
- MS/CCL/HCl, MS/CCF/HCl systems show maximum of 93.95% and 91.1% IE was observed at 313K, 323K respectively. This indicates CCL &CCF performed excellently at higher temperature.
- MS/HCl/CCL & MS/HCl/CCF utilized in the current study followed Langmuir and Temkin adsorption isotherm which indicated the monolayer formation with heterogeneity in the surface of the electrode.
- Thermodynamic parameters showed that the inhibition as a spontaneous with adsorption of inhibitors on the metal surface.
- Values of activation energy infer the strong adsorption of inhibitor molecules on mild steel surface.
- Values of Tafel constant b_a and b_c confirm that the CCL & CCF extracts act like mixed type inhibitor.

- Polarization curves obtained in the presence of the extract indicate that it controls both anodic and cathodic reactions.
- Increase in R_p and R_{ct} values and decrease in I_{corr} and C_{dl} values confirm that the CCL & CCF extracts are adsorbed on the mild steel surface and inhibition process is followed by monolayer adsorption.
- IE by mass loss methods were found to be greater than electrochemical measurements.
- Optical Electron Microscope results illustrated the strong adsorption of the inhibitor on the metal surface.
- FT-IR spectroscopic studies revealed that the phytochemical constituent of the plant extracts were adsorbed on the surface.
- CCL & CCF in HCl medium efficiently inhibit mild steel corrosion efficiency and proved to be zero cost inhibitor, eco-friendly environmentally friendly.

In the current investigation the ***Clystoma callistegioides*** **(leaf & flower)** extract plays a major role in reducing the metal dissolution as well as hydrogen evolution and protect the mild steel surface from corrosion. Thus ***Clystoma callistegioides*** **(leaf & flower)** extract were proved to be zero cost, eco-friendly and highly economical.

REFERENCES

REFERENCES

- Al-Sehaibani. H., (2000), “Evaluation of Extracts of Henna Leaves as Environmentally Friendly Corrosion Inhibitors for Metals”, *Materialwissenschaft and Werkstofftechnik*, 31:1060 – 1063.
- Al-Turkustani A.M., Arab S.T., and Al-Qarni L.S.S., (2011), “Medicago Sative plant as safe inhibitor on the corrosion of steel in 2.0M H2SO4 solution”, *Journal of Saudi Chemical Society,* 15:73–82.
- Ambrish Singh & Ishtiaque Ahamad & Singh. V. K & Mumtaz Ahamed Quraishi(2010),”Inhibition effect of environmentally benign *Karanj* (Pongamia pinnata) seed extract on corrosion of mild steel in hydrochloric acid solution” , *J Solid State Electrochem* 15:1087–1097.
- Ambrish Singh, Vinod Kumar Singh, M. A. Quraishi ,(2013),“Corrosion in HCl Solution Using Pipali (*Piper longum*) Fruit Extract”,*Arabian Journal for Science and Engineering,* 38: 85-97.
- Badiea. A.M., Mohana. K.N., (2009), “The effect of some plant extracts on the corrosion
  behavior of low carbon steel in industrial water”, *Journal of materials engineering and performance.*23:110-118
- Bammou, L., Belkhaouda, M., R. Salghi, O. Benali , A. Zarrouk ,H. Zarrok , B. Hammouti ,(2014), “Corrosion inhibition of steel in sulfuric acidic solution by the *Chenopodium Ambrosioides* Extracts”, *Journal of the Association of Arab Universities for Basic and Applied Sciences*. 104
- Benali.O , H. Benmehdi , O. Hasnaoui , C. Selles , R. Salghi. *(2013), “*Green corrosion inhibitor: inhibitive action of tannin extract of *Chamaerops humilis* plant for the corrosion of mild steel in 0.5M H2SO4”, *J. Mater. Environ. Sci. 4: 127-138.*
- C.A. Loto and A.P.I. Popoola, (2011), Effect of Tobacco and Kola Tree Extracts on the Corrosion Inhibition of Mild Steel in Acid Chloride *Int. J. Electrochem.* Sci., 6: 3264 – 3276.

- Chetouani A, Hammouti B, Benkaddour M., (2004), “Corrosion inhibition of iron in hydrochloric acid solution by jojoba oil”, *Pigment & Resin Technology,* 33(1) :26 – 31.
- El-Etre .A.Y(2006), “Khillah extract as inhibitor for acid corrosion of SX 316 steel” *Applied Surface Science 252: 8521–8525.*
- Emeka E. Oguzie;Evaluation of the inhibitive effect of some plant extracts on the acid corrosion of mild steel; *Corrosion Science,* 50(11):2008, 2993-2998.
- Eddy N O, Ebenso E E, (2008), “Adsorption and inhibitive properties of ethanol extracts of *Musa sapientum* peels as a green corrosion inhibitor for mild steel in H2SO4”, *Afr. J. Pure. Appl. Chem.,* 2(6) :46-54.
- Eddy. N. O., Odoemelam. S. A. and Odiongenyi. A. O., (2008) “Ethanol extract of Musa Acuminate peel as an eco-friendly inhibitor for the corrosion of mild steel in sulphuric acid”, *Advances in natural and applied Sciences,*: 35-42.
- Emeka E. Oguzie, Chinonso B. Adindu , Conrad K. Enenebeaku , Cynthia E. Ogukwe , Maduabuchi A. Chidiebere , and Kanayo L. Oguzie, (2012), “Mechanism of Corrosion Inhibition of Mild Steel by Acid Extracts of *Piper guineense”, J. Phys. Chem. C,* 116 (25):13603–13615
- Farooqi, I H, Quraishi, M A, Saini, P A, (1997), “Natural compounds as corrosion inhibitors for mild steel in industrial cooling systems” *Eurocorr '97, 2 Trondheim; Norway: 247-252, 22-25.*
- Gopal Ji, Shadma Anjum, Shanthi Sundaram, Rajiv Prakash, (*2015)*, “*Musa paradisica* peel extract as green corrosion inhibitor for mild steel in HCl solution” *Corrosion Science, Volume 90, January 2015, Pages 107-117*
- Guy D. Davis, Anthony Von Fraunhofer J; (2003), “Tobacco plant extract as environmentally benign corrosion inhibitors”, *Materials Performance,* 56-60.
- Gopal ji , Sudhish Kumar Shukla , Priyanka Dwivedi , Shanthi Sundaram , and Rajiv Prakash , (2011), “Inhibitive Effect of *Argemone mexicana* Plant Extract on Acid Corrosion of Mild Steel”, *Ind. Eng. Chem. Res.,*50 (21):11954–11959
- Hui Cang, Zhenghao Fei, Jinling Shao, Wenyan Shi, Qi Xu. (2013),”Corrosion Inhibition of Mild Steel by *Aloes* Extract in HCl Solution Medium,”*Int. J.Electrochem. Sci.,* 8:720 – 734.

- Iloamaeke I. M, Onuegbu T. U., Umeobika U. C., Umedum N. L.Green Approach to Corrosion Inhibition of Mild Steel Using *Emilia Sonchifolia* and *Vitex Doniana*In 2.5M HCl Medium, International Journal of Science and Modern Engineering (IJISME) , Volume-1, Issue-3, February 2013
- Karthikaiselvi. R., Subhashini. S., Rajalakshmi. R., (July 2009), *Biodegradable green inhibitor (Myristica Frangans) as a corrosion inhibitor of mild steel in 1M HCl, JCSE, Volume 12.*
- Leelavathi S., R. Rajalakshmi Evaluation of *Cassia alata* leaves extract (Candle Bush) as Corrosion inhibitor for Mild Steel in Hydrochloric acid medium Advances in Materials and Corrosion 1 (2012): 47-56 ,2012
- Loto C.A., and Mohammed A.I., (2000), "The effect of *Cashew juice* extract on corrosion inhibition of mild steel in hydrochloric acid and corrosion prevention and control", 133(3): 50-56.
- Loganayagi C , Kamal C , and Sethuraman MG, (2014), "An Active Principle of *Opuntia elatior* as an Eco-Friendly Inhibitor of Corrosion of Mild Steel in Acid Medium", *ACS Sustainable Chem. Eng.*, 2 (4):606–613
- Maduabuchi A. Chidiebere , Cynthia E. Ogukwe , Kanayo L. Oguzie , Chukwuemeka N. Eneh , and Emeka E. Oguzie, (2012), "Corrosion Inhibition and Adsorption Behavior of *Punica granatum* Extract on Mild Steel in Acidic Environments" *Ind. Eng. Chem. Res.*, 51 (2):668–677
- Maheshwari.D Subhashini.S, Rajalakshmi.R, Viswanathan, Marikkannu C and Sivakamasundhari.S.(2003), The performance of *Cajanus Cajan* seed extract on corrosion inhibition of mild steel in 1M HCl, *National Conference On Control Of Industrial Pollution And Environmental Degradation*,534-539.
- Manohari.G and Rajalakshmi R., Ninth seminar proceedings, *Tamilnadu state council for science and technology*, (2001), India 31
- Nnabuk Okon Eddy, Patricia A. Ekwumemgbo, Paul A. P. Mamza"Ethanol extract of *Terminalia catappa* as a green inhibitor for the corrosion of mild steel in H2SO4"Green Chemistry Letters and Reviews,1751-7192:2(4):2009,223-231.
- Oguzie. E.E "Corrosion inhibition of aluminium in acidic and alkaline media by *Sansevieriatri fasciata* extract"49(3):2007,1527-1539.

- Okafor. P.C., Ikpi. M.E., Uwah. I.E., Ebenso. E.E., Ekpe. U.J., Umoren. S.A.; Inhibitory action of *Phyllanthusamarus* extracts on the corrosion of mild steel in acidic media; Corrosion Science, 50(8):2008,2310-2317.
- Okafor P.C,I.E.Uwah,U.J.Ekpe,O.O.Ekerenam, (2009), "*Combretum bracteosum extracts* as eco-friendly corrosion inhibitor for mild steel in acidic medium", Pigment&Resin technology,38(4): 236-241.
- Olasehinde, E. F., Olusegun S. J. , Adesina, A. S., Omogbehin, S. A., Momoh-Yahayah, H.Inhibitory Action of *Nicotiana tabacum* Extracts on the Corrosion of Mild Steel in HCl: *Nature and Science* 2013;11(1)
- Onuegbu T. U., Umoh E.T., Onuigbo U. A ,*Eupatorium Odoratus* As Eco-Friendly Green Corrosion Inhibitor Of Mild Steel In Sulphuric Acid , *International Journal Of Scientific & Technology Research* Volume 2, Issue 2, February 2013
- Patel N. S, S Jauhariand, G N Mehta, S. S. Al-Deyab, I. Warad, B. Hammouti. Mild Steel Corrosion Inhibition by Various Plant Extracts in 0.5 M Sulphuric acid, *Int. J. Electrochem. Sci.*, 8 (2013) :2635 – 2655
- Pandian Bothi Raja , Mehran Fadaeinasab , Ahmad Kaleem Qureshi , Afidah Abdul Rahim, Hasnah Osman , Marc Litaudon , and Khalijah Awang, (2013), "Evaluation of Green Corrosion Inhibition by Alkaloid Extracts of *Ochrosia oppositifolia* and Isoreserpiline against Mild Steel in 1 M HCl Medium", *Ind. Eng. Chem. Res.*, 52 (31):10582–10593
- Punita Mourya, Sitashree Banerjee, M.M. Singh, (*2014)*, "Corrosion inhibition of mild steel in acidic solution by *Tagetes erecta* (Marigold flower) extract as a green inhibitor", *Corrosion Science, Volume 85, Pages 352-363*
- Pavithra M. Krishnegowda , Venkatarangaiah T. Venkatesha, Punith Kumar M. Krishnegowda, and Shylesha B. Shivayogiraju, (2013),"*Acalypha torta* Leaf Extract as Green Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution" ,*Ind. Eng. Chem. Res.*, 52 (2), pp 722–728.
- Parikh K. S., Joshi K. J., (2004). "Use of Heena & Babul: Picking inhibitors for mild steel in 5% hydrochloric acid" , *Chemical engineering world*, 39: 64-68.

- Rajalakshmi R., and Safina A.S. “Inhibitive propertives of Leaf Sheath extract of *Cocos Nucifera* as green inhibitor for mild steel in HCl medium”, *Asian* Journal of Chemistry, 24 (10):4401 - 4407.
- Ramananda Singh.M. A green Approach: *(2013), “*A corrosion inhibition of mild steel by *Adhatoda vasica* plant extract in 0.5 M H2SO4”, *J. Mater. Environ. Sci. 4: 119-126.*
- Rajalakshmi R., and Safina A.S., (2012), “Staminate flower of *Cocos Nucifera* as green inhibitor for mild steel in HCl medium”, *E-Journal of Chemistry,* 9 **:**1632-1644.
- Rajalakshmi R., Subhashini S., Prithiba A., .(2010) “Acid extracts of *Ervatamia coronaria* leaves for corrosion inhibition of mild steel”, *Asian Journal of chemistry* 22 (7):5034-5040.
- Rajalakshmi. R., Subhashini. S., Leelavathi. S., Femina Mary. R., (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).
- Sakthivel P, Nirmala P V, Uma Maheswari S, Antony A A A, Kalaignan G P, Gopalan A, Vasudevan T; (1999), “Inhibitive action of *Pongamia* and *Annona* on mild steel in acid medium*” Bull.Electro Chem, 15(2): 83-86.*
- Sethuraman M.G, Bothi Raja P,”Corrosion inhibition of mild steel by *Daturametel”, Pigment &Resin Technology,*34(6):2005, 327-331.
- Sethuraman M.G., Ajesh T.P., and Vinodkumar K.P., (2001), “The effect of *Solanum trilobatum extract* on the corrosion of mild steel in HCl medium” *,10th National Convention of Electrochem.,* 13-14.
- Sheyreese M. Vincent., Cyril B. Okhio., (2005), “Inhibiting corrosion with *Green Tea”, Journal of Corrosion Science and Engineering,* 7(36): 354-359. 77
- Shivakumar S.S., K.N. Mohana.Studies on the Inhibitive Performance of *Cinnamomum zeylanicum* Extracts on the Corrosion of Mild Steel in Hydrochloric Acid and Sulphuric Acid Media *.J. Mater. Environ. Sci. 4 (3):(2013): 448-459*
- Subha. R., Saratha. R.; Naturally occurring substance (*Calendula officinalis* flower) as a corrosion inhibitor of mild steel in 1M HCl solution; JCSE, Vol: 10, Preprint 9 ,3rd Sep 2006.

- Subhashini. S., Rajalakshmi. R. and Kowshalya. V.N., Eco-friendly corrosion inhibitor from *poultry waste* for mild steel in acid medium, *Material Science Research India, Vol: 5, No. 2,* Pg: 423-428, Dec 2008.
- Saviour A. Umoren, Zuhair M. Gasem , and Ime B. Obot, (2013), "Natural Products for Material Protection: Inhibition of Mild Steel Corrosion by Date *Palm Seed Extracts* in Acidic Media", *Ind. Eng. Chem. Res.,* 52 (42):14855–14865
- *Smita A.Verma and Mehta G.N., (1998), Tranaction of the SAEST 32 (4): 160-162.*
- Uwah IE, Okafor PC, Ebiekpe VE, (*2013)*, "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, Volume 6, Issue 3, Pages 285-293*
- Umoren S. A. and Ebenso E. E.,(2008), "Studies of the anti-corrosive effect of *Raphia hookeri* exudate gum-halide mixtures for aluminium corrosion in acidic medium," *Pigment and Resin Technology*, 37(3):173–182.
- Umoren.S.A, Eduok .U.M, Solomon.M.M, Udoh.A.P (2011), "Corrosion inhibition by *leaves and stem extracts of Sida acuta* for mild steel in 1 M H2SO4 solutions investigated by chemical and spectroscopic techniques", *Arabian Journal of Chemistry,* 37(3):173–182.
- Vasudha V.G., Shanmuga PriyaK. *PolyalthiaLongifolia*as a Corrosion Inhibitor for Mild Steel in HCl Solution, January (2013) *Res.J.Chem. Sci,* Vol. 3(1), 21-26
- Vijayalakshmi.P.R, Rajalakshmi .R, Subhashini S, (2010), " *Cocos nucifera* shell as a potential inhibitor for mild steel corrosion in acidic medium, Asian J.Chem, 22(6): 4537 – 4548.
- Vijayalakshmi.P.R, Rajalakshmi.R and Subhashini.S (2010) "Inhibitory action of *Borassus Flabellifier Linn*.(Palmyra Palm) Shell Extract on Corrosion of Mild steel in Acidic Media". E-journal of chemistry,7(3):1055-1065
- Yan Li, Peng Zhao,Qiang Liang and Baorong Hou., (2005), "Berberine as a natural source inhibitor for mild steel in 1 M H2SO4.", *Applied Surface Science,*252: 1245-1254.