Assessment of the Inhibitive Action of Bakery Waste for Corrosion of Mild Steel In Acid medium

By

S. LEELAVATHI
(06 PAC 11)

A Dissertation Submitted To The

AVINASHILINGAM UNIVERSITY FOR WOMEN,

COIMBATORE – 641043.

In Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE IN APPLIED CHEMISTRY

APRIL-2008

Assessment of the Inhibitive Action of Bakery Waste for Corrosion of Mild Steel In Acid medium

By

S. LEELAVATHI
(06 PAC 11)

A Dissertation Submitted to the

AVINASHILINGAM UNIVERSITY FOR WOMEN,

COIMBATORE – 641043.

In Partial Fulfilment of the Requirements

for the Degree of

MASTER OF SCIENCE IN APPLIED CHEMISTRY

APRIL-2008

Certified as Bonafide Research Work

29.4.08
Signature of the H.O.D

29.4.08
Signature of the Guide

ACKNOWLEDGEMENT

It is with the choicest blessings and divine grace of the ***God Almighty*** that any human endeavour is achieved. In addition to the will of the Supreme Divinity, the success of the project lies in the hands of many persons who have helped and guided me in completing this project. I take this opportunity to express my sincere thanks and gratitude to each and every one of them who had supported me.

I wish a grateful thanks to Hon***. Dr. K. Kulandaivel,*** M.A., M,A.,(Ohio State), Ph.D.(Madras), Former Chancellor, Avinashilingam University for Women, Coimbatore, for providing the opportunity to conduct my investigation in this esteemed University.

I record my heartfelt thanks to ***Mr. T.K. Shanmuganandam,*** B.A., B.L., Chancellor, Avinashilingam University for Women, Coimbatore, for the provision of a conductive and congenial ambience for the execution of research work.

I extend my respectful thanks to ***Dr. Saroja Prabhakaran***, M.A., Dip.M.Ed.,(Chennai), Ph.D.,(Mother Teresa), Vice Chancellor, Avinashilingam University for Women, Coimbatore, for providing all the facilities essential to carry out and complete the study.

I thank immensely ***Dr. Gowri Ramakrishnan***, M.Sc.,(Madras), M.Phil., Ph.D.,(Avinashilingam), Registrar, Avinashilingam University for Women, Coimbatore, for the timely help rendered to carry out the work.

My overwhelming gratitude and sincere thanks goes to ***Dr. (Mrs). R. Parvatham,*** M.Sc., Dip. Ed., M.Phil.,(Madras), Ph.D.,(Avinashilingam), Dean and Head, Department of Bio-Chemistry, Faculty of Science, Avinashilingam University for Women, Coimbatore, for her for her support and encouragement.

I record with pleasure my deep sence of gratitude to ***Dr. Mrs. R. Shyamala,*** M.Sc., Dip. Ed., (Madras), M.Phil., (Bharathiar), Ph.D., (Avinashilingam), Professor and Head, Department of Chemistry, Avinashilingam University for Women, Coimbatore,for her motivationand help in the conduct of the study.

I feel extremely proud and privileged to have been able to work under the able guidance of ***Dr. (Mrs). R. Rajalakshmi,*** M.Sc., B.Ed., (Madurai Kamaraj), M.Phil., (Bharathiar), Ph.D., (Avinashilingam), Reader, Department of Chemistry,Avinashilingam University for Women, Coimbatore, for her meticulous care, guidance, patience, unflinching encouragement, innovative ideas, constructive thoughts, constant support and motivation right from the selection of the topic to the completion of the work.

My sincere thanks to ***Dr. (Mrs). S. Subhashini,*** M.Sc., M.H.Ed., (Annamalai), M.Phil (Bharathiar), Ph.D., (Avinashilingam), Reader, Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women (Deemed University), Coimbatore for her timely and valuable help, sustained encouragement, expert suggestions and motivation all through the project.

I also wish to thank all the ***Staff Members of the Chemistry Department,*** Avinashilingam University for Women, Coimbatore, who rendered their help whenever required.

I cordially thank my ***beloved parents, caring brother*** for their encouragement, enduring help and lovable care which have been the source of strength.

I am forever grateful to my ***friends*** for their moral support and multifarious assistance through out the work.

S. LEELAVATHI

CONTENTS

LIST OF ABBREVIATIONS

E.S	⌋	Egg shell
H_2SO_4	⌋	Sulphuric Acid
C.R	⌋	Corrosion Rate
I.E	⌋	Inhibition Efficiency
MS	⌋	Mild Steel
Conc	⌋	Concentration
I_{corr}	⌋	Corrosion Current Density
E_{corr}	⌋	Corrosion Potential
b_c	⌋	Cathodic Tafel Slope
b_a	⌋	Anodic Tafel Slope
R_p	⌋	Polarization Resistance
R_{ct}	⌋	Charge Transfer Resistance
C_{dl}	⌋	Double Layer Capacitance
LPR	⌋	Linear Polarization Resistance
ml	⌋	Milli litre
hr	⌋	Hour
mV	⌋	Milli volt
θ	⌋	Surface coverage

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

INTRODUCTION

GIST OF CORROSION

Corrosion is a natural process and is a result of the inherent tendency of metals to revert to their more stable compounds, usually oxides. Most metals are found in nature in the form of various chemical compounds called ores. In the refining process, energy is added to the ore, to produce the metal. It is this same energy that provides the driving force causing the metal to revert back to the more stable compound.

Corrosion is the destructive attack of a material by reaction with its environment

CORROSION AND THE SENSES

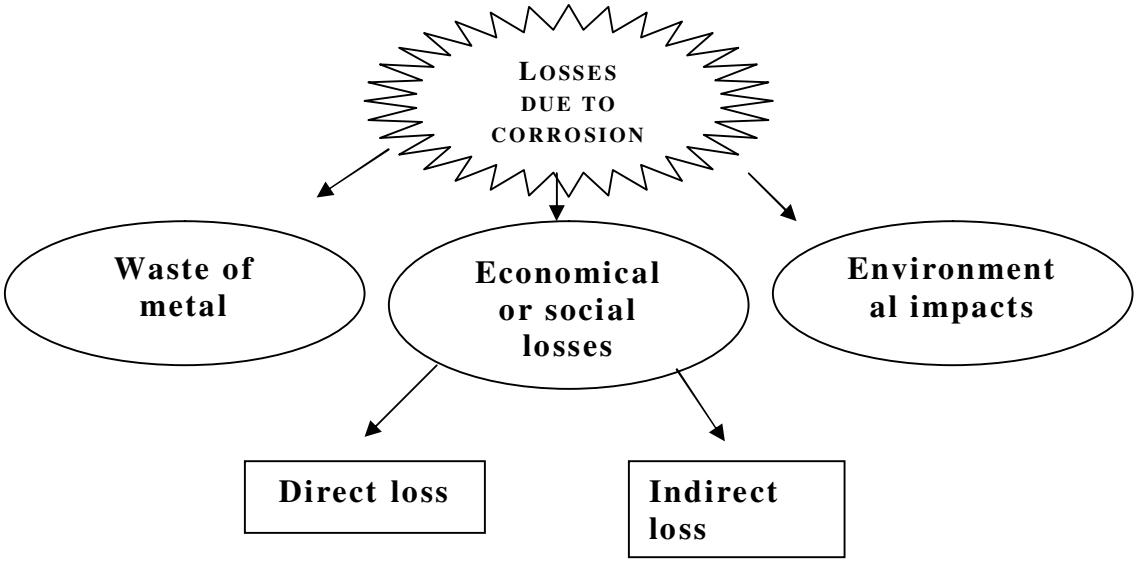
A good operator can see, taste, and smell changes in water quality and has the "sixth sense" to detect differences in quality before they become problems. It is this sixth sense that makes the science of corrosion control an art in an effective treatment program.

Color : Iron corrosion stains bathroom vanities and white laundry with a familiar rust color. In homes, copper corrosion results in blue–green stains that show up in sinks, baths, and blonde hair.

Taste and odor : Corrosion can cause a metallic taste and sometimes a musty odor. At times this odor can be attributed to bacterial problems.

LOSSES DUE TO CORROSION

"Corrosion is a natural impact of atmospheric environments like marine, industrial, urban and rural and affects the structural stability of buildings. The annual loss due to corrosion can be compared with that of other natural calamities like earthquakes and cyclones, only its impact is indirect. Loss due to corrosion has been reported to account for more failures in terms of cost and tonnage than any other environment."



1. Waste of metal resources

Aside from its direct costs in dollars, corrosion is a serious problem, because it definitely contributes to the depletion of our natural resources. As resources are consumed, in the future, conservation and recycling will become watchwords – not catchwords.

2 .Environmental impacts

Corrosion is not only expensive but also pose a significant risk to human life and safety. The fatal accident like the leak of methyl cyanide in a plant in Bhopal, India, cost many thousands of lives and blinded many thousands permanently.

3. Economical or social losses

This includes direct and indirect losses. Being wide in its range of effect and almost inseparable from the technological activity, corrosion has a wide impact on the economics of technology.

Corrosion is one of the main causes of breakdowns in machinery and material leading to loss of man-power, material and money. This has been a matter of great concern both to the industrials and the state.

Also, as the world is beginning to depend more and more on light equipment such as computers, high energy batteries and sophisticated telecommunication equipment, another aspect of loss due to corrosion has been identified; while these are less subject to gross rusting, they are very sensitive to microscopic level corrosion. The fact that these circuits consists of very little material to begin with, means that small amounts of corrosion create disproportionately larger problems.

COST OF CORROSION

The **cost of corrosion is estimated to be around $364 billion as of 2004.** This does not include the indirect cost and other consequential damages. If this is taken into account, it would go up several times from the present level of 3.1% of GDP," said Houston-based NACE International president George Hays during his presentation at the NACE International India Section conclave in Mumbai.

CORROSION IN INDIA

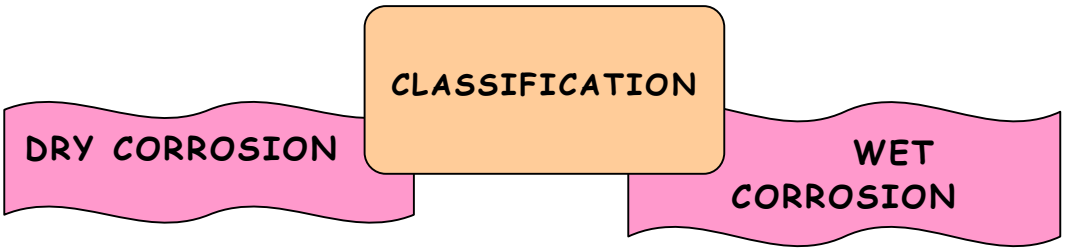
"As for **the cost of corrosion in India alone, it is estimated to touch Rs 36,000 crore,"** The country is losing Rs 80,000 crore per annum on account of corrosion in various sectors and at least 25 percent of this can be saved by way of proper management said Mr.Hays at Mumbai.

INDUSTRIAL MISSION STATEMENT

We place great emphasis on providing practical cost effective solutions, which are based on many years of experience in all aspects of the Corrosion Prevention Industry. While we realize and accept the importance of theory, however, there is no substitute for experience, and therefore our designs are based on a combination of both technical and practical experience.

"The control of corrosion, at all levels, involves optimizing costs, doing neither too little nor too much. To reach an optimum decision the cost of corrosion control should be balanced in such a way that the total cost over the structure's lifetime is minimized.

CLASSIFICATION OF CORROSION:



1.Direct Chemical corrosion (Dry Corrosion)

It involves direct chemical reaction of a metal with its environment. There is no transport of electric charge and the metal remains film free. This would include corrosion in gaseous environment when the reaction product is volatile, corrosion in liquid metals, fused halides and organic liquids.

2 .Electrochemical corrosion (Wet Corrosion)

This occurs when aqueous solutions or liquid electrolytes are present. Here two partial reactions occur, one at each electrode. The anodic reaction is always the dissolution of the metal.

$$M \longrightarrow M^{n+} + n^{e-}$$

Metal | Metal ion | Oxidation

Cathodic reaction may be

i) Hydrogen evolution
ii) Oxygen absorption
iii) Metal deposition

Of these the first two are more probable. If the corrosive medium is highly acidic, hydrogen evolution is more likely.

$$2\,H^+ + 2\,e^- \rightleftharpoons H_2\,(g)$$

If the solution is sufficiently aerated, oxygen absorption occurs.In fairly acidic medium,

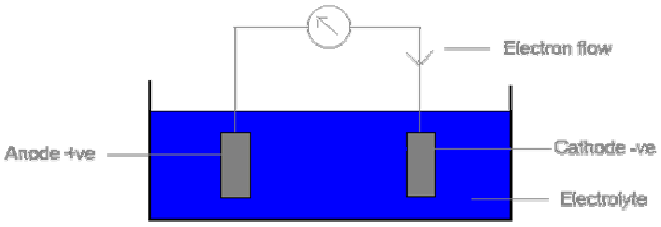
$$O_2 + 4\,H^+ + 4e^- \rightleftharpoons 2\,H_2O$$

In alkaline or neutral medium,

$$O_2 + 2\,H_2O + 4e^- \rightleftharpoons 4\,OH^-$$

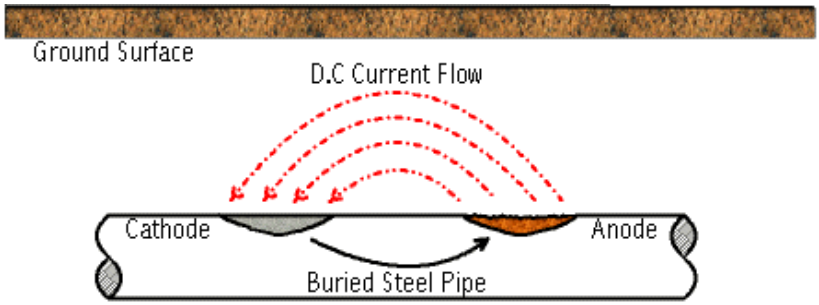
During corrosion more than one oxidation or one reduction may occur. For example if more than one reduction occurs, then the oxidation viz., corrosion will be faster than when only one reduction occurs. This is because the total rate of oxidation must be equal to that of reduction.

MECHANISM OF CORROSION



Corrosion is an electrolytic action involving an exchange of electrons and ions. It can take place between dissimilar metals or between areas of the same metal or alloy component where there are differences in electrochemical potential. These occur naturally with the effects of oxides, impurities, alloy phases and metallurgy, but any corrosive situation requires a conducting electrolyte (moisture, salt water, caustic, etc.) to establish the electrical circuit. A typical corrosion cell can be represented by:

ELECTROCHEMICAL CORROSION THEORY

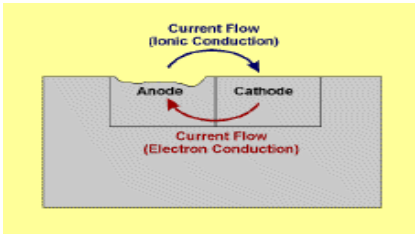


Electrochemical corrosion involves two half-cell reactions; an oxidation reaction at the **anode** and a reduction reaction at the **cathode**. For iron corroding in water with a near neutral pH, these half cell reactions can be represented as:

Anode reaction: $2Fe \Rightarrow 2Fe^{2+} + 4e^-$

Cathode reaction: $O_2 + 2H_2O + 4e^- \Rightarrow 4OH^-$

There are obviously different anodic and cathodic reactions for different alloys exposed to various environments. These half cell reactions are thought to occur (at least initially) at microscopic anodes and cathodes covering a corroding surface. Macroscopic anodes and cathodes can develop as corrosion damage progresses with time.



Schematic representation of current flow (conventional current direction) in a simple corrosion cell

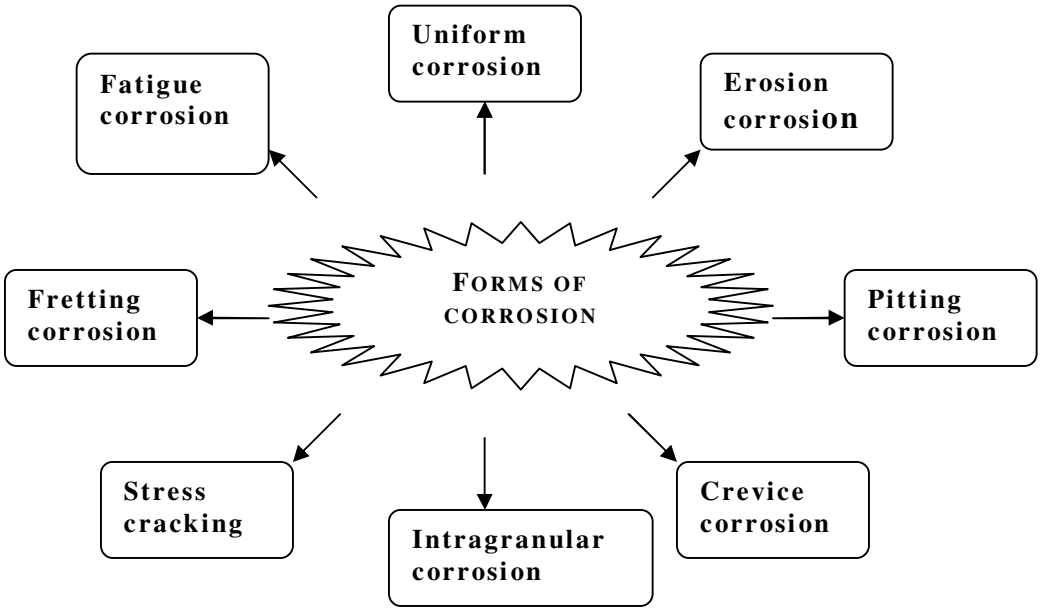
From the above theory it should be apparent that there are four fundamental components in an electrochemical corrosion cell:

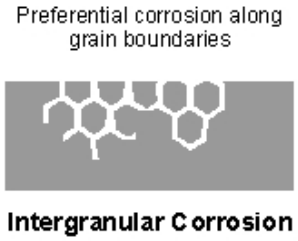
- *An anode.*
- *A cathode.*
- *A conducting environment for ionic movement (electrolyte).*

An electrical connection between the anode and cathode for the flow of electron current.

If any of the above components is missing or disabled, the electrochemical corrosion process will be stopped. Clearly, these elements are thus fundamentally important for corrosion control.

FORMS OF CORRROSION

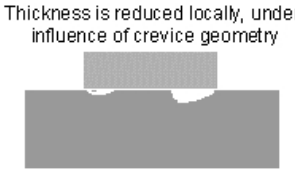




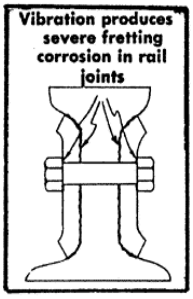
Intergranular Corrosion

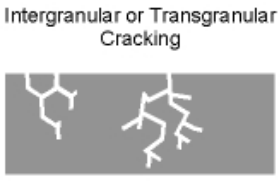
Pitting Corrosion

Uniform Corrosion

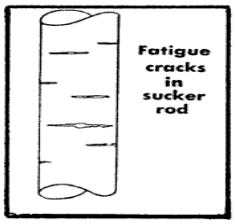


Crevice Corrosion





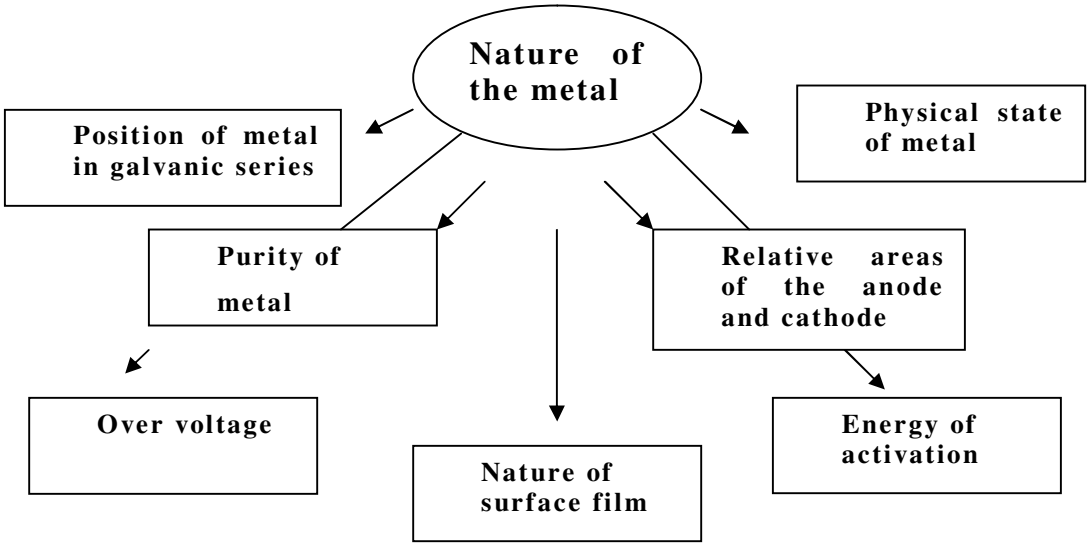
Stress Corrosion Cracking

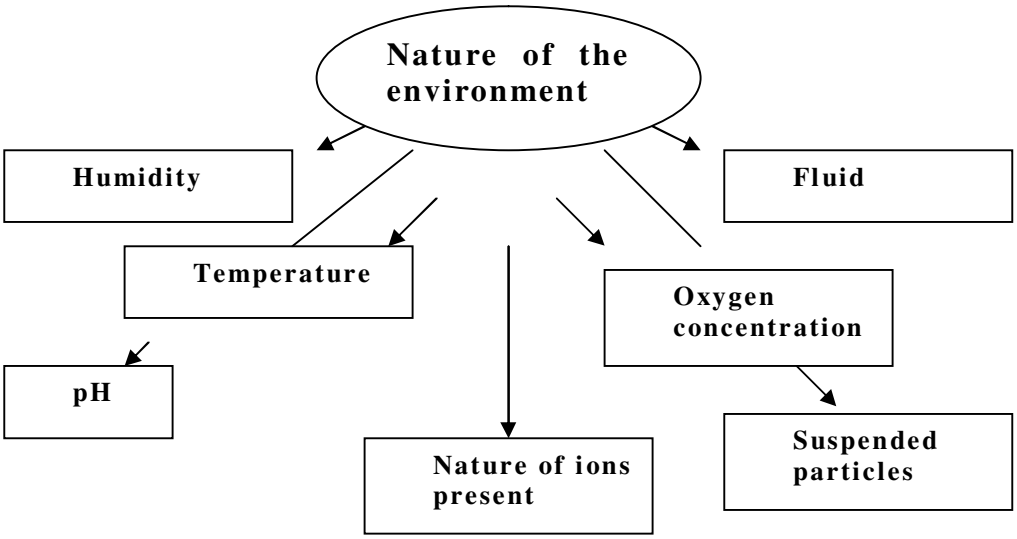


FACTORS INFLUENCING CORROSION

The rate and extent of corrosion depends mainly on

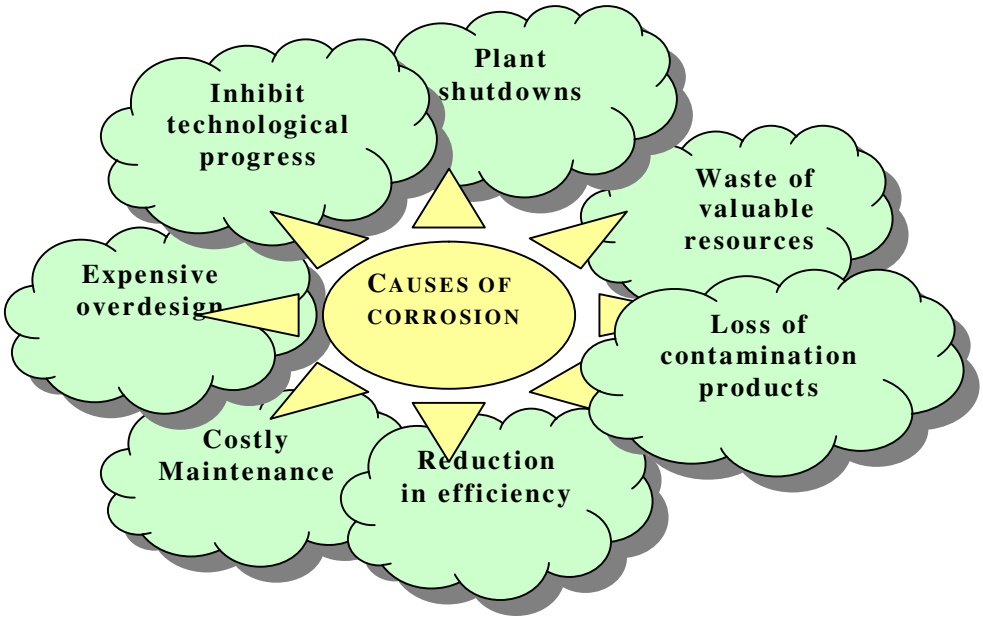
- *Nature of metal*
- *Nature of the environment*





CONSEQUENCES OF CORROSION

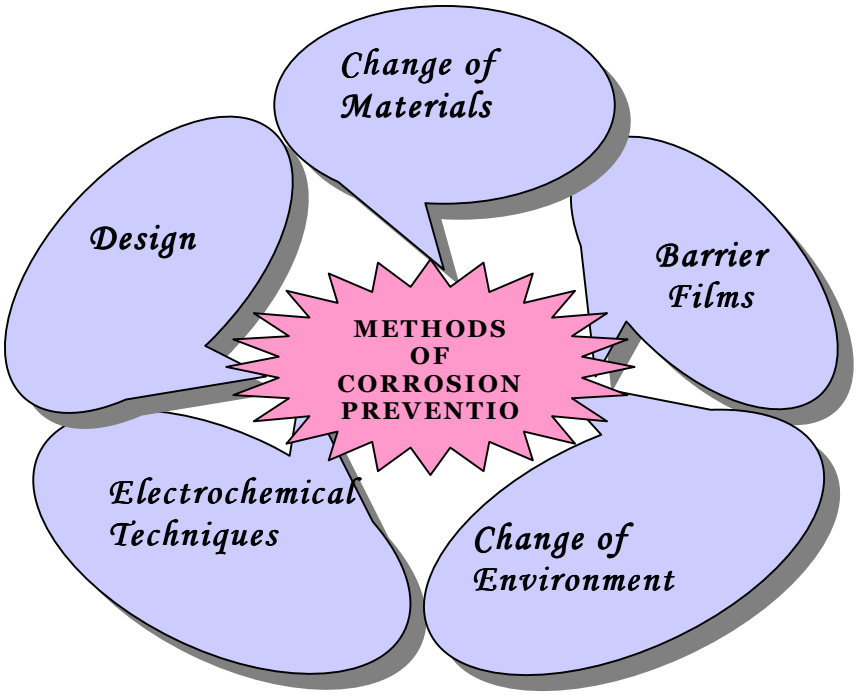
The serious consequences of the corrosion process have become a problem of worldwide significance.



CORROSION MANAGEMENT

- Increase awareness of large corrosion costs and potential savings
- Change the misconception that nothing can be done about corrosion
- Change policies, regulations, standards, and management practices to increase corrosion savings through sound corrosion management
- Improve education and training of staff in recognition of corrosion control
- Advance design practices for better corrosion management
- Advance life prediction and performance assessment methods
- Advance corrosion technology through research, development, and implementation.

CORROSION PREVENTION



Change of Materials :Complete or partial change of materials used

Change of Environment :Either a complete change in environment or a partial alteration by modification of pH etc

Barrier Films : Either organic coatings or electroplating etc.

Electrochemical

Techniques : Sacrificial coatings, cathodic or anodic protection

Design : Allowances for general corrosion and control of factors such as temperature, velocity etc

CLASSIFICATION OF CORROSION PROTECTION METHODS

❖ Active Corrosion Protection

The aim of active corrosion protection is to influence the reactions which proceed during corrosion, it being possible to control not only the package contents and the corrosive agent but also the reaction itself in such a manner that corrosion is avoided. Examples of such an approach are the development of corrosion-resistant alloys and the addition of inhibitors to the aggressive medium.

❖ Passive Corrosion Protection

In passive corrosion protection, damage is prevented by mechanically isolating the package contents from the aggressive corrosive agents, for example by using protective layers, films or other coatings. However, this type of corrosion protection changes neither the general ability of the package contents to corrode, nor the aggressiveness of the corrosive agent and this is why this approach is known as passive corrosion protection. If the protective layer, film etc. is destroyed at any point, corrosion may occur within a very short time.

❖ Permanent Corrosion Protection

The purpose of permanent corrosion protection methods is mainly to provide protection at the place of use. The stresses presented by climatic, biotic and chemical factors are relatively slight in this situation. Machines are located, for example, in factory sheds and are thus protected from extreme variations in temperature, which are frequently the cause of condensation. Examples of passive corrosion protection methods are:

- *Tin plating*
- *Galvanization*
- *Coating*
- *Enameling*
- *Copper plating*

❖ Temporary Corrosion Protection

The stresses occurring during transport, handling and storage are much greater than those occurring at the place of use. Such stresses may be manifested, for example, as extreme variations in temperature, which result in a risk of condensation. Especially in maritime transport, the elevated salt content of the water and air in so-called seasalt aerosols may cause damage, as salts have a strongly corrosion-promoting action. The following are the main temporary corrosion protection methods:

- *Protective coating method*
- *Desiccant method*
- *VCI method*

CORROSION CONTROL METHODS

"It is better to control rather than to prevent corrosion, since it is impossible to eliminate corrosion" **(Jain & Jain, 1992).** Some of the corrosion control methods are,

1. Design improvement
2. Change of metal

    By selection of the material

    By using pure metal

    By alloying

    By annealing

3. Change of environment

    By removal of harmful constituents

    - Deaeration
    - Dehumidification

    By addition of inhibitors

By change of operating variables such as temperature, pH, viscosity, etc.,

4) Change of metal electrode potential

Cathodic protection

- Sacrificial anodic protection
- Impressed current cathodic protection

5) Use of protective coatings

CORROSION INHIBITORS

The use of chemical inhibitors to decrease the rate of corrosion processes is quite varied. In the oil extraction and processing industries, inhibitors have always been considered to be the first line of defense against corrosion. A great number of scientific studies have been devoted to the subject of corrosion inhibitors. However, most of what is known has grown from trial and error experiments, both in the laboratories and in the field.

Rules, equations or theories to guide inhibitor development or use are very limited. A synergism, or cooperation, is often present between different inhibitors and the environment being controlled, and mixtures are the usual choice in commercial formulations.

DEFINITION OF INHIBITORS

- Inhibitor is a chemical substance, which when added in small concentration to an environment, minimizes or prevents corrosion **(Riggs, 1973)**.
- Inhibitors are substances which when added in small quantity to a corrosive environment lower the corrosion rate **(Raj Narayan, 1988)**.

CLASSIFICATION OF INHIBITORS

INTERFACE INHIBITORS

They inhibit by forming a film at the metal – environmental interface. Interface can be classified into liquid and vapour phase inhibitors.

a) Vapour – phase inhibitors (VPIs)

Temporary protection against atmospheric corrosion, particularly in closed environments can be achieved using vapour phase inhibitors. VPIs are more effective for ferrous than non-ferrous metals.

b) Liquid phase inhibitors

They are further classified as anodic, cathodic and mixed inhibitors.

i) Anodic inhibitors

Anodic inhibitors are usually used in near-neutral solutions where sparingly soluble corrosion products, such as oxides, hydroxides or salts are formed. When its concentration is not sufficient, corrosion may be accelerated, rather than inhibited. They are also called passivating inhibitors.

ii) Cathodic inhibitors

Cathodic inhibitors either slow the cathodic reaction itself or selectively precipitate on cathodic on cathodic areas to increase the surface impedance and limit the diffusion of reducible species to there areas. They provide inhibition by three different mechanisms.

Cathodic poisons

Cathodic precipitates

Oxygen scavenger

- ***Cathodic poisons*** are used advantageously as corrosion inhibitors by stifling the cathodic reduction processes that must balance the anodic corrosion reaction (eg.,) silicates, borates, phosphates.
- ***Cathodic precipitators*** increase the alkalinity at cathodic sites and precipitate insoluble compounds on the metal surface (eg.,) carbonates of calcium and magnesium.
- ***Oxygen scavenger*** is that chemical which reacts with dissolved oxygen to reduce corrosion such as sulfite and bisulfite ions combines with oxygen to form sulfate.

iii) Mixed inhibitors

About 80% of inhibitors are organic compounds that cannot be designated specifically as anodic or cathodic and are known as mixed inhibitors (eg.,) polyphosphates. They protect the metal in three possible ways.

Physical adsorption

Chemisorption

Film formation

NEED FOR SELECTION OF NATURAL COMPOUND AS INHIBITOR

Inhibitors can be used to great advantage to suppress the corrosion of metals in many environments; there are certain limitations of this type of corrosion prevention which should be recognized. First, it may not be possible to add inhibitors to all corrosive systems because they may contaminate the environment. Further, many inhibitors are toxic and their application is limited in those mediums which will not be used directly or indirectly in the preparation of food or other products which will come in contact with humans. Inhibitors are primarily used in closed systems where the corrosive environment is either contained for long periods or re-circulated. Inhibitors are usually not practical in “once -

through" system. Finally, inhibitors generally rapid lose their effectiveness as the concentration and temperature of the environment increase.

`"It is only through the elimination of waste and the increase in our national efficiency that we can hope to lower cost of living, on the one hand, and raise our standards of living, on the other. The elimination of waste is a total asset. It has no liabilities".

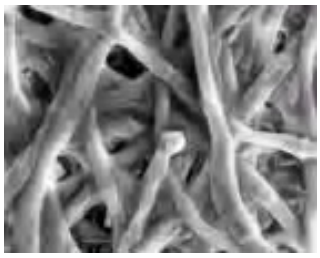
Keeping the above quote in mind, our present study aims at evaluating the corrosion inhibition study using animal waste materials. Thereby elimination of waste and corrosion inhibition is done in one hand (or) hit in one stone.

EGG SHELL PROFILE

EGG SHELL : The egg's outer covering, accounting for about 9 to 12% of its total weight depending on egg size. The shell is the egg's first line of defense against bacterial contamination.

The shell is largely composed of calcium carbonate (about 94%) with small amounts of magnesium carbonate, calcium phosphate and other organic matter including protein.

Scanning electron micrographs of egg shell membrane, highlighting the unique structure. The fibres show the source of the unique and highly valued type of collagen present in the membrane.



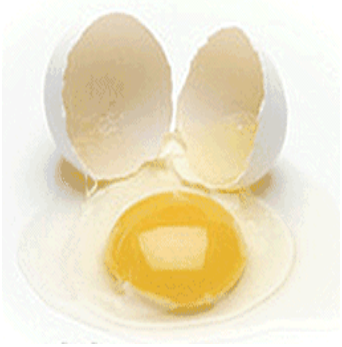


FIG 1

EGG SHELL – HITCH

Eggshell waste is a serious matter in the "egg-breaking" industry. Companies are paying up to $100,000 a year to dispose of eggshells in landfills -- and the fills are reaching capacity. On top of that, many landfill owners do not want eggshells because the protein-rich membrane which adheres to the shell attracts rats and other vermin.

IS IT WASTE?

Egg shell Product	***Application***
Collagen	***Cosmetics***: (facial treatment; anti-ageing/wrinkle creams); ***Biomedical***: wound dressings; surgical implants; intrusive device coatings.
Gelatin	Food and confectionery constituent; ice-cream texturiser.
Sialic Acid	Pre-cursor for many anti-inflammatory drugs

CRUCIAL ROLE

"The key to making pure hydrogen is separating out the carbon dioxide,"

That brought them to eggshells, which mostly consist of calcium carbonate -- one of nature's most absorbent materials. It is a common ingredient in calcium supplements and antacids. With heat processing, calcium carbonate becomes calcium oxide, which will then absorb any acidic gas, such as carbon dioxide.

Calcium carbonate –- a key ingredient in the eggshells -- captures 78 percent of carbon dioxide by weight, that means, given equal amounts of carbon dioxide and eggshell, the eggshell would absorb 78 percent of the carbon dioxide.

NEW IMPERATIVE ROLE

Efforts have been taken to prove that bakery waste egg shells can act as corrosion inhibitor in sulphuric acid media for mild steel. The inhibitive effect of egg shells extract for the corrosion of mild steel in 0.5M sulphuric acid have been investigated.

OBJECTIVES

- To select an ecofriendly "*zero cost*" inhibitor for corrosion of MS in acid medium.
- To utilize egg shell extract – bakery waste as corrosion inhibitor for MS in acid medium.
- To study the effect of concentration of the egg shell extract at room temperature on corrosion inhibition of MS in acid medium
- To carry out immersion studies using the selected egg shell extract.
- To find the stability of egg shell extract at higher at higher temperatures.
- To calculate Ea and free energy of adsorption, ΔS and ΔH using temperature studies results .
- To fit the result into experimental data.

- To evaluate the IE of the egg shell extract using electrochemical measurements.
- To understand the mechanism of inhibition using electrochemical measurements.
- To compare the efficiency of the egg shell by various techniques

REVIEW OF LITERATURE

REVIEW OF LITERATURE

The present study on "Corrosion inhibition of MS using egg shell extract – bakery waste as an eco-friendly inhibitor for MS in acid medium" is reviewed under the following topics.

- Natural products as inhibitors
  - Effect of natural product as inhibitors on mild steel.
- Corrosion behaviour 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.

- They can easily be obtained from ordinary and cheap resources.
- Non-toxic.
- Eco friendly.
- They have high surface activity.
- Bio degradable.

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.

✠ The effect of *cashew juice* extract on corrosion inhibition of mild steel in HCl was investigated by **Dr. C.A. Loto and A.I. Mohammed (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.

✠ **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 inhibitor efficiency increased with increase in concentration and temperature. The presence of Solanaces alkaloid in the plant was identified as responsible for inhibition.

✠ An extract of *Neem (Azadiracta indica)* has been investigated for corrosion inhibition and bacterial activity. The inhibitive efficiency has been studied by weight loss method, Tafel polarization and Impendence measurements. The low weight loss in the presence of *Neem* extract is in good agreement with and corrosion current resistance values**.** The extract also showed biocidal activity inhibition**.(Manimegalai et al., 2001)**

✠ **(Ramesh et al., 2001)** studied the inhibitive action of acid extract of *Andrograph's paniculata* on the corrosion of mild steel in hydrochloric acid using weight loss method and the results revealed that this plant extract has the potential to serve as corrosion inhibitor .

✠ **Ibrahim Hashi Omar et al., (2002)** investigated the effects of various plant extracts on the dissolution of mild steel in HCl. The additives investigated were *Papaia, Poinciana pulcherrima, Cassia occidentalis* and *Datura stramonium* seeds and *Calotropis procera*. Weight-loss determinations and electrochemical measurements were performed. All extracts reduced the corrosion of steel with an efficiency of 88%–96% in 1 N HCl and with a slightly lower efficiency in 2 N HCl. The inhibition action is mostly due to the products of the hydrolysis of the protein content of these plants.

✠ **Rajalakshmi et al.,(2002)** investigated the performance of acid extracts of *ficus benghalensis* bark on the corrosion inhibition of mild steel in 1M HCl and 0.5M H_2SO_4 by weight loss and electro chemical techniques. The presence of anthrocyanin compounds,flavanoidal compounds and reducing sugars in the bark extract could inhibit the corrosion of mild steel in acid medium.

✠ **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.

✠ **H. Ashassi-Sorkhabi , M. R. Majidi (2002)** explained the inhibition effect of *amino acids* (alanine, glycine and leucine) against steel corrosion in HCl solutions using potentiodynamic polarization method. Corrosion data such as corrosion rate, corrosion potential (E_{corr}) and corrosion resistance (R_p) were determined by extrapolation of the cathodic and anodic Tafel region. The effect of inhibitor concentration and acid concentration against inhibitor action was investigated. The inhibition effect ranged from 28 to 91%.

✠ **Maheswari et al., (2003)** have 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 0.7 concentration at 65º C and the efficiency of 92.84% at 0.7 concentration of 5% extract.

✠ **Prathiba et al.,(2003)** investigated the *jack been* seed (*canavalia ensiformis*) as inhibitor for mild steel in 1M HCl medium and revealed that the efficiency increased with increasing concentration of the inhibitor and immersion time.A maximum of 95% was observed at 12 hrs for 0.75% of 5% extract.

✠ **Chitra et al., (2003)** studied the *Phaselous aureus* seeds extract on the corrosion of mild steel in 1M HCl and found that the inhibition efficiency increases with increase in inhibitor concentration and immersion time. An efficiency of 95.6% has been observed at 0.7% concentration at room temperature and slightly decreased to 93.58% at 65^{o}C.

✠ The inhibitive effects of aqueous extracts of *Jasminum auriculatum* (leaves), *Momordica Charantia* (fruits) and *Hibiscus* (flower) on the corrosion of mild steel for cooling water system, using 3% NaCl water, have been investigated by means of weight loss and electrochemical polarization and impedance techniques**.** All the extracts were found to inhibit corrosion and their inhibition efficiencies were Jasminum auriculatum (80%) Momordica charantia (79%) and Hibiscus (76%). Polarization measurements show that extract of Jasminum was anodic while the extracts of Momordica and Hibiscus were found to be cathodic. **(Farooqi, I H; Quraishi, M A .,2004).**

✠ **K. O. Orubite and N. C. Oforka (2004)** analysed the inhibition of the corrosion of mild steel in hydrochloric acid solutions by extract of the leaves of *Nypa fruticans Wurmb.* It has been studied using weight loss and hydrogen gas evolution techniques. Inhibition was found to increase with increasing concentration of the leaves extract. The inhibition action of *N. fruticans* was compared with that of 1,5-diphenylcarbazone. The highest inhibition efficiency of 75.11% was observed with N. fruticans at 30 °C.

✠ Natural Compounds *Onion* (Allium Cepa), *Garlic* (Allium Sativum) and *Bitter Gourd* (Momordica Charantia) as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid were proved by **Parikh, K S Joshi K J .,(2004)** .Variable parameters like inhibitor concentration, immersion period, temperature, and stirring rate were incorporated. 1% inhibitor concentration in 5% HCl gave 82%, 98% and 88% inhibition efficiency respectively.

✠ **A.Y. El-Etre et al., (2004)** proved that the aqueous extract of the leaves of *henna (lawsonia)* is tested as corrosion inhibitor of C-steel, nickel and zinc in acidic, neutral and alkaline solutions, using the polarization technique. It was found that the extract acts as a good corrosion inhibitor for the three tested electrodes in all tested media. The extract acts as a mixed inhibitor. The degree of inhibition depends on the nature of metal and the type of the medium.

✠ The effects of natural *Artemisia oil* on the corrosion of steel in molar hydrochloric acid were studied by the measurements of weight loss, electrochemical and EIS polarisation. The results obtained revealed that Artemisia oil reduced the rate of corrosion. The corrosion inhibition efficiency increased with the increase of inhibitor concentration. . Potentiodynamic polarisation studies clearly revealed that the presence of the natural Artemisia oil did not alter the mechanism of the hydrogen evolution reaction and acted essentially as a cathodic inhibitor. **(A. Bouyanzer, B. Hammouti.,2004)**

✠ **Parikh. K S JoshiK J.,(2004)** explained that dry leaves of *'Mehndi' (Heena; Lawsonia Intermis) and 'Babul' (Acacia Arabica)* were chemically extracted with 5 percent hydrochloric acid solution. Variable experimentel parameters like effect of inhibitor concentration, temperature, immersion period and stirring rate were studied, 1 percent inhibitor concentration in 5 percent hydrochloric acid environment gave 83 percent and 85 percent inhibition efficiency respectively.

✠ The corrosion behaviour of plant extract *Ricinus communis (castor-oil plant)* was studied by means of weight loss, electrochemical polarization and impedance measurements. It was found from weight loss measurements that the inhibition efficiency was about 84% in 300 ppm of the plant extract. Polarization measurements indicated that the plant extracts generally act as cathodic inhibitors. **Palaniswamy. N et al., (2005)** indicated that Ricinus communis might alleviate the corrosion process in mild steel.

✠ **A.Y. El-Etre et al.,(2005)** analyzed the inhibitive effect of the extract of *khillah (Ammi visnaga)* seeds, on the corrosion of SX 316 steel in HCl solution by using weight loss measurements and potentiodynamic technique. It was found that the presence of the extract reduces markedly the corrosion rate of steel in the acid solution.

✠ **E.E.Oguzie et al., (2005)** investigated the efficacy of *Telfaria occidentalis* extract as a corrosion inhibitor for mild steel in 2M HCl and 1M H_2SO_4 solutions. Inhibition efficiency increased with extract concentration but decreased with rise in temperature. It was found to be a promising inhibitor.

✠ **Yan Li et al., (2005)** explained that *Berberine* was extracted from *coptis chinensis* and its inhibition efficiency on corrosion of mild steel in 1 M H_2SO_4 was investigated through weight loss experiment and electrochemical techniques, surface analysis in the presence of inhibitor was done by scanning electronic microscope (SEM) with energy disperse spectrometer (EDS). The weight loss results showed that berberine is an excellent corrosion inhibitor for mild steel immersed in 1 M H_2SO_4.

✠ **Sheyreese M. Vincent et al., (2005)** investigated 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. He found that both the leaf as well as plant waste are excellent sources of corrosion inhibitors and can replace a wide variety of current toxic and polluting industrial inhibitors including tobacco.

✠ **A.M. Abdel-Gaber et al.,(2005)** observed that the effect of extracts of *Chamomile* (Chamaemelum mixtum L.), *Halfabar* (Cymbopogon proximus), *Black cumin* (Nigella sativa L.), and *Kidney bean* (Phaseolus vulgaris L.) plants on the corrosion of steel in aqueous 1 M sulphuric acid using electrochemical impedance

spectroscopy (EIS) and potentiodynamic polarization techniques. Potentiodynamic polarization curves indicated that the plant extracts behave as mixed-type inhibitors.

✠ Corrosion inhibition of mild steel in 2M HCl and 1M H_2SO_4 by leaf extracts of *Occimum viridis* was studied using the gasometric technique at temperatures of 30^o and 60^oC. The results indicated that the extracts inhibit the corrosion process in both acid media and inhibition efficiency increased with concentration. Temperature studies revealed a decrease in efficiency with rise in temperature **(Emeka E. Oguzie 2005).**

✠ The inhibition effect of *Zenthoxylum alatum* plant extract on the corrosion of mild steel in 5% and 15% aqueous hydrochloric acid solution has been investigated by weight loss and electrochemical impedance spectroscopy (EIS)**. L.R. Chauhan and G. Gunasekaran (2006)** proved that the effect of temperature on the corrosion behaviour of mild steel in 5% and 15% HCl with addition of plant extract was studied in the temperature range 50–80 °C.

✠ **Afidah A. Rahim et al.,(2006)** proved that the inhibitive behaviour on steel using flavanoid monomers that constitute *mangrove tannins* namely catechin, epicatechin, epigallocatechin and epicatechingallate in an aerated HCl solution via electrochemical methods. The monomers were found to be mainly cathodic inhibitors and the inhibition efficiency was dependent on concentration.

✠ *Natural oil* extracted from *Pennyroyal Mint* (Mentha pulegium, PM) was evaluated as corrosion inhibitor of steel in molar hydrochloric acid using weight loss measurements, electrochemical polarisation and EIS methods. The inhibition efficiency was found to increase with oil content to attain 80%.PM oil acts as a cathodic inhibitor.The increase in temperature leads to an increase in the inhibition efficiency of the natural substance. **(A. Bouyanzer, B. Hammouti 2006)**

✠ **Abo el-enin S et al., (2006)** studied that the aqueous extract of a natural compound, namely *Date Pits* (DP, hard stone of date palm) as an acid corrosion inhibitor for mild steel. The inhibition efficiency is evaluated by different techniques such as weight loss, polarization measurements (Tafet plot and Linear polarization) and scanning electron microscope (SEM).

✠ The inhibitive effect of *cocoa* (Theobroma Cacao) and *kolanut* (Cola Acuminata) extracts on the corrosion of mild steel in seawater at room temperature has been investigated. The study was carried out using the gravimetric technique. The results showed kola and cocoa leaves extracts as potential inhibitors of mild steel corrosion in seawater and marine environment. **(L.E. Umoru I.A. Fawehinmi 2006)**

✠ The inhibitive action of the aqueous extract of *olive leaves* (Olea europaea L.) toward the corrosion of C-steel in 2 M HCl solution was investigated by **A.Y. El-Etre et al.,(2007) .** It was found that the extract acts as a good corrosion inhibitor for the tested system. The inhibition efficiency increases with increasing extract concentration.

✠ **C. Thinaharan and G. Venkateswaran (2007)** studied that *Gallic acid* (GA) was found to provide corrosion inhibition to carbon steel. Inherent stability to radiation degradation as compared to other reductant and coupled with its anionic nature with respect to removal using ion exchange column makes it suitable for using as both reductant as well as corrosion inhibitor .

✠ **A. Tounsi, H et al.,(2007**) investigated that the effect of some *lactones* as inhibitors for the corrosion of mild steel in 1 M hydrochloric acid at different concentrations at 308 K using weight loss measurements, potentiodynamic polarization and impedance spectroscopy (EIS) methods. EIS measurements show an increase of the transfer resistance with the inhibitor concentration.

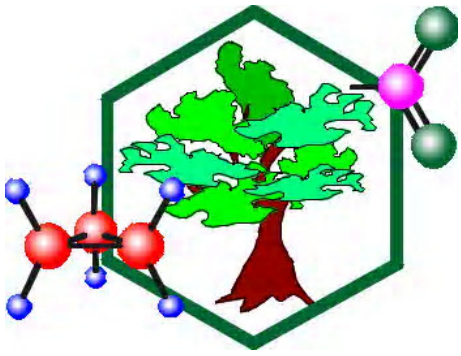
✠ **Mathur Gopalakrishnan et al.,(2007)** explained the corrosion inhibitive effect of the extract of *black pepper* on mild steel (MS) in 1 M H_2SO_4 media .It was evaluated by conventional weight loss studies (303–323 K), electrochemical studies viz., Tafel polarization, ac impedance and scanning electron microscope (SEM) studies. Results of weight loss study reveal that black pepper extract acts as a good inhibitor even at high temperatures.

✠ The inhibitive effect of ethanol extracts of *Garcinia kola* (EXG) for the corrosion of mild steel in H_2SO_4 solutions was proved by **P.C. Okafor et al.,(2007).** The inhibition efficiency has been evaluated using the hydrogen evolution technique at 30-60°C.

✠ The effect of *ascorbic acid* (AA) on the corrosion of mild steel in sulphuric acid solution has been investigated by open circuit potential (OCP) and polarization measurements. AA was observed to shift the OCP to more positive potentials with increasing concentration. The trend of inhibition efficiency with concentration showed that efficiency increased rapidly at low concentrations. **(E. E. Oguzie et al., 2007).**

✠ **E.E. Ebenso et al., (2007)** evaluated the effect of different parts of *Carica papaya* (leaves (LV), seeds (SD), heart wood (HW) and bark (BK)) as eco-friendly and non-toxic mild-steel corrosion inhibitors in H_2SO_4 media on the corrosion of mild steel. Inhibition efficiency increased with extracts concentration but decreased with temperature. The plant extracts can be used in chemical cleaning and picking process.

✠ *Natural products* as corrosion inhibitor for metals in corrosive media were inferred by **Sethuraman et al., (2007).** Plant extracts have become important as an environmentally acceptable, readily available and renewable source for wide range of inhibitors. They are the rich sources of ingredients which have very high inhibition efficiency.



MATERIALS AND METHODS

MATERIALS AND METHODS

In the present investigation, efforts have been taken to study the inhibitive efficiency of the extract of egg shell as corrosion inhibitor for mild steel in 0.5M sulphuric acid.

SELECTION OF THE SAMPLE

Due to low cost and easy availability, mild steel is a material of choice to fabricate various reaction vessels, pipes, tanks, etc., in sugar, petrochemical, brewery, food, paper, textile and marine industries. MS suffers from severe corrosion in aggressive environment, which needs to be protected. Hence the study of corrosion inhibition of MS in aqueous aggressive media is the subject of pronounced technological significance. Thus the investigation was carried out using mild steel.

PREPARATION OF THE SPECIMENS

A rectangular steel bar was cut into pieces of area 5x1 cm^2. The specimens were polished mechanically, degreased, cleaned successively in deionized water, dried, stored in a dessicator and used for all studies.

The locally produced mild steel specimens were found to have the following elemental composition.

ELEMENTAL ANALYSIS

TABLE 1

S. NO.	ELEMENT	% OF CHEMICAL COMPOSITION
1	CARBON	0.081
2	MANGANESE	0.296
3	SILICON	0.016
4	PHOSPHOROUS	0.032
5	SULPHUR	0.014
6	CHROMIUM	0.021
7	MOLYBDENUM	0.019
8	NICKEL	0.016
9	IRON	99.505

TEST MEDIA

The experiment was carried in 0.5M sulphuric acid. Since it is one of the most commonly and widely used acids in industries.

EQUIPMENTS USED

Solartron 1280 B

Thermostat

UNI-BLOC Digital balance.

INHIBITOR PREPARATION

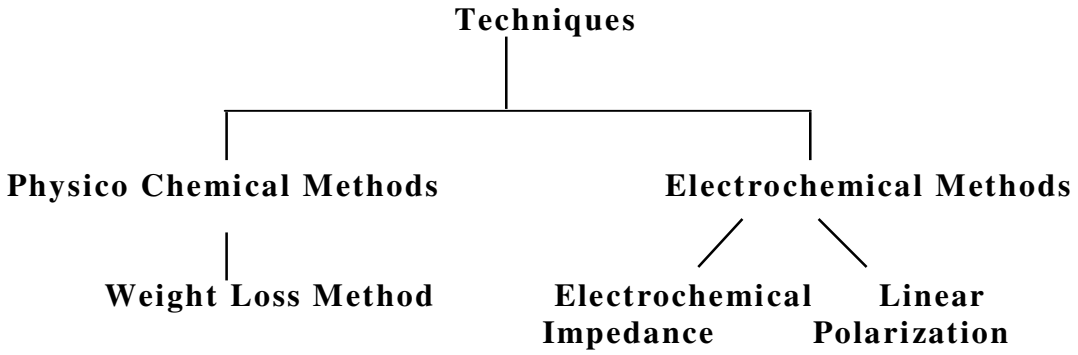
The inhibitor selected for the present study is the ***extract of egg shells***.The egg shells were collected from a near by bakery shop and air dried. About 25g of the shells were weighed and refluxed in 500ml of 0.5 M sulphuric acid for 3hrs. It was kept overnight and filtered to get 5% extract.

EGG SHELL EXTRACT IN ACID MEDIUM

FIG 2

TECHNIQUES EMPLOYED

Corrosion monitoring techniques have been classified into two main categories.



PHYSICO CHEMICAL METHOD (WEIGHT LOSS METHOD)

The MS coupons were weighed in UNIBLOC balance. weighed samples in triplicate were immersed in 100 ml of acid solution (with and without inhibitor) for a specific time viz., ½ hr,3hr,6hr,12 hr and 24hr. the specimens were removed and washed with saturated sodium bi carbonate solution and water , dried and reweighed.

The experiments were also performed with different concentrations of inhibitor and at various temperatures (303K-343K).

DETERMINATION OF CORROSION RATE

Many expressions are available to express corrosion rate. The widely used one is mills per year. The rate of corrosion was calculated using the formula.

$$\text{C.R. (mpy)} = \frac{534W}{DAT}$$

Where

W is the weight loss in g

D is the density of specimen in g/cm^2

A is the area of the specimen in cm^2

T is the exposure time in hr

DETERMINATION OF PERCENTAGE OF INHIBITOR EFFICIENCY

The inhibitor efficiency was obtained from the following formula.

$$IE = \frac{W_0 - W}{W_0} \times 100$$

Where

IE – Inhibitor efficiency in percentage

W_0 – Corrosion rate without inhibitor

W – Corrosion rate with inhibitor

DETERMINATION OF THERMODYNAMIC PARAMETERS

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

$$\text{Log of inhibitor concentration } \mathbf{(log\ C)} = \mathbf{log}\left[\frac{\theta}{1-\theta}\right] - \mathbf{log\ B}$$

log B = -1.74-(ΔG/2.303 RT)

R = Gas constant 8.134 J/mole

T = Temperature

C = Concentration of the inhibitor

θ = Surface coverage

The change in heat of adsorption ΔH and change in enthalpy ΔScan be calculated using Gibbs Helmholtz equation.

$$\mathbf{\Delta G = \Delta H - T\Delta S}$$

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

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 terms of adsorption isotherm. The

knowledge of the adsorption behaviour of the inhibitor is important for the definition of its active mechanism for this reason; the dependence of surface coverage on concentration is studied through the following adsorption isotherms.

Langmuir[(log θ/1- θ)Vs log C]

Temkin (θ Vs log C)

ACTIVATION ENERGY (EA):

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 (Ea) was calculated using the following formula.

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

Where R=gas constant 8.34 J/mole

POTENTIODYNAMIC POLARIZATION AND IMPEDANCE MEASUREMENTS: The corrosion monitoring techniques like

- *Potentiodynamic polarization(Tafel polarization)*
- *Electrochemical impedance spectroscopy(EIS)methods*

have been used in the present investigation. For all the two techniques, **solartron Electrochemical Measurement Unit** (1280B) model was used with a software package of **Z plot and Corrware**. The system includes a potentiostat, personal computer and Frequency Response Analyser.

For potentiodynamic polarization studies, the experiments were carried out over a potential range of -200mV to +200mV with respect to reference electrode and its current response was measured at a scan rate of 1mVsec^{-1}.

FIG 3 SOLARTRON 1280 B

Impedance measurements were carried out at corrosion potential. The A.C. amplitude of 10mV was applied and the frequency was varied from 10 kHz to 10 mHz. The real and imaginary parts of the impedance were plotted in Nyquist plot. From the Nyquist plots and Bode plots, the Charge Transfer Resistance (R_{ct}) and Double Layer Capacitance (C_{dl}) values were calculated.

MEASUREMENT OF CORROSION CURRENT (I_{corr}):

Values of corrosion current were obtained by Tafel extrapolation method. In Tafel extrapolation method, plots of η Vs log current were made and an extrapolation of linear portion to the corrosion potential gave the corrosion current and the slope of the linear portion of the anodic and cathodic curves gave b_a and b_c respectively.R_p was obtained from the linear polarization resistance curves.

DETERMINATION OF INHIBITOR EFFICIENCY:

The inhibitor efficiency was obtained from the equation,

$$IE = \frac{I_{corr\ (b)} - I_{corr\ (i)}}{I_{corr\ (b)}} \times 100$$

$I_{corr\ (b)}$ - corrosion current in the absence of inhibitor

$I_{corr\ (i)}$ - corrosion current in the presence of inhibitor

$$IE = \frac{R_{p\ (inhibited)} - R_{p\ (blank)}}{R_{p\ (inhibited)}} \times 100$$

R_p (blank)-linear polarization resistance in the absence of inhibitor

R_p (inhibited) -linear polarization resistance in the presence of inhibitor

$$IE = \frac{R_{ct\ (inhibited)} - R_{ct\ (blank)}}{R_{ct\ (inhibited)}} \times 100$$

$R_{ct\ (blank)}$ - charge transfer resistance with the absence of inhibitor

$R_{ct\ (inhibited\ )}$ - charge transfer resistance with the presence of inhibitor

RESULTS AND DISCUSSION

RESULTS AND DISSCUSSION

Corrosion behavior of MS specimen at different concentration of an acid extract of egg shells-bakery waste was studied in 0.5 M sulphuric acid. The results of the study on *"Assessment of the inhibitive action of bakery waste for corrosion of mild steel in acid medium"* is discussed in the light of the objective set forth. The inhibition efficiency of the extracts depends on the concentration of the extract, time of immersion and temperature.

In the present investigation the conventional weight loss measurements and sophisticated electrochemical measurements were carried out.

In weight loss measurements, concentration of the egg shell extract, period of immersion & temperature were varied and inhibition efficiency was calculated. Temperature studies were carried out to calculate activation energy and thermodynamic parameters. The data are fitted in to Langmuir adsorption isotherm. Findings of the current investigation are presented in tables & figures with discussion.

EVALUATION OF EGG SHELL EXTRACT AS AN EFFECTIVE INHIBITOR

Dissolution rate of mild steel was studied for different concentration of the inhibitor at various period of immersion and the results are presented in the table1. Results indicated a significant decrease in the corrosion rate with 0.1% to 0.5%extract of egg shell. Analysis of the table revealed that the inhibition efficiency increases with increase in concentration of extract .The results are graphically represented in fig 4. 97.8%was the maximum efficiency observable with 0.5% concentration of the extract. At all test durations 0.5% extract showed maximum efficiency.

The inhibition of corrosion is due to adsorption of the constituents of the extract. The adsorbed molecules block the active site on the metal surface thus preventing the dissolution of iron. With increase in concentration of the extract the surface coverage by the inhibitor increases and the inhibition caused to MS corrosion increased.

FIG 4

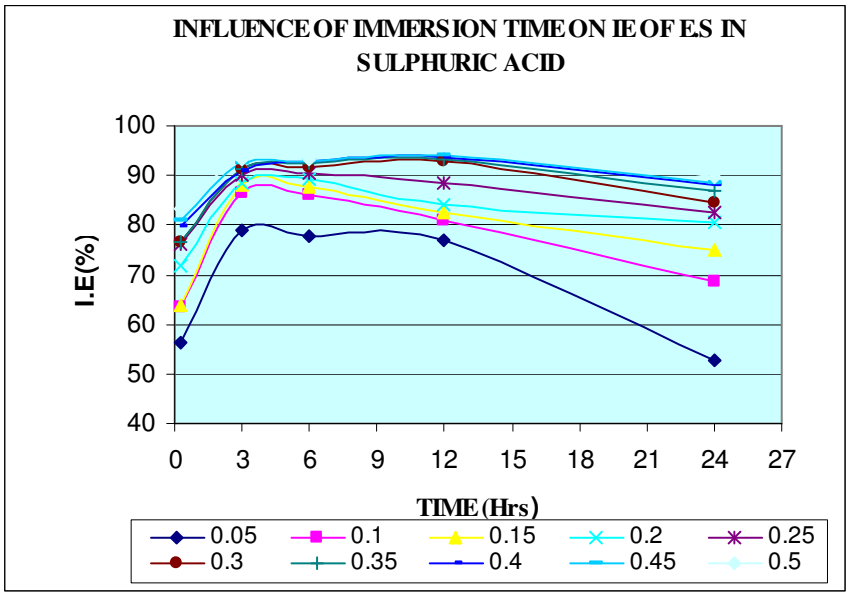
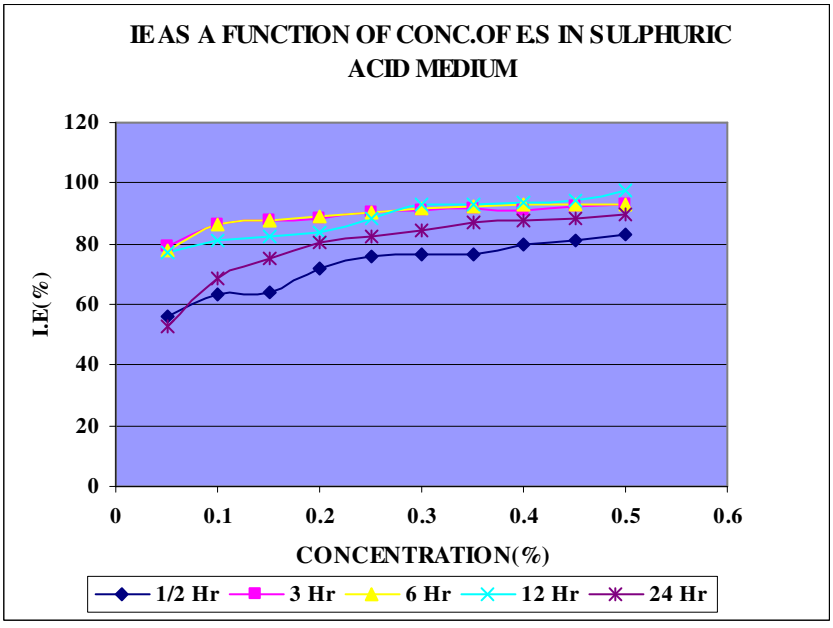

INFLUENCE OF IMMERSION TIME ON IE OF E.S IN SULPHURIC ACID
I.E(%)
100
90
80
70
60
50
40
0
3
6
9
12
15
18
21
24
27
TIME (Hrs)
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5

FIG 5


IE AS A FUNCTION OF CONC.OF E.S IN SULPHURIC ACID MEDIUM
I.E(%)
120
100
80
60
40
20
0
0
0.1
0.2
0.3
0.4
0.5
0.6
CONCENTRATION(%)
1/2 Hr
3 Hr
6 Hr
12 Hr
24 Hr

2. EFFECT OF PERIOD OF IMMERSION

Considering the technical process for a inhibitor, the optimum period of immersion has to be mentioned. To investigate the effect of inhibition with exposure time, experiments were carried at various time intervals (½ hr, 3 hrs, 6 hrs, 12hrs, 24 hrs) with & without egg shell extract by weight loss method.

As the time of immersion increases from ½ hr to 12 hr the IE also increases from 83% to 97% at 0.5% concentration. After 12 hrs there is slight decrease in IE. This may be explained as adsorption of inhibitor molecules on MS surface increases with time. Prolonged immersion may result in the desorption of the extract from MS surface.

3. EFFECT OF TEMPERATURE

Temperature can influence the interaction between the mild steel and the acid in the presence and absence of the inhibitor. To determine the activation energy and free energy of adsorption of the corrosion process studies were conducted using egg shell extract at various temperatures 313K - 353K.IE & CR of MS at various temperatures are listed in the table 3 & depicted in figure 6.Temperature studies results can be discussed in the point of view of concentration of extract & temperature of medium. As the concentration of the extract increases the IE increases for all the temperatures.

TABLE.2 INFLUENCE OF CONCENTRATION OF E.S EXTRACT ON CORROSION OF MS IN 0.5 M H_2SO_4

S.no	Conc in molar	½ hr		3 hrs		6 hrs		12hrs		24 hrs	
		CR mpy	IE %	CR mpy	IE %	CR mpy	IE %	CR mpy	IE %	CR mpy	IE %
1.	blank	6506.5	-	1622.5	-	1542.4	-	1588.8	-	1116.5	-
2.	0.05%	2843.3	56.3	340.7	79	344.13	77.6	365.9	76.9	530.03	52.53
3.	0.1%	2450.8	63.5	218.1	86.55	213.9	86.1	300.7	81	350.3	68.6
4.	0.15%	2354.9	63.8	194.7	87.9	188.1	87.7	279.4	82.4	278.5	75
5.	0.2%	1840.3	71.7	187.2	88.4	164.6	89.3	252.9	84	214.91	80.7
6.	0.25%	1552.4	76.1	159.3	90.1	146.5	90.4	180.8	88.6	195.5	82.5
7.	0.3%	1526.3	76.5	159.8	91.2	126.0	91.8	109.8	93	172.79	84.5
8.	0.35%	2581.6	76.6	138.9	91.4	128.8	92.3	106.6	93.2	145.95	86.9
9.	0.4%	1777.4	79.6	124.2	91	117.6	92.9	97.97	93.8	134.6	87.9
10.	0.45%	1343.7	81	124.1	92.3	109.2	92.9	92.48	94.1	127.4	88.5
11.	0.5%	1229.7	83.2	111.6	93.1	98.91	93.1	34.92	97.8	134.6	89.5

TABLE.3 ROLE OF TEMPERATURE ON CORROSION OF MS IN THE PRESENCE OF VARIOUS CONCENTRATION OF THE E.S EXTRACT

s.no	Conc in molar	313K		323K		333K		343K		353K	
		CR mpy	IE %	CR mpy	IE %	CR mpy	IE %	CR mpy	IE %	CR mpy	IE %
1.	blank	4720.292	-	6810.05	-	8418	-	15740.4	-	26102	-
2.	0.05%	1472.25	68.81	3030.86	55.49	3702	56.01	8524.7	43.87	14990.3	41.39
3.	0.1%	705.60	80.05	2090.63	69.3	3384.6	59.79	8076.4	46.79	14312.6	44.56
4.	0.15%	867.45	81.61	1454.81	78.64	2772.6	67.06	7729.3	49.08	13689	46.97
5.	0.2%	865.25	81.68	1386.75	79.68	2466.5	70.7	7365.6	51.48	13076.7	47.65
6.	0.25%	864.3	81.62	1064.81	84.36	1961.5	76.69	5817.5	51.07	13342.7	48.31
7.	0.3%	860.5	81.67	1174.83	82.74	1936.2	76.99	7398.7	51.26	12634.5	51.06
8.	0.35%	818.11	82.66	1071.04	84.27	1681.5	80.02	7316.8	51.89	12808.9	50.38
9.	0.4%	780.61	83.46	986.44	85.51	1680.7	80.03	6922.5	54.4	12157.4	52.91
10.	0.45%	703.28	85.08	880.91	87.06	1498.4	82.03	6426.2	57.66	12007.4	53.49
11.	0.5%	548.83	87.39	838.17	87.69	1364.1	83.79	6088.7	59.89	11877.4	53.99

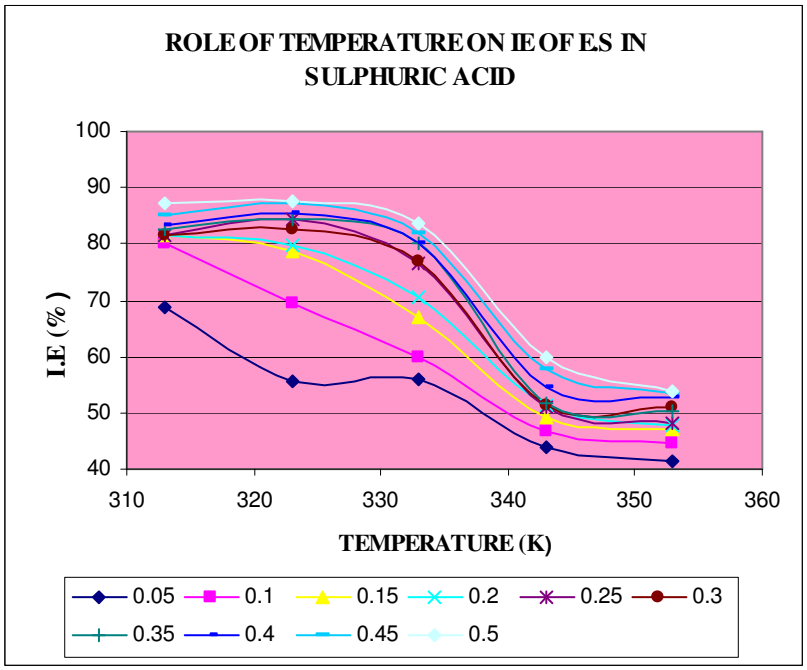

ROLE OF TEMPERATURE ON IE OF E.S IN SULPHURIC ACID
I.E (%)
100
90
80
70
60
50
40
310
320
330
340
350
360
TEMPERATURE (K)
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5

FIG 6

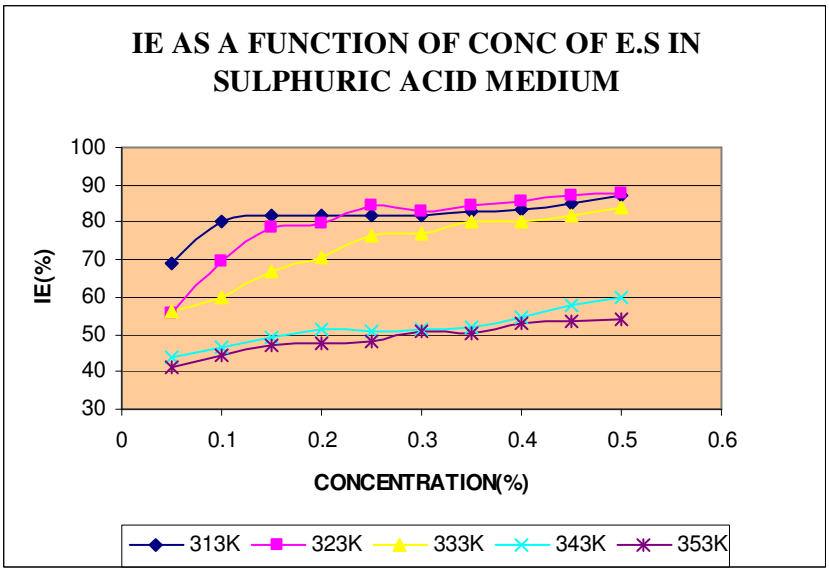

IE AS A FUNCTION OF CONC OF E.S IN SULPHURIC ACID MEDIUM
IE(%)
100
90
80
70
60
50
40
30
0
0.1
0.2
0.3
0.4
0.5
0.6
CONCENTRATION(%)
313K
323K
333K
343K
353K

FIG 7

As the temperature increases from 303K to 323K, the IE also increases from 83% to 88% at 0.5% concentration. After 323K, IE decreases with increasing temperature. This may be explained as adsorption and desorption of inhibitor molecules continuously occurs at the metal surface and equilibrium exists between these two processes at a particular temperature. With the increase of temperature the equilibrium between adsorption and desorption process is shifted leading to a higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant. This explains the lower inhibitor efficiency at higher temperature.

ADSORPTION ISOTHERMS

It has been generally accepted that 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 electrochemical reactions in the adsorptions process is the adsorption isotherm.

Basic information on the interaction between the investigated inhibitors of egg shell extract & mild steel surface can be provided by the adsorption isotherms.

The values of surface coverage (θ) is calculated using the formula $\theta = IE/100$ where IE is the inhibitor efficiency obtained from weight loss measurements.

The θ values for different concentrations of inhibitor for acid solution were tested graphically by fitting to various isotherm like

Langmuir [log (θ/ 1- θ)] Vs Log C & Temkin

LANGMUIR ADSORPTION ISOTHERM

A plot of log (θ/ 1- θ) Vs Log C gave a straight line. Figure No 8.This result demonstrated that the inhibition of MS using the egg shell extract was attributed to adsorption of this extract on MS surface .It also confirms the monolayer adsorption.

FIG 8

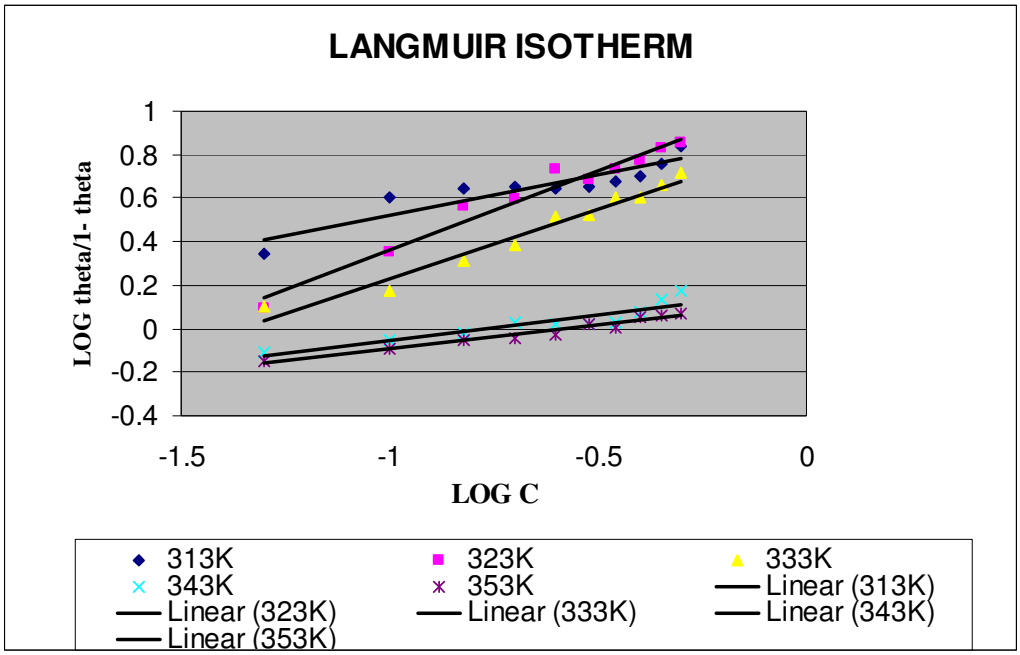

LANGMUIR ISOTHERM
LOG theta/1- theta
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-1.5
-1
-0.5
0
LOG C
313K
323K
333K
343K
353K
Linear (313K)
Linear (323K)
Linear (333K)
Linear (343K)
Linear (353K)

TABLE.4 DEPENDENCE OF LOG(θ/1-θ) ON LOG C FOR ES EXTRACT IN 0.5M H_2SO_4

Log C	LOG(θ/1-θ)				
	313K	323K	333K	343K	353K
-1.30103	0.343636	0.095757	0.104912	-0.10703	-0.15108
-1	0.603418	0.353595	0.172294	-0.05584	-0.09488
-0.82391	0.647162	0.566042	0.30874	-0.01598	-0.0527
-0.69897	0.64919	0.593426	0.382552	0.025718	-0.04085
-0.60206	0.647451	0.7319	0.517196	0.018591	-0.02937
-0.52288	0.6489	0.680675	0.524518	0.021893	0.018417
-0.45593	0.678246	0.728944	0.602603	0.032848	0.006601
-0.39794	0.702943	0.770949	0.602875	0.076634	0.050609
-0.34679	0.756059	0.827884	0.659425	0.134124	0.060726
-0.30103	0.840747	0.852692	0.713409	0.174102	0.069461

ACTIVATION ENERGY

The kinetic parameter of the systems under consideration was evaluated using the data obtained from weight loss method for various concentration of the extract at different temperature.

Activation energy of corrosion reaction was calculated from Arrhenius equation

$$\text{Log } K = - Ea / 2.303 RT + C$$

Where K = corrosion rate

The plot of log K against 1 / T gave straight lines.

FIG 9

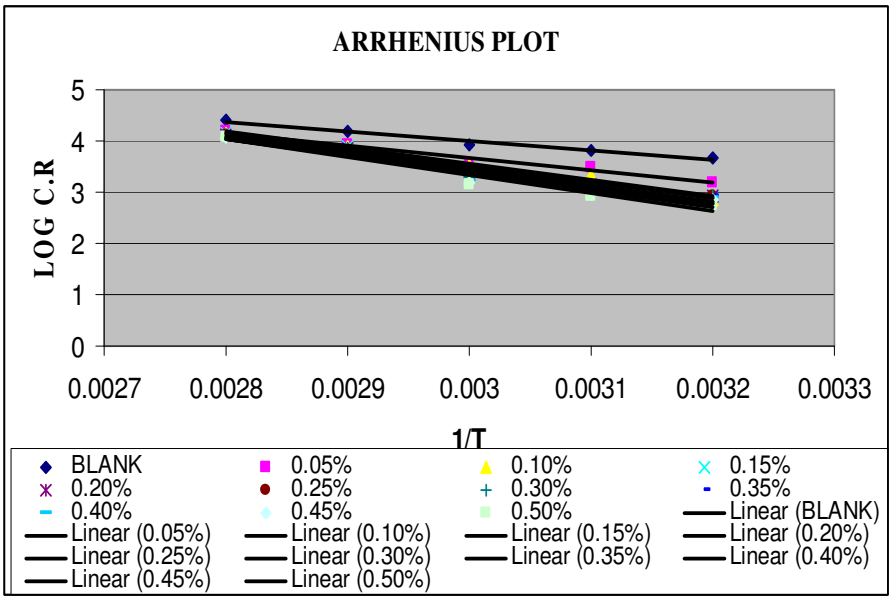
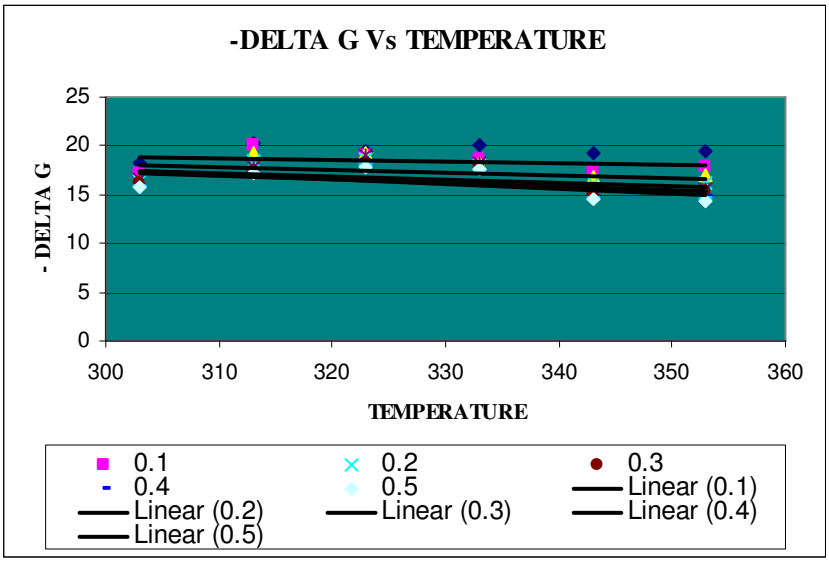


TABLE.5 VALUES OF ΔG, ΔH AND ΔS FOR VARIOUS CONCENTRATION OF ES EXTRACT FOR MS IN 0.5M H_2SO_4

CONC (%)	ACTIVATION ENERGY (Ea) KJ/mol	FREE ENERGY OF ADSORPTION (-)ΔG KJ/mol						HEAT OF ADSORPTION (-ΔH) KJ/mol	ENTROPY CHANGE (ΔS) J/mol
		303	313	323	333	343	353		
BLANK	35.40881		-	-	-	-	-		
0.05	47.19579	18.28	20.28	19.39	20.05	19.26	19.53	15.85	11
1	61.30723	17.29	20.03	19.13	18.56	17.62	17.87	23.00	14
0.15	59.7678	16.30	19.24	19.35	18.31	16.73	16.97	22.70	14.91
0.2	59.02872	16.49	18.50	18.75	17.99	16.18	16.20	25.94	26.2
0.25	59.6376	16.50	17.91	19.01	18.23	15.50	15.63	28.71	35.31
0.3	59.98417	16.10	17.45	18.20	17.77	15.00	15.41	27.17	32.09
0.35	61.72847	15.72	17.22	18.08	17.84	14.63	14.88	27.83	34.89
0.4	61.86442	15.83	17.02	17.99	17.47	14.54	14.79	28.60	37.6
0.45	63.71403	15.76	17.03	18.02	17.50	14.58	14.51	29.46	40.34
0.5	67.62388	15.87	17.27	17.89	17.56	14.54	14.26	31.76	47.34

FIG 10



From the table 5 it is understood the energy of activation changes in the presence of the inhibitor. For adsorption inhibitors the observed rate shows not only the effect of temperature on the metal dissolution, but also the variation of surface coverage with temperature at constant concentration. Accordingly the energy of activation changes. In the present study the energy of activation decreased in the presence of inhibitor. This is explained by Riggs. According to him the dissolution process is not determined only by the reaction of the metal from the bare surface but involves also the adsorbed inhibitor and consequently the E_a (Energy of Activation) can assume values greater or smaller than those calculated in the absence of the inhibitor. It also suggested that the inhibitor does not change the temperature co-efficient of the reaction and firmly held on the metal surface.

THERMODYNAMIC PARAMETERS:

With the help of the temperature studies results, thermodynamic parameters such as ΔG, ΔH and ΔS were calculated. Standard free energy values of adsorption at different temperatures were derived from Langmuir plot using the relation,

Log of inhibitor concentration log C= log θ/ 1- θ – log B

log B = - 1.74 – (ΔG /2.303 RT)

The values of thermodynamic parameters are represented in the table 5 for various concentrations of egg shell extract .the variation of ΔG with temperature were shown in figure 10.The entropy of adsorption (ΔS) & enthalpy of adsorption (ΔH) can be calculated from the plot of

ΔG Vs T. ΔS &ΔH were obtained from the slope and intercept respectively .The negative values of ΔG show that the adsorption of the inhibitor is a spontaneous process under the experimental conditions. The negative heat adsorption and positive entropy substantiate the spontaneous adsorption of inhibitor on the metal surface. The change of ΔH &ΔS with concentration of the inhibitor suggests that the process is enthalpic and entropic controlled.

POLARISATION STUDIES

ELECTROCHEMICAL MEASUREMENTS

Electrochemical measurements were carried out using the electrochemical analyzer Solartron 1280 B. Electrochemical techniques such as linear polarization, Tafel intercept method & electrochemical impedance spectroscopy were carried out.

LINEAR POLARIZATION & TAFEL INTERCEPT RESULTS

The values of Tafel constants b_a & b_c, corrosion current density I_{corr} & corrosion potential E_{corr} corresponding IE are given in table 6. From the table it is inferred that I_{corr}

decreases with increases in concentration of egg shell extract in acid medium. This result confirms the inhibitive action of egg shell extract in 0.5M H_2SO_4.

Inhibition efficiency calculated using I_{corr} was found to be maximum at 0.5% concentration .The change in Tafel constant b_a & b_c with respect to the blank, indicate that the inhibitors under study behave like ***mixed type inhibitors.*** It was also supported by the polarization studies carried out using egg shell inhibitors (fig 11).

The corrosion current potential obtained in the presence of egg shell extract indicate that corrosion potential were not significantly changed in the presence of inhibitor and it could suggest that the adsorption of these inhibitor on cathodic and anodic sites. The values of E_{corr} also reflect the mixed behavior of inhibitor under study.

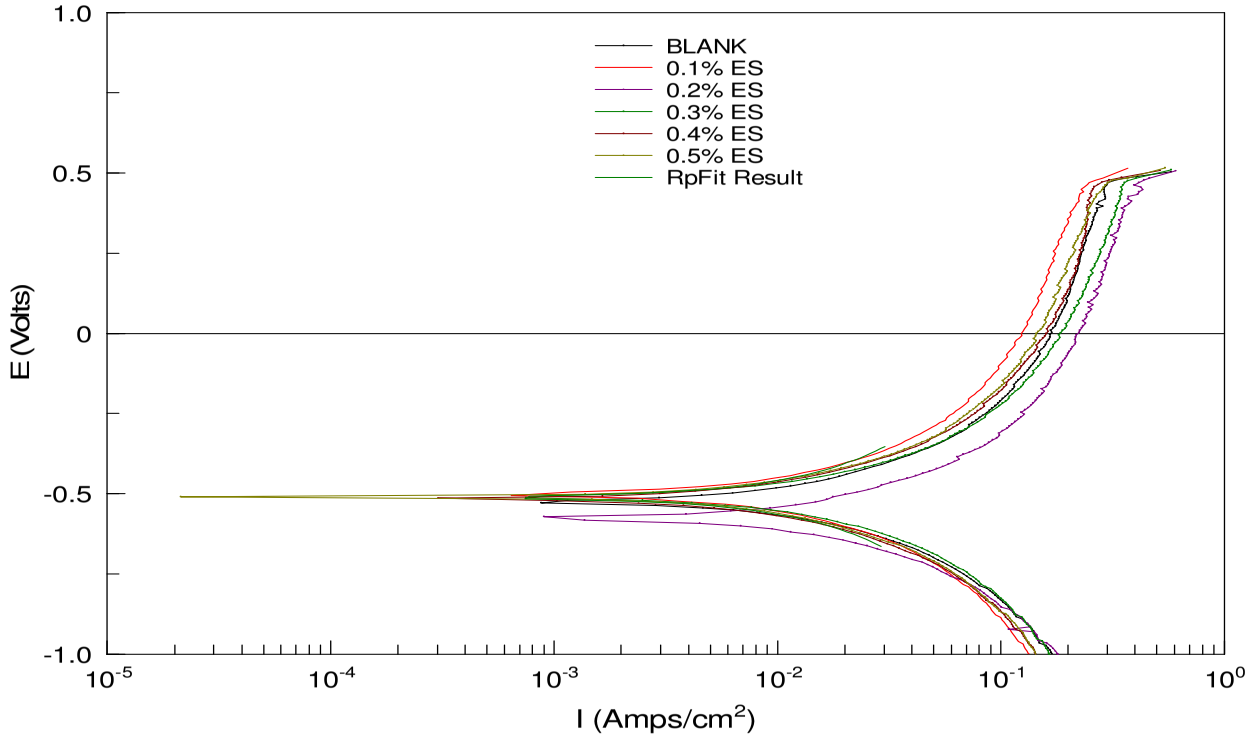
TABLE.6 ELECTRO CHEMICAL PARAMETERS OF MS IN THE PRESENCE OF E.S EXTRACT IN THE ACID MEDIUM

S.No	Conc of inhibitor	I_{corr} (mA/cm^2)	b_a mV/dec	b_c mV/dec	E_{corr} mV/sec	IE(%)
1	Blank	0.006488	182.6	166	-517	-
2	0.1%	0.003072	153.5	133.5	-492	52.65
3	0.2%	0.00198	186	143.5	-570	69.48
4	0.3%	0.001785	176	123.5	-503	72.48
5	0.4%	0.001459	180	130.5	-513	77.51
6	0.5%	0.001244	157.2	109.4	-519	80.82

TABLE. 7 TABULATION OF R_{ct},R_p,AND C_{dl} & THEIR RESPECTIVE IE IN THE PRESENCE OF E.S EXTRACT

S.No	conc	Rct(Ω cm^2)	IE(%)	Rp (Ω $/cm^2$)	IE(%)	Cdl (μ F cm^{-2})	θ
1	blank	15.10		4.26		1.96	-
2	0.1%	35.81	57.83	4.3	0.93	0.966	0.5071
3	0.2%	48.96	69.15	5.3	19.62	0.703	0.6413

POTENTIODYNAMIC POLARIZATION OF MILD STEEL IN 1M H_2SO_4 IN THE PRESENCE OF INHIBITOR E.S EXTRACT



POLARISATION CURVES FOR THE MS IN THE PRESENCE OF EGG SHELL EXTRACT

FIG 11

Linear polarisation resistance in the presence and absence of egg shell extract are presented in the table 7.From the table it is clear that the value of R_p increases with increase in concentration of the egg shell extract. Hence the IE increases with increase in concentration. Maximum IE in the presence of egg shell extract was found be 19.62% at 0.2% concentration.

The results of Tafel polarization & LPR inferred the effectiveness of egg shell extract on MS surface.

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Impedance measurements of MS in the presence & absence of egg shell extract were recorded in the figure12. The impedance parameter such as R_{ct} & C_{dl} with the concentration of the egg shell extract are represented in table 7.Increase in concentration of egg shell extract increases the charge transfer resistance value (R_{ct})The maximum IE was found to be 69.15% at 0.2% concentration in the presence of egg shell extract.

The decrease in double layer capacitance (C_{dl}) with increase in concentration of egg shell extract indicate the adsorption of the compound on the metal surface. Table 7 infers that the surface coverage (θ) was found to be 0.6413 at 0.2% concentration for egg shell extract . The IE obtained using I_{corr} , R_p , R_{ct} & C_{dl} are plotted in the table 7 , & graphically represented in figure 12 and 13.

Impedance diagrams have a semicircular appearance; it shows that the corrosion of mild steel is controlled by charge transfer process. From the electrochemical measurements it was clear that egg shell extract is acting profoundly as an excellent inhibitor to reduce acid corrosion of MS.

NYQUIST PLOT FOR CORROSION OF MILD STEEL IN THE PRESENCE OF EGG SHELL EXTRACT

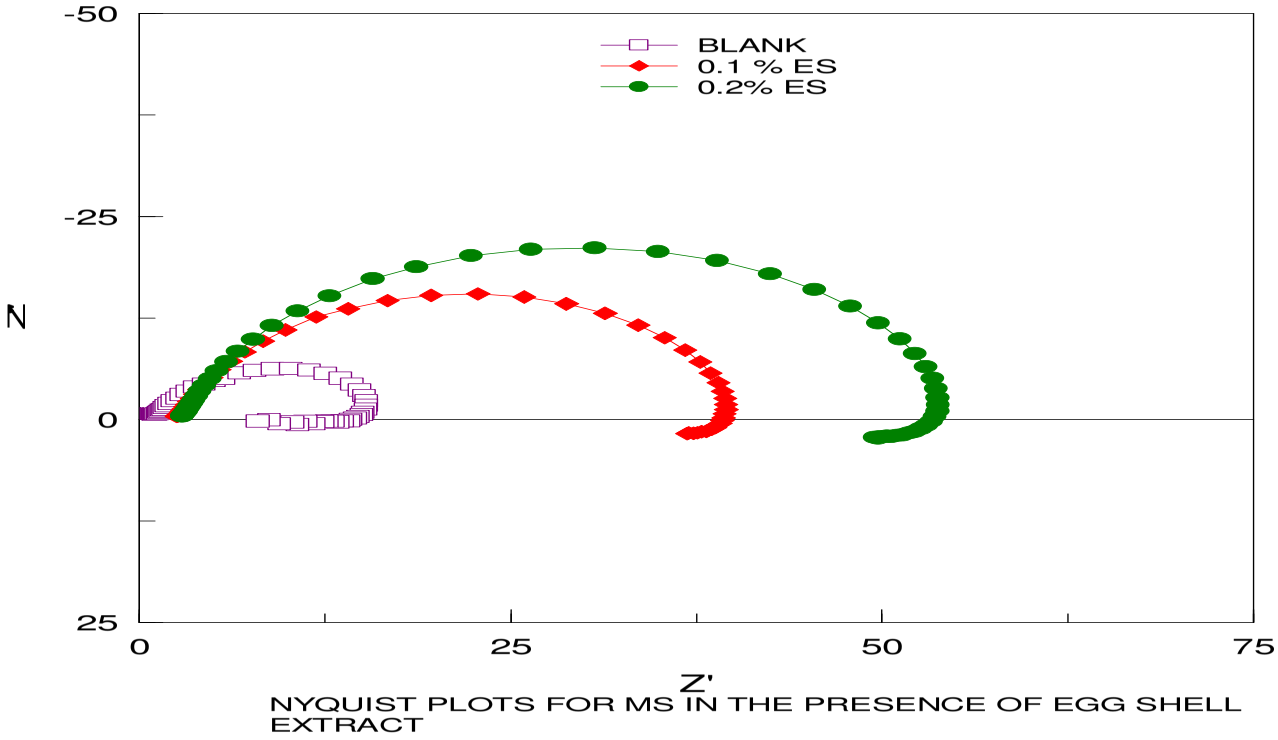


FIG 12

BODE PLOT FOR CORROSION OF MILD STEEL IN 0.5M H_2SO_4 IN THE PRESENCE OF EGG SHELL EXTRACT

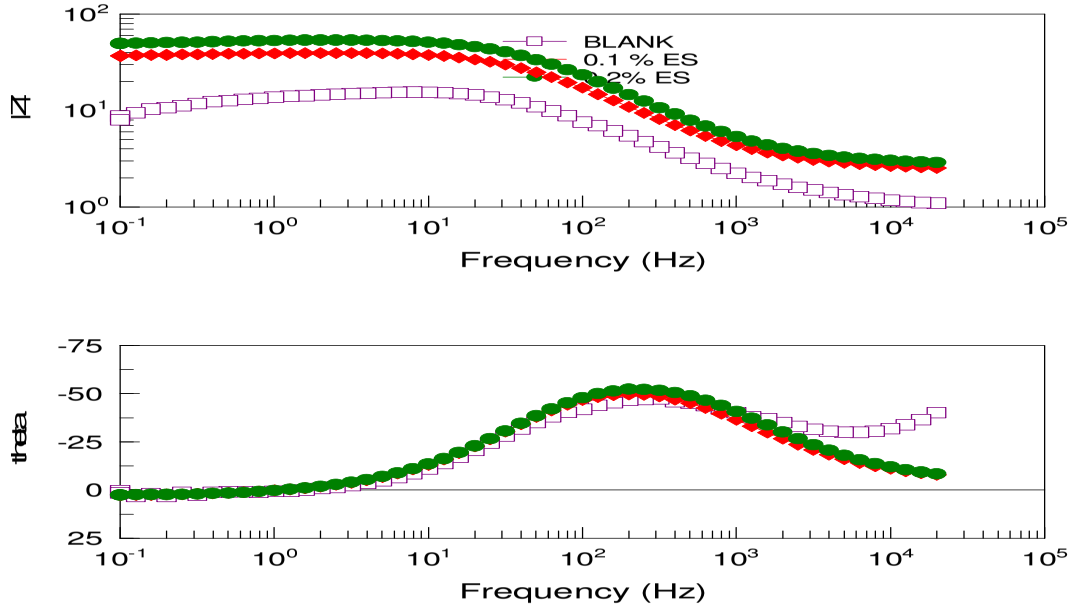


FIG 13

TABLE.8 PERFORMANCE EVALUTION OF E.S EXTRACT IN 0.5M H_2SO_4 USING WEIGHTLOSSMETHOD

S.NO	CONCENTRATION(%)	INHIBITION EFFICIENCY(%)		
1.	0.5	TIME OF IMMERSION (6 hr)	ROOM TEMPERATURE (303K)	HIGH TEMPERATURE (323 K)
		97.8	83.2	87.6

TABLE.9 PERFORMANCE EVALUTION OF E.S EXTRACT IN 0.5M H_2SO_4 USING WEIGHT LOSS & ELECTROCHEMICAL METHOD

S.NO	CONC (%)	INHIBITION EFFICIENCY(%)					
1.	0.2	TIME OF IMMERSION	ROOM TEMP	HIGH TEMP	R_{ct}	Θ X 100	I_{corr}
		80.7	71.7	79.6	69.1	64.1	69.4

PERFORMANCE EVALUTION OF E.S EXTRACT IN 0.5M H_2SO_4 USING WEIGHT LOSSMETHOD

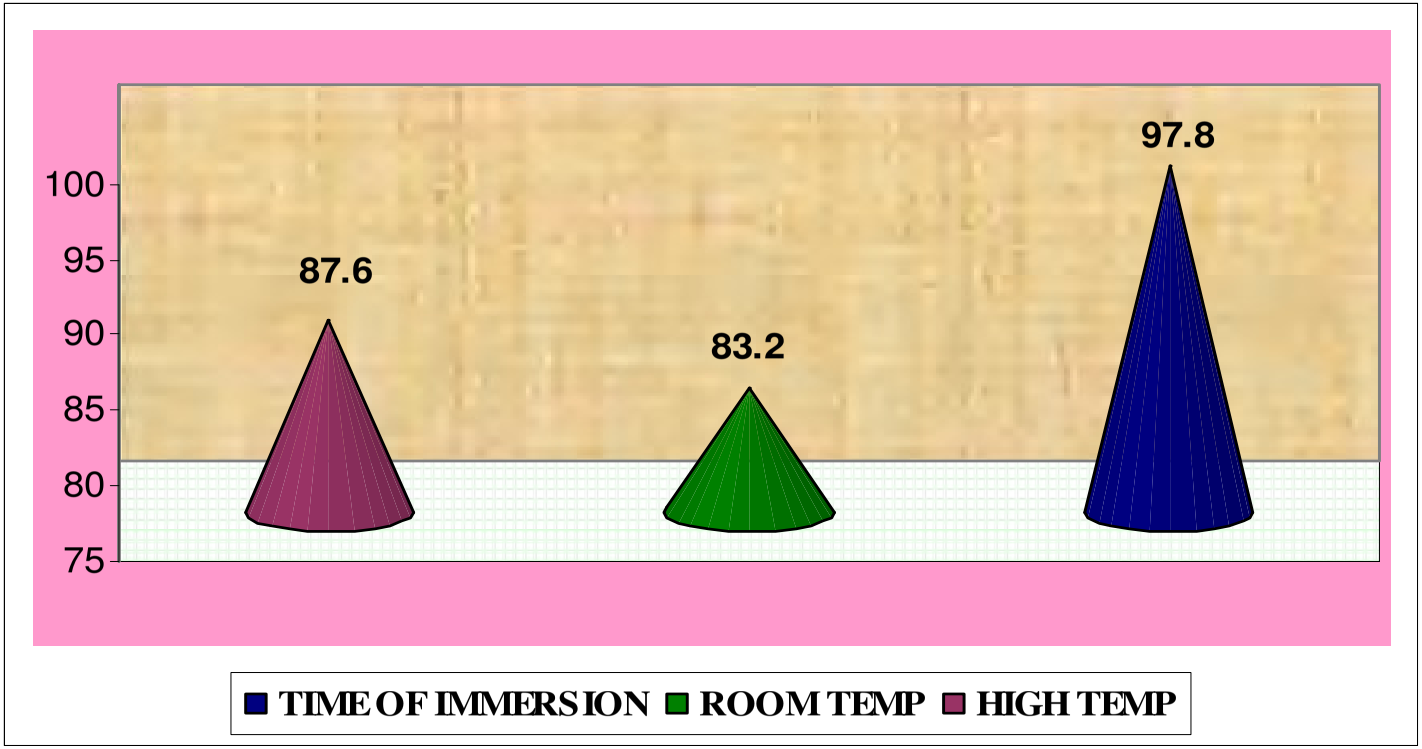


FIG 14

PERFORMANCE EVALUTION OF E.S EXTRACT IN 0.5M H_2SO_4 USING WEIGHT LOSS & ELECTROCHEMICAL METHOD

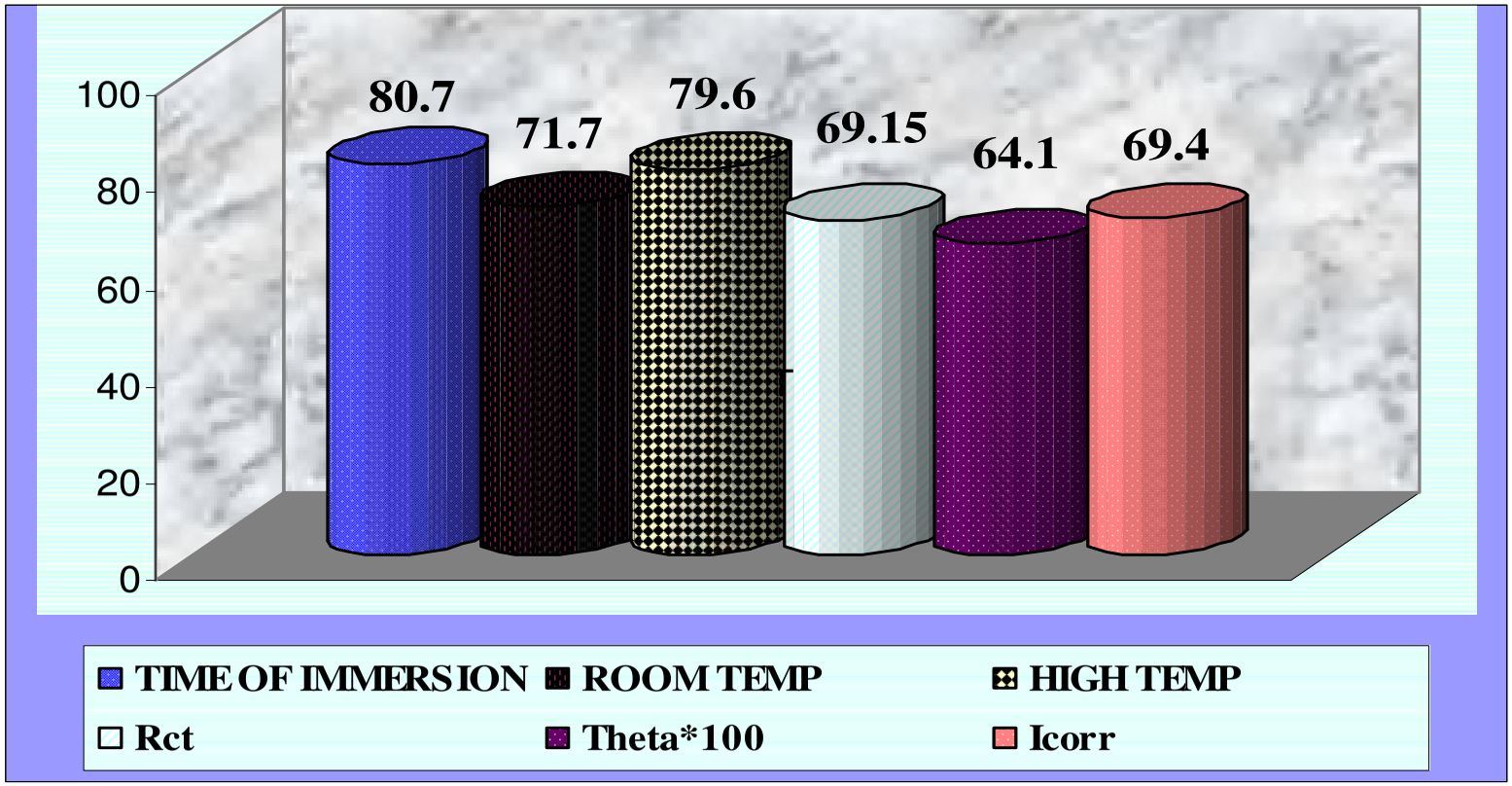


FIG 15

COMPARISON OF IE OBTAINED BY VARIOUS TECHNIQUES

I.E values obtained from I_{corr} values for different concentration of compounds under study do not show absolute agreement with those obtained from weight loss measurements. This observation can be explained in the following ways. Weight loss measurements are experiment of long duration, which helps in the formation of a thick, inherent & continuous film on the surface. This leads to the complete shielding of the metal surface from the corrosive environment .Whereas polarization studies are experiments of short duration & the time will not be enough for the formation of a thick & continuous film. This leads to low value of inhibitor efficiency in some cases. **(Quaraishi et al., 1996).**

MECHANISM OF INHIBITION

The corrosion of mild steel in acid medium was well controlled by the extract of egg shells 0.5% of the extract found to 97.85% of efficiency. This shows the effectiveness and sustainability of the inhibitor.

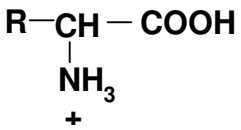
The egg shells are mostly consists of calcium carbonate. On heat processing with acid, calcium carbonate becomes insoluble calcium oxide. Thus the extract is rich in various amino acids constituents listed below.

Water, %	**29-35**
Alanine, %	**0.45**
Arginine, %	**0.56-0.57**
Ash, %	**89.9-91.1**
Aspartic Acid, %	**0.83-0.87**
CaCO3, % of total Ca	**90.9**
Calcium, %	**35.1-36.4**

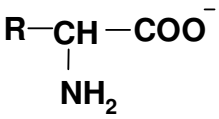
Crude Fat, %	**0.10-0.20**
Cystine, %	**0.37-0.41**
Glutamic Acid, %	**1.22-1.26**
Glycine, %	**0.48-0.51**
Histidine, %	**0.25-0.30**
Isoleucine, %	**0.34**
Leucine, %	**0.57**
Lysine, %	**0.37**
Magnesium, %	**0.37-0.40**
Methionine, %	**0.28-0.29**
Phenylalanine, %	**0.38-0.46**
Phosphorus, %	**0.12**
Potassium, %	**0.10-0.13**
Proline, %	**0.54-0.62**
Protein, %	**1.4-4**
Serine, %	**0.64-0.65**
Sodium, %	**0.15-0.17**
Sulphur, %	**0.09-0.19**
Threonine, %	**0.45-0.47**
Tyrosine, %	**0.25-0.26**
Valine, %	**0.54-0.55**

The inhibitive nature of amino acids was studied by **M.Abdullah and A.M.Vita(1997).** The mixture of amino acids is a promising inhibitor for mild steel corrosion. The lone pair of electrons available on the N,O and Sulphur atoms present in the amino acid might have readily formed co-ordinate bond with the empty d orbitals of iron. Thus they form a thin film on the metal surface preventing the dissolution of the metal. The adsorption of the constituents is further confirmed by the adsorption isotherm, negative free energy and exothermic nature of adsorption. Due to the presence of mixture of amino acids the inhibition was more effective.

In acidic medium some of the amino acids are present as cations and some as anions depending on their iso electric point.

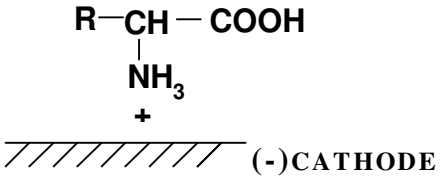


CATIONS



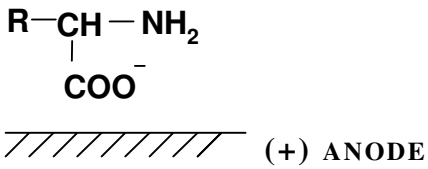
ANIONS

The cations and anions are get adsorbed on the cathodic and anodic sites respectively on the metal surface. The adsorption can be pictorially represented as



(-)CATHODE

MILD STEEL



(+) ANODE

MILD STEEL

SUMMARY AND CONCLUSION

SUMMARY AND CONCLUSION

Efforts have been taken to study the inhibitive effect of egg shell extract on corrosion of mild steel in 0.5 M H_2SO_4 by weight loss &electrochemical techniques .Studies were carried out at various concentration of acid extract of egg shell at different time of immersion at room temperature by weight loss method. Effect of temperature was studied to evaluate the kinetic & thermodynamic parameters .Suitable adsorption isotherm were also fitted for egg shell inhibition. Electrochemical technique-linear polarization technique were performed. Inhibitor efficiency obtained by weight loss & electrochemical technique was compared. A possible mechanism of inhibition process was also suggested.

The results obtained during the study were summarized as follows.

1. The acid extract of bakery waste - egg shell could bring out a maximum of 97.8 % IE in 0.5 M H_2SO_4.
2. The extract was temperature resistant in nature and the IE obtained was 83.2% at room temperature which changed to 87.6% for 323K after which it is declined.
3. Optimum time of immersion for the egg shell extract was found to be 97.8% for 12 hrs.
4. The inhibitor used in the current study followed Langmuir adsorption isotherm which indicated the monolayer formation with heterogeneity in the surface of the electrode.
5. Thermodynamic parameters showed that the inhibition is a spontaneous adsorption of inhibitors on the metal surface.
6. Values of activation energy infer the strong adsorption of inhibitor molecules on the mild steel surface.
7. Values of Tafel constant b_a and b_c confirm that the egg shell extract act like mixed type inhibitor.
8. Polarization curves obtained in the presence of the extract indicate that it controls both anodic and cathodic reactions.

9. Increase in R_p and R_{ct} values and decrease in I_{corr} and C_{dl} values confirm that egg shell extract is adsorbed on the mild steel surface and inhibition process is followed by monolayer adsorption.
10. IE by weight loss methods were found to be greater than electrochemical measurement.
11. Bakery waste – egg shell extract in H_2SO_4 medium efficiency inhibits the corrosion and proves to be zero cost inhibitor, ecofriendly and environmentally friendly inhibitor.
12. Cost effective and non toxic to the environment.

BIBLIOGRAPHY

BIBLIOGRAPHY

- Abdel-Gaber A.M,Abd-El-Nabey.,B.A., Sidahmed.I.M,El-Zayady. A.M. and. Saadawy M (2005).,Inhibitive action of some *plant extracts* on the corrosion of steel in acidic media.CorrosionScience .,48 (9) 2765-2779.
- Abo el-enin s. A,(2006) Testing of *eco-friendly compound* as acid corrosion inhibitor for mild steel, Afinidad journal,63, (522) 130-135.
- Abdallah.M ,vita.M (1998).,J.electrochemical society of India.vol 46-4,185-190.
- Afidah A. Rahim,E. RoccaJ. Steinmetz,M.J. Kassim,R. Adnanand M. Sani Ibrahim(2006) Mangrove tannins and their flavanoid monomers as alternative steel corrosion inhibitors in acidic medium., Corrosion Science ,49,(2), 402-417.
- Ashassi-Sorkhabi H. Majidi. .,M.R, and Seyyedi K. (2002) Investigation of inhibition effect of some *amino acids* against steel corrosion in HCl solution . Applied Surface Science , 225 (1-4) 176-185.
- Bouyanzer A., Hammoutiand B. Majidi L , (2006) Pennyroyal oil from *Mentha pulegium* as corrosion inhibitor for steel in 1 M HCl. Materials Letters ,60 (23), 2840-2843.
- Bouyanzer, A,Hammouti, . B. (2004) A study of anti-corrosive effects of *Artemisia oil* on steel, Pigment & Resin technology, 33, (5) 287-292.
- Chauhan L.R. and Gunasekaran. G., (2006) Corrosion inhibition of mild steel by *Zenthoxylum alatum* plant extract in dilute HCl medium ,Corrosion Science, 49, (3) 1143-1161.
- Chitra S.P., (2003). The effect of *Phaselous aureus* seeds extract on the corrosion of mild steel in 1M HCl Presented at Eleventh National Congress on Corrosion Control, Vadodara, 17-19.
- El-Etre A.Y. Abdallah .,M. and El-Tantawy Z.E.,(2004) Corrosion inhibition of some metals using *lawsonia* extract, Corrosion Science ,47 (2) 385-395.
- El-Etre A.Y.,(2007) Inhibition of acid corrosion of carbon steel using aqueous extract of *olive leaves,* Journal of Colloid and Interface Science ,314,(2)78-583.

- El-Etre A.Y.;(2005), *Khillah* extract as inhibitor for acid corrosion of SX 316 steel, Applied Surface Science ,252, (24), 8521-8525.
- Emeka E. Oguzie., (2006). Studies on the inhibitive effect of *Occimum viridis* extract on the acid corrosion of mild steel. Materials Chemistry and Physics, Article in press, 99, (2-3) 441-446.
- Fabrizio Zucchi.,Ibrahim Hashi Omar.,(2002). *Plant extracts* as corrosion inhibitors of mild steel in HCl solutions. Surface Technology , 24 (4), 391-399.
- Keny S.J., Kumbhar A.G,Thinaharan., C. and Venkateswaran G. (2007),*Gallic acid* as a corrosion inhibitor of carbon steel in chemical decontamination formulation ,Corrosion Science , 50 (2) 411-419.
- 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.
- Maheswari .D Subhashini.S,Rajalakshmi.R, Viswanathan ,Marikkannu C and Sivakamasundari.S.(2001),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.
- Manimegalai.M,Rajeswari.P,Mohan.S and Palanisamy.N (2001),The effect of corrosion inhibition on mild steel with extract of *Neem*(azadiracta indica) 10^{th} National Convention of electro- chemistry,10-12.
- Oguzie E.E.;(2005) Inhibition of acid corrosion of mild steel by *Telfaria Occidentalis*. Pigment & Resin technology, 34, (6) 321-326.
- Oguzie, E. E. Li Y. and Wang F. H. (2007 ,Effect of *ascorbic acid* on mild steel dissolution in sulphuric acid solution investigated by electrochemical polarization and surface probe techniques ,Journal of Applied Electrochemistry, 37, (10), 1183-1190.
- Okafor P.C., Osabor V.I., Ebenso E.E.,(2007) Eco-friendly corrosion inhibitors: inhibitive action of ethanol extracts of *Garcinia kola* for the corrosion of mild steel in H_2SO_4 solutions. Pigment & Resin technology 36, (5) 299-305.

- Okafor, P.C Ebenso. E.E. (2007) ,Inhibitive action of *Carica papaya* extracts on the corrosion of mild steel in acidic media and their adsorption characteristics, Pigment & Resin technology,volume 36 (3) 134-140.
- Orubite K. O. and Oforka N. C..(2004) Inhibition of the corrosion of mild steel in hydrochloric acid solutions by the extracts of leaves of *Nypa fruticans* Wurmb , Journal of Applied Sciences & Environmental Management, 58, (11) 1768-1772
- Pandian Bothi Raja and Mathur Gopalakrishnan Sethuraman (2007) ,Natural products as corrosion inhibitor for metals in corrosive media -Areview, Materials Letters,62, (1)113-116.
- Pandian Bothi Raja and Mathur Gopalakrishnan, Sethuraman (2007),Inhibitive effect of *black pepper* extract on the sulphuric acid corrosion of mild steel, Materials Letters **,**Article in Press **.**
- 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 .
- Parikh, K S., Joshi, K J.(2004), Natural Compounds *Onion* (Allium Cepa), *Garlic* (Allium Sativum) and *Bitter Gourd* (Momordica Charantia) as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid ,39(2)., 29-35.
- Prathipa .A,Subhashini.S,Rajalakshmi.R, Sathiyanarayanan.S,Marikkannu C and Sivakamasundari.S (2002) Inhibition effect of *Ervatamia Coronaira* leaves extract on mild steel,ISAEST-VII,C138-C141.
- Quarashi M.A ,Khan M.A.W., Ajmal.M., influence of some thiazole derivatives on the corrosion of mild steel in hydrochloric acid , anticorrosion methods & materials, vol : 43.
- Rajalakshmi .R,Sathiyanarayanan.S,Marikkannu C and Sivakamasundari.S (2002)
- The performance of acid extracts of *ficus benghalensis* bark on the corrosion inhibition of mild steel.,ISAEST-VII 142-145.
- Ramesh S.P., Vinodkumar K.P., and Sethuraman M.G., (2001). Extract of *Andrographis paniculata* as corrosion inhibitor of mild steel in acid medium. Bulletin of Electrochemistry. **17,** (3) 141-144.

- Sathiyanathan R. Ananda louise ; Mohamed Essa M. ; Maruthamuthu S ; Selvanayagam M. ; Palaniswamy N. ; (2005)., Inhibitory effect of *Ricinus communis* (Castor-oil plant) leaf extract on corrosion of mild steel in low chloride medium .Journal of the Indian Chemical Society , 82,. 357-359.
- 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.
- Subhashini.S ,Sathiyanarayanan.S,Marikkannu C and Sivakamasundari.S (2002) ,
- Inhibitive effect of acid extract of *sesbania grandiflora* seeds on the corrosion of mildsteel,.ISAEST-VII 146-148.
- Tebbji K.,. Faska N,. Tounsi A, Oudda, H. Benkaddour H. and Hammouti B.,(2007).The effect of some *lactones* as inhibitors for the corrosion of mild steel in 1 M hydrochloric acid ,Materials Chemistry and Physics, 106(2-3), 260-267.
- Umoru L.E., Fawehinmi A. and Fasasi A.Y. (2006)Investigation of the Inhibitive Influence of *Theobroma Cacao* and *Cola Acuminata Leaves*,Journal of Applied Sciences Research 2, (4) 200-204.
- Yan Li, Peng Zhao,Qiang Liang and Baorong Hou.,(2005), .*Berberine* as a natural source inhibitor for mild steel in 1 M H_2SO_4.,Applied Surface Science**,** 252, (5) 1245-1253.

WEBSITES:

- www.corrosioncost.com
- www.sciencedirect.com
- www.corrosion-doctors.org/monitorbasics/types.htm
- http://www.corrosion-club.com
- www.wileyinterscience.com
- www.emeraldinsight.com
- www.catinist.com