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# INTRODUCTION

## 1.1 PREAMBLE

The tremendous advancement in material science has led to increasing utilisation of metals and alloys in all facets of technology. Metals possess many unique fundamental properties such as lustre, strength, hardness etc., that, when exploited, makes them an ideal material for use in a diverse range of industrial applications. The advent of modern civilization along with advancement of scientific technology has created an impetus in designing newer materials for novel applications.

**Mild steel and Aluminium alloys** are noted to have multifarious applications in various industries due to their low cost and easy availability. In the history of the use of metals, the past 150 years have been closely associated with alloys of metals such as Iron, Aluminium & Copper. Our highly developed civilization could not exist without them. Yet corrosion is their Achilles heel.

Ferrous and non-ferrous metals differ in the pace at which they tend to corrode in a natural environment. Unprotected ferrous metals are exceedingly vulnerable to corrosion commonly referred to as rust, a continuous process that occurs instantaneously under the right conditions. Non ferrous metals like aluminium, zinc, copper and brass are found to corrode at a lesser speed than ferrous metals. This is due to the rapid formation of a thin protective oxide layer on their surface though they are susceptible to corrosion when exposed to atmospheric conditions. Aluminium alloys are highly favoured because of their non toxic corrosion product, stability, low density, high thermal & electrical conductivity **(Fink, 1936)**.

Corrosion, an ubiquitous legacy, is the damage of material resulting from exposure and interaction with the environment. It is a global problem that must be confronted for safety, environment and economic reasons. Safety concerns are of utmost importance in every society and in all situations. Environmental concerns include corrosion caused pollution, depletion of resources such as those needed for replacement of the corroded structures and disposal of the corroded structures. To combine the technological progress with environmental safety is one of the key challenges of the millennium.

ISO 8044 describes corrosion as physiological interaction, which usually of an electrochemical phenomenon between man and his environment, which result changes in properties of metal and which may often lead to the impairment of function of metal in the environment or technical system of which these form a part.

## **1.2 CONSEQUENCES OF CORROSION**

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal. The effects of corrosion are both direct, in that corrosion affects the useful service lives of our possessions, and indirect, in that producers and suppliers of goods and services incur corrosion costs, which they pass on to consumers. Some of the major harmful effects of corrosion are

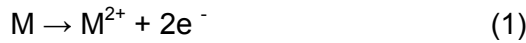
- ❖ Loss of mechanical strength and structural failure or breakdown due to reduction of metal thickness
- ❖ Hazards or injuries to people arising from structural failure or breakdown
- ❖ Loss of time in availability of profile-making industrial equipment.
- ❖ Reduced value of goods due to deterioration of appearance.
- ❖ Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings.
- ❖ Loss of technically important surface properties of a metallic component.
- ❖ Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products.

## **1.3 ELECTROCHEMICAL PRINCIPLE OF CORROSION**

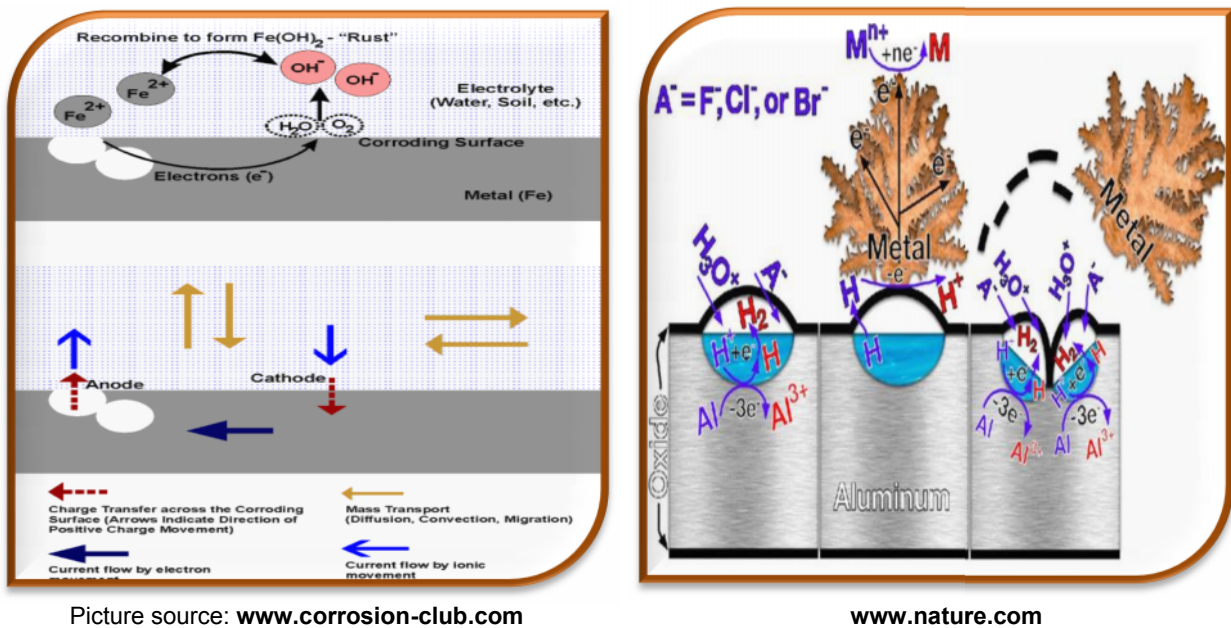
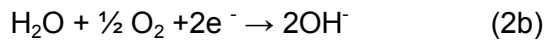
Metals being in a meta stable state tend to lose their acquired energy by reverting to compounds more or less similar to their original states. Virtually all corrosion reactions are electrochemical in nature. The anodic reaction comprises of the metal going into solution as metal ions. As metal atoms undergo oxidation they release electrons whose negative charge would quickly build up in the metal and prevent further anodic reaction, or corrosion. At a cathodic site the electrons react with some reducible component of the electrolyte and are removed from the metal. The corroding piece of metal is described as “mixed electrode” because of the occurrence of simultaneous anodic and cathodic reactions on its surface. The mixed electrode is a complete electrochemical cell on the metal surface.

The most general and important electrochemical reactions in the corrosion of metal consist of

Anodic reaction (corrosion)

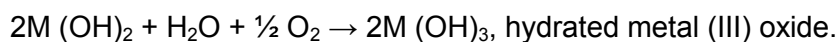
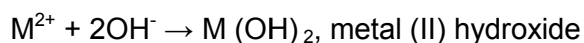


Cathodic reactions (simplified)



**Figure – 1.1 Schematic representation of electrochemical corrosion process for Mild Steel and Aluminium**

The most common reaction that occurs in acids is 2a and oxygen reduction (i.e. 2b) takes place in the pH range 6.5 – 8.5. In the latter case, corrosion is usually accompanied by the formation of solid corrosion products.



Further hydration and oxidation reactions may occur and the reddish rust that is obtained eventually is a complex mixture whose exact constitution will depend on other trace elements present in it. The precipitated rust is porous in nature and tends to act as a sort of harmful poultice promoting further corrosion.

For other metals or different environments different types of anodic and cathodic reactions are possible. As a result of anodic oxidation, solid corrosion products may be

produced directly on the surface of the metal aiding the formation of a highly protective surface film. This film tends to retard further corrosion i.e. the surface is said to be in a passive state.

#### 1.4 FORMS OF CORROSION

Corrosion occurs in several different forms and classification is typically based on one of the three factors:

- ❖ *Nature of the corrodent:* Corrosion can be classified as “wet” or “dry.” A liquid or moisture is necessary for the former, and dry corrosion usually involves reaction with high-temperature gases.
- ❖ *Mechanism of corrosion:* This involves either electrochemical or direct chemical reactions.
- ❖ *Appearance of the corroded metal:* Corrosion is either uniform i.e. the metal corrodes at the same rate over the entire surface, or localized, in which case only small areas are affected.

Further classification is based on distinction between macroscopically localized corrosion and microscopic local attack. Macroscopic forms of corrosion affect large areas of metal and are usually visible to the naked eye or can be noticed with the help of a low-power magnifying device. In the case of microscopic forms of corrosion, considerable damage of the metal occurs before it is visible to the naked eye as the amount of metal dissolved is minute in nature.

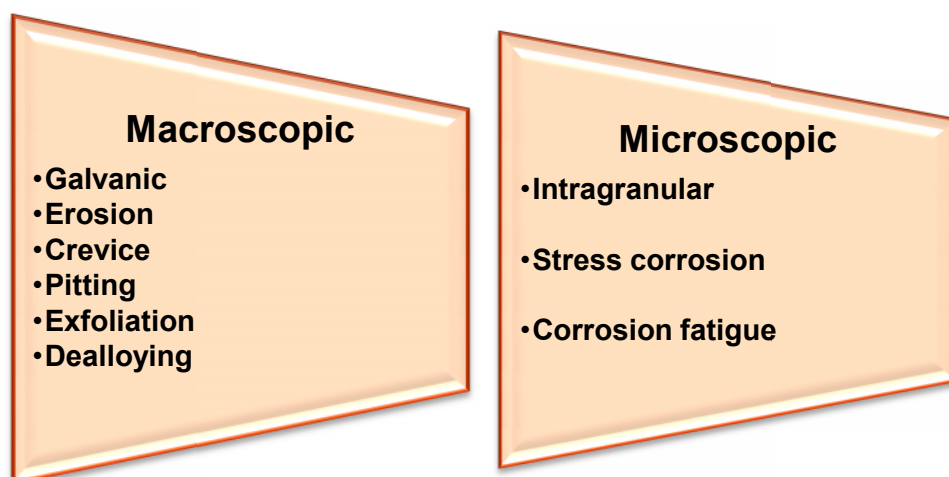


Figure 1.2 Classification of macroscopic and microscopic forms of corrosion

#### 1.5 STRATEGIC IMPACT OF CORROSION DAMAGE

Lack of awareness on the economic impact of corrosion coupled with the poor selection of protection measures has resulted in the astounding cost of corrosion.

Corrosion survey and corrosion audit of plant assets is the need of the hour to perceive the impact of corrosion and contain it in reasonable limits. Assessment on corrosion and its cost have been carried out since ancient times, but only recently serious attempts have been made to estimate the total cost caused by it to the community.

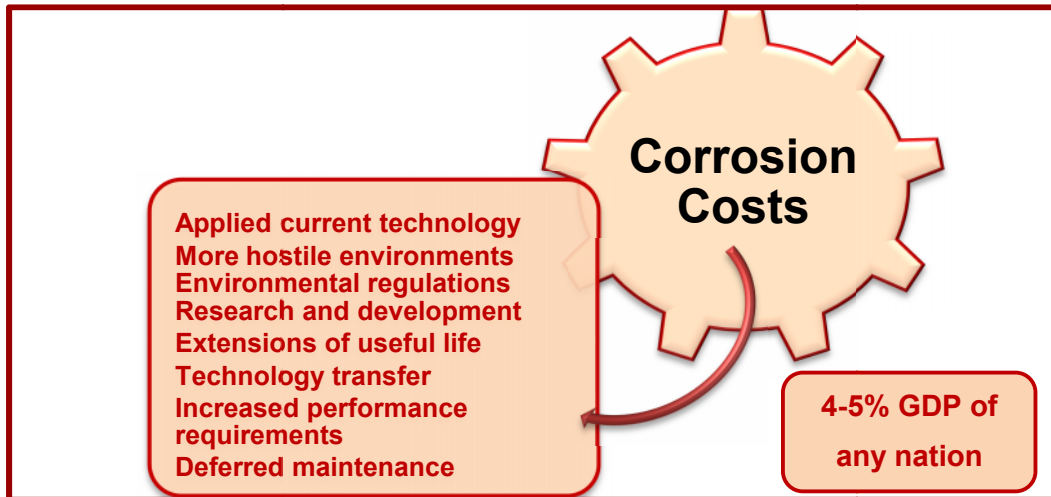


Figure 1.3 Factors affecting the costs of corrosion

### 1.5.1 Economical Front

The indirect losses result due to deterioration in quality of product, loss of efficiency, plant shut down, over design of the system etc. The annual cost of corrosion is approximately 1 to 5 percent of the GDP of any nation. India's corrosion loss has been estimated at more than **USD 40 billion a year - about 4 percent of the size of the total economy** - Sudhir Vasudeva, CMD, ONGC, 2012.

. **Recent NACE assessment reports that the total annual cost of corrosion in USA amounts to \$ 1 trillion (NACE)**

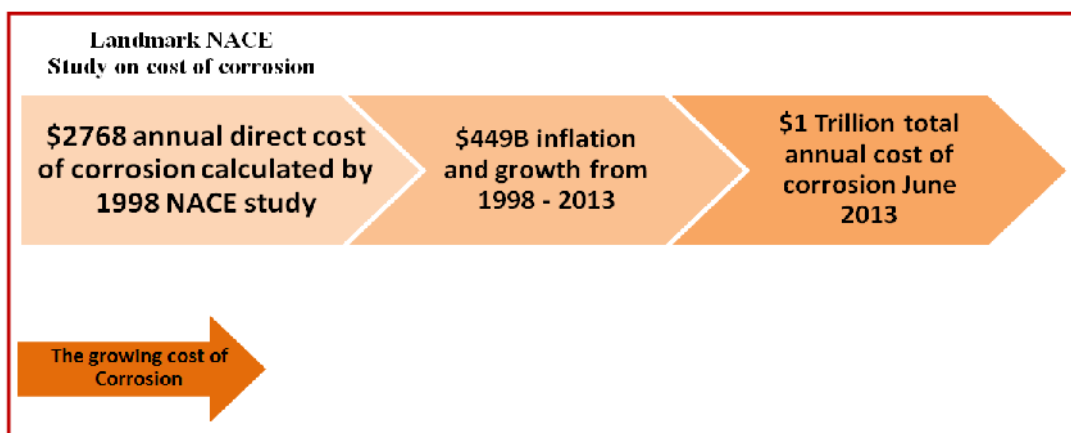


Figure 1.4 NACE Assessment of growing cost of Corrosion

### 1.5.2 Environmental and Health Front

Huge life, material losses and large scale environmental pollution are some of the results due to corrosion. Recent years have witnessed an increasing utilisation of metal prosthetic devices in the body, namely pins, plates, hip joints, pace makers and other implants. In spite of development of new alloys and better techniques of implantation, corrosion continues to create problems. Some of the examples due to corrosion are: failures through broken connections in pace makers, inflammation caused by corroded products in the tissue around implants and fracture of weight bearing prosthetic devices.

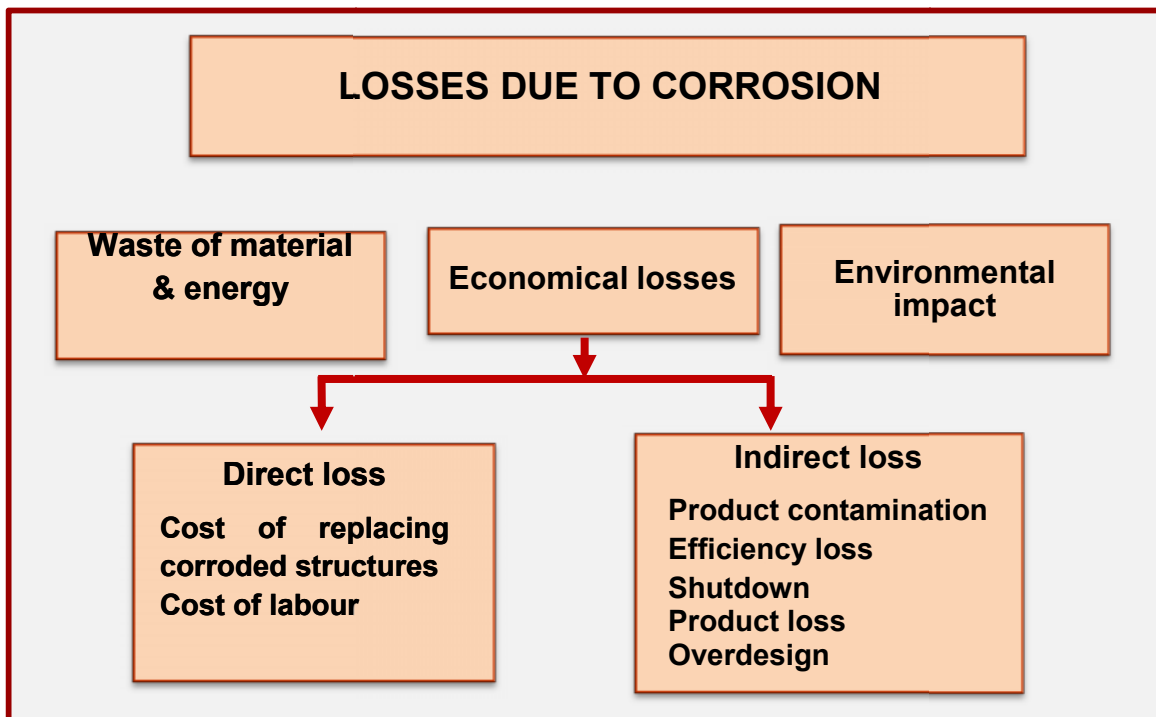


Figure 1.5. Losses due to Corrosion

### 1.6 CORROSION CONTROL - A UNIVERSAL NECESSITY

Researchers and practitioners in the field of corrosion engineering apply more attention to metallic corrosion than was done earlier due to increasing use of materials in all fields of technology. In view of modern age of technological development and use of metallic materials in all aspect of technology, corrosion phenomena, their prevention and control have become a perpetual struggle between man and nature

It is essential to apply more attention to metallic corrosion than was done earlier due to

- ❖ Increasing use of metals in all facets of technology
- ❖ Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown.

- ❖ Increasing pollution of air and water resulting in more corrosive environment.
- ❖ Use of new high strength alloys which are usually more susceptible to certain types of corrosive attack.
- ❖ Safety standard of operating equipment, which may fail due to corrosion

## 1.7 CORROSION MITIGATION

Corrosion in different environments is one of the serious problems facing industry and its mitigation has been approached in from various angles. Since the types of corrosion are so numerous and the conditions under which corrosion occurs are so different that diverse methods are used to control corrosion. Some of the corrosion control methods are

**a. Design considerations:** The essential factor that should be taken into consideration while designing for corrosion control is to avoid crevices where deposits of water-soluble compounds and moisture can accumulate.

**b. Cathodic protection:** It is an electrical method of mitigating corrosion on metallic structures that are exposed to electrolytes such as soils and waters. In this method, a defined quantity of direct current can be forced to flow from auxiliary anodes, through the electrolyte, and onto the metal structure to be protected.

**c. Protective coatings:** Application of coatings and linings are nowadays found play a significant role in corrosion prevention. Metallic coatings such as thermal sprayed zinc, aluminium or aluminium-zinc alloys, stainless steel, and chromium can be used to protect against corrosion or provide increased wear or abrasion resistance.

### 1.7.1 INHIBITORS

**One of the extensively used methods in minimizing corrosion is the usage of corrosion inhibitors.**

Corrosion, in electrolytic phases, is an electrochemical process and any phase constituent leading to retardation of this process is called an inhibitor. Corrosion inhibitor is a substance that when added in small quantities to the aqueous corrosive environment, effectively minimises the corrosion of a metal. The most effective inhibitor is the one which has the most stable adsorption type, which in turn depends on the molecular structure of the inhibitor. Inhibitors slow down the corrosion processes by either:

- ❖ Increasing the anodic or cathodic polarization behaviour;
- ❖ Reducing the movement or diffusion of ions to the metallic surface;
- ❖ Increasing the electrical resistance of the metallic surface.

Several chemical compounds that are found to exhibit inhibitive properties are listed by the scientific and technical corrosion literature. Of these, only very few are actually used in practice due to considerations of cost effectiveness, availability and environmental issues. The most popular classification of corrosion inhibitors are

- ❖ Passivating Inhibitors
- ❖ Cathodic inhibitors
- ❖ Precipitation inhibitors
- ❖ Organic inhibitors
- ❖ Volatile corrosion inhibitors

### **Choosing a Corrosion Inhibitor**

When choosing the corrosion inhibitor, several things need to be considered.

- ❖ Protection timeframe
- ❖ Method of application (dip, spray, brush, etc.)
- ❖ Type of protection required (in process, storage or shipping)
- ❖ Storage, packaging and/or shipping conditions (temperature, humidity & seasonal conditions)
- ❖ Environmental, health and safety requirements
- ❖ Type of product (Oil/Solvent or Water-based) desired

### **Oil/Solvent-Based Inhibitors**

Corrosion inhibitors of this type rely principally on the formation of barrier coatings to prevent water from contacting metal surfaces. Oil-based inhibitors are preferred for long term usage due to their heavy film and the water rejecting properties they possess.

### **Water-Based Inhibitors**

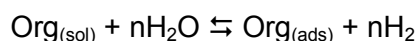
Water-based corrosion inhibitors rely on modifying the characteristics of the metal surfaces to decrease their susceptibility to oxidation and corrosion formation. Water-based corrosion inhibitors generally have very desirable characteristics. The chemical films formed are thin and typically transparent when dry. Application methods for these coatings include spray, brush or immersion. They are cleaner to use and eliminate concerns of solvent fumes.

### **1.7.2 SELECTION OF INHIBITOR**

Appropriate selection of the inhibitor mainly depends on the type of acid, concentration, temperature, the extent of dissolved organic or inorganic substances in

solution and the type of metallic material exposed to acid corrosion. The use of organic inhibitors in acid solution is very common, particularly in view of the high corrosion rate.

Nitrogen containing organic compounds are widely used as effective and efficient metallic corrosion inhibitors. The inhibitive action of these organic compounds may be ascribed to the mobile electron pairs,  $\pi$ -orbital character of free electrons and electron density around nitrogen atoms. The efficiency of an organic compound acting as an inhibitor is largely dependent on its adsorption onto the metal surface by replacement of water molecules at the interface and can be represented as



The presence of functional groups such as = NH, -N = N-, -CHO, R-OH, R = R etc are also found to play a significant role in the adsorption of the inhibitor molecule.

#### Nature of Adsorption of Inhibitors

While formulating an organic inhibitor system, it is essential to know the inhibition mechanism of the concerned molecules and the application field. It has been generally accepted that organic molecules inhibit corrosion by adsorption at the metal / solution interface and the degree of adsorption are dependent upon the

- ❖ chemical structure of the molecule
- ❖ chemical composition of the corrosive solution
- ❖ nature of the metal surface and
- ❖ electrochemical potential at the metal / solution interface (**Riggs, 1973**).

### 1.7.3 NATURAL PRODUCTS AS CORROSION INHIBITORS – A PRACTICAL APPROACH

In acidic media, one of the most suitable methods for protection against corrosion is the use of inhibitors (**Trabanelli, 1991**). In recent years, the use of naturally occurring substances as inhibitors is considered as replacement for synthesised organic inhibitors mainly due to its biodegradability and eco- friendliness.

Green inhibitors displaying improved environmental properties will be the inhibitors most widely used in future. The need of the hour is to harness the abundant natural resources to find a viable solution to mitigate corrosion. This motivated us to assess the effectiveness of *Spathodea campanulata* (leaves and flowers) and *Tecoma capensis* (leaves and flowers) in minimising the corrosion of mild steel and aluminium in acidic media. The selected plant species were authenticated by Botanical Survey of India (**BSI**)

## 1.8 PLANT DESCRIPTION

### 1.8.1 *Spathodea campanulata*

*Spathodea campanulata*, commonly called African tulip tree, is a large, fast-growing tree that is native of tropical African forests where it typically grows to as much as 80' tall. It is noted for producing an often extraordinary bloom of reddish-orange, tulip-like. This tree has now been extensively planted as an ornamental in tropical areas around the world including **INDIA**. It has been reported to be an invasive colonizer in the South Pacific, Puerto Rico, and Brazil. (Bittencourt *et al.* 2003).



#### Scientific Classification:

Kingdom : *Plantae*

Order: *Lamiales*

Family: *Bignoniaceae*

Genus: *Spathodea*

Species: *S.campanulata*

Common Name: Flame of forest

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### 1.8.2 *Tecoma capensis*

*Tecomaria capensis* (Bignoniaceae) also known as Cape-honey suckle is a climber common to the tropical zone-**INDIA**, Australia, Africa. It is grown as an ornamental plant in gardens. *Tecoma capensis* has been categorised as an invasive species by several countries namely; Anguilla, Australia and New Zealand, Tanzania. (Wotherspoon and Wotherspoon, 2002). (Dawson *et al*, 2008). (Healy, 1958) and Queensland, Australia (Queensland Herbarium, 2002).

#### Scientific Classification:

Kingdom : *Plantae*

Order: *Lamiales*

Family: *Bignoniaceae*

Genus: *Tecoma*

Species: *T.capensis*

Common Name: Cape honeysuckle

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## **1.9 OBJECTIVES**

- ❖ To identify a viable natural resource of plant origin that can act as a corrosion inhibitor.
- ❖ To characterise the identified plant based inhibitors using various analytical techniques.
- ❖ To establish the utility of the corrosion inhibitors for mild steel (MS)/ aluminium (AA1100) in 1M hydrochloric acid medium using mass loss and electrochemical techniques.
- ❖ To ascertain the adsorption of the phytochemical constituents on MS / AA1100 surface by surface analysis method.
- ❖ To corroborate the experimental determination of corrosion inhibition using theoretical modelling of phytochemical constituents of the investigated extracts by means of Hyperchem 7.5