

Review of Corrosion Inhibitors for Industrial Applications

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Abstract: Corrosion is more than just an inevitable natural process; it is also one of the most serious engineering problems in modern society. Losses incurred as a result of corrosion are estimated in billions of dollars each year. As an effort to combat these losses, technological options have to be exercised in order to provide protection against corrosion. The inhibition science has started in 1930's. This technology has changed and developed over the last decades. Several successful efforts have been made using corrosion inhibitors to overcome this serious problem.

Corrosion inhibitors are compounds used in low concentration to Slowdown or prevent the corrosion process. The effectiveness of an inhibitor depends on its ability to react with the surface of a metal to form a protective film; thereby reducing or providing protection against corrosion. The current inhibitors are toxic and expensive; therefore a new non-toxic and inexpensive materials or methods to reduce corrosion are needed.

Keywords: Corrosion, natural inhibitor, industrial corrosion, corrosion prevention.

1. INTRODUCTION

The paper focuses on the corrosion inhibitors for chemical industries. There is an increasing concern about the toxicity of corrosion inhibitors in industry. The toxic materials are not only affecting living organisms but also poison the earth over a long term. Similar to coatings, corrosion inhibitors represent another essential technology for the mitigation of corrosion. It further parallels the field of coating; however the research in corrosion inhibitors should focus on:

1. Identify new and better inhibitor materials that are environmentally friendly.
2. Understand how they function.
3. Examine new methods to clearly and rapidly characterize their service – life potential.

Chromate based compound inhibitors used within a wide range of industries. But the use of chromate causes health and environmental problems. It is not easy to find a suitable replacement because chromate materials showed excellent performance in so many environments. The applications of the inorganic compound (Nitrate, phosphate, Vanadate, etc.) are limited because of the high maintenance cost and reduced safety levels accompanied with their use. Most of the efficient inhibitors used in industry are organic compounds that mainly contain nitrogen; sulphur atoms and multiple bonds in the molecules through which they are adsorbed on the metal surface.

The selection of the appropriate inhibitors depends on the type of chemicals in the industry, concentration, temperature, and the type of metallic material. The extent of adsorption of an inhibitor depends on the nature of the metal surface, the chemical structure of inhibitor, and the type of aggressive solution. Several researches have confirmed the use of some plants' extracts; which are available naturally in plenty at low cost, are non-toxic, and achieve high inhibition efficiency as corrosion inhibitor. The use of low cost eco-friendly compounds as corrosion inhibitors is essential to reduce the high cost of corrosion process.

In 1949 the direct cost of corrosion in USA was estimated at 5 billion dollars per year. At 1971, in a survey carried out by T.P Hoar in England on behalf of the department of Trade and Industry, suggested that the direct losses due to corrosion would be 1.25% of the gross national product. A recent estimate of the National Commission on Material Policy in USA

comes up with an estimate of 15 billion dollars per year. The total annual costs of fires, floods, hurricanes, tornadoes and earthquakes in North America do not exceed the lowest estimate on the direct costs of corrosion.

A National Bureau of Standards report in 1966 stated that 40% of US steel production was used to replace items rendered useless due to corrosion (40 millions tons of steel/year). 50% of the world's zinc production is sacrificed to protect steel. Corrosion costs in the oil and gas industry estimated \$200/mile of pipe line per year in the USA.

2. CORROSION PROCESS AND MECHANISM

2.1 Definition:

Corrosion is deterioration of materials by chemical or electrochemical attack within the working environment. The term corrosion is sometimes also applied to the deterioration of plastics and other non-metallic materials, which are susceptible to swelling, crazing, cracking softening, etc., is essentially physiochemical rather than electrochemical in nature (Fontana, 1986, Green and Perry, 2007).

Thus, generally, the definition of corrosion is the reaction of engineering materials (metals) with their environment leading to a consequent deterioration in properties of materials (Shreir, et al., 1998).

2.2 Chemistry of Corrosion:

The surface of all metals (except for gold) in air is covered with oxide film. When such metal is immersed in an aqueous solution, the oxide film tends to dissolve. All corrosion reactions are electrochemical in nature. The rate of corrosion process depends on the two conjugate reactions at the metal surface:

A) Anodic reaction:



The anode is the site at which metal is corroded. The metal is dissolved and transferred to the solution as metal ions positively charged. The electrons flow, as electrical current, to the cathode where they are consumed (Roberge, 1999).

B) Cathodic Reaction:



The cathode is the site at which the electrons react with some reducible component of the electrolyte and detached from the metal.

The rate of the anodic and cathodic reactions must be equivalent according to Faradays' Laws, being determined by the total flow of electrons from the anode to cathode which is called the "corrosion current", I_{corr} . Since the corrosion current must also flow through the electrolyte by ionic conduction, conductivity of the electrolyte will be influenced by the way in which corrosion cells operate. The corroding piece of metal is described as "a mixed electrode", since simultaneous anodic and cathodic reaction are proceeding in each surface. The mixed electrode is a complete electrochemical cell on one metal surface (Abdel Hamid, et al., 2005, Revie, 2011, Roberge, 1999).

The electrochemical reactions in the corrosion in case of iron as an example are:

Anodic reaction (corrosion)



Cathodic reaction



Or



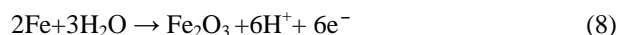
The cathodic reaction (4) takes place in acidic solutions. At the pH range (6.5 – 8.5), the most important reaction is oxygen reduction (Reaction 5). In the later case corrosion is usually accompanied by the formation of solid corrosion debris from the reaction between the anodic and cathodic products:



The pure iron (II) hydroxide is white but the material initially produced by corrosion is normally a greenish color due to partial oxidation in air.



Further hydration and oxidation reactions can occur and the reddish rust eventually formed. Because the rust, precipitated as a result of secondary reaction, is porous, absorbent, and tends to act as a sort of harmful poultice; the environment tends to enrich further corrosion. For other metals or different environments, different types of anodic and cathodic reaction may occur. If solid corrosion products are produced directly on the surface as the first result of anodic oxidation, this may provide a highly protective surface film which retards further corrosion. The surface is then set to be "passive". For an example, of such process would be the production of an oxide film on iron in water, this reaction which occurs in oxidizing conditions or at elevated temperatures:



2.3 Potentials and Polarization measurements:

Since the corrosion reactions involve the transfer of electrons and ions between the metal and the solution at reaction rates equivalent to electric currents. The rates of these reactions depend on the potential difference between the metal and the solution, i.e. the potential of the metal. As the potential of the metal becomes more positive, the rates of anodic reactions increase and the rates of cathodic reactions decrease. The converse effect on the reaction rates occurs as the potential of the metal becomes more negative. From the relationships between the potential of a metal and the currents flowing (equivalent to rates of the corrosion reactions) the corrosion behavior can be understood. The relationships between potential and current (termed polarization curves) can be determined using a potentiostat. The potentiostat employs a working electrode, a reference electrode, and a counter electrode (El Dahan, et al., 1999, Roberge, 1999, Rozenfeld, 1982).

The reference electrode most commonly used is the saturated calomel electrode. The potential depends on the concentration of chloride ions. A saturated solution of potassium chloride is used because this minimizes the junction potential between the test solution and the solution in the reference electrode. The change in potential induced in the working electrode by the passage of current is measured against the reference electrode. In order to minimize the inclusion in the measured potential of any potential drop occurring in the solution due to its resistance, the reference electrode is brought into contact with the test solution through a tube which ends in a fine capillary known as a Luggin capillary. In the potentiostatic method, the potential of the working electrode is controlled at a fixed value with a potentiostat. This instrument uses a feed-back circuit to pass appropriate current to the working electrode to keep the measured potential against the reference electrode at the desired value, regardless of variations in current corresponding to changes in the rates of the corrosion reactions. The potentiostatic method of polarization has the advantage that it can follow more closely the behavior of metals during the formation and breakdown of passivating films, where the behavior primarily depends on the potential of the metal, and very large changes in currents could occur at constant potential (Roberge, 1999, Rozenfeld, 1982).

2.4 Polarization Behavior of Corrosion Metals:

A corroding metal in a solution consumes a potential, the corrosion potential, such that the rate of the anodic reaction of metal dissolution is equal to the rate of the cathodic reactions of hydrogen and/or oxygen reduction. If the potential of the corroding metal is displaced slightly from the corrosion potential, **E_{corr}**, then the potential **E** is initially a linear function of the current density **i** (the current per unit area). This linear relationship holds for a potential displacement of up to about 10 mV. The slope of the linear polarization curve **dE/di** is termed the polarization resistance **R_p**. The polarization resistance is inversely proportional to the rate of corrosion expressed as the equivalent corrosion current density **i_{corr}**, i.e:

$$i_{\text{corr}} = \mathbf{B} / \mathbf{R}_p \quad (9)$$

Where **B** is a constant.

Measurement of the polarization resistance provides a valuable way of rapid determination of the instantaneous rate of corrosion of a metal, as used in several commercial instruments. As the potential displacement is above 10 mV, the polarization curve increasingly deviates from the linear region exhibits a linear dependence on the logarithm of the current density as shown in Figure 1

This behavior is characterized by the occurrence of a single electrochemical reaction on the metal surface. Indicating that the displacement of potential is high since one of the corrosion reactions, either anodic or cathodic, has been retarded until its rate is negligible compared to the rate of the reaction being accelerated. Then the relationship between the observed potential E and current density i is given by Equation 10:

$$E - E_r = i_0 + b \log i \quad (10)$$

The difference between the observed potential E and the reversible potential E_r is the over potential. The term i_0 is the exchange current density, i.e. the current density of the opposing reactions at the reversible potential. The constant b which is the slope $dE/d \log i$ of the polarization curve is termed the Tafel slope and is related to the kinetics of the corrosion reaction. The observed Tafel regions of the polarization curves extrapolated to the corrosion potential E_{corr} , intersect there to give the value of the corrosion current density i_{corr} (Abo El-Enin, et al., 2005, El-Enin, et al., 2008, Revie, 2011, Sharma and Eddy, 2011).

2.5 Factors Influencing Corrosion Process:

2.5.1 pH Value of Solution:

The corrosion rate of most metals is affected by pH (Green and Perry, 2007):

- (a) Acid-soluble metals such as iron; at pH range 4 to 10, the corrosion rate is controlled by the rate of transport of oxidizer (dissolved O_2) to the metal surface.
- (b) Amphoteric metals such as Al and zinc, dissolve rapidly in either acidic or basic solution.
- (c) Noble metals such as gold and platinum are not affected by pH-value.

2.5.2 Oxidizing Agents:

Oxidizing agents are often powerful accelerators of corrosion. Oxidizing agents that accelerate corrosion of some materials may also retard corrosion of others through the formation on their surface layers of adsorbed oxygen which makes the metal more resistant to chemical attack. This property of chromium is responsible for the principle corrosion-resisting characteristics of the stainless steels.

2.5.3 Temperature:

The rate of corrosion tends to increase with rising temperature. Temperature also has a secondary effect through its influence on the solubility of air (O_2), which is the most common oxidizing substance influencing corrosion.

2.5.4 Velocity:

An increase in the velocity of relative movement between a corrosive solution and metallic surface accelerates corrosion.

2.5.5 Filming:

Once corrosion has started, its progress often is controlled by the nature of films; such as passive films that may form on the metallic surface. Insoluble corrosion products may be completely impervious to the corroding liquid and therefore completely protective. Films that are discontinuous may tend to localize corrosion in particular areas.

2.5.6 Impurities:

The effects of impurities are varied and complex. An impurity in a stream may act as an inhibitor if this impurity is removed by some process change, a marked rise in corrosion rate can result. Other impurities, of course, can have very deleterious effects on materials e.g. chloride ion can break down the passive acid film on stainless steels.

2.5.7 Other Effects:

Stream concentration may have important effects on corrosion rate in equipment such as reactors, and evaporators. The concentration is important during plant shutdown; presence of moisture that collects during cooling can turn innocuous chemicals into dangerous corrosives.

2.6 Forms of Corrosion:

The various forms of corrosion and their causes are easily recognized (Green and Perry, 2007, Revie, 2011, Sharma and Eddy, 2011, Shreir, Burstein and Jarman, 1998, Younan and Abo El-Enin, 2004, Younan, et al., 2001).

2.6.1 General Corrosion:

General Corrosion or uniform corrosion is characterized by a corrosion reaction that proceeds at a similar rate over the entire exposed surface. Practically, all metallic materials used in industry have sufficient heterogeneity to produce minute anodic and cathodic areas in their exposed surfaces. As a result of electrochemical reaction between these areas, corrosion occurs and appears to be uniform. The general corrosion causes the greatest amount of damage to metals. Its rate depends on the specific condition of the environment such as the corrosivity of the environment which can be decreased by reducing temperature, pressure, velocity and/or composition.

2.6.2 Localized Corrosion:

Pitting and crevice corrosion are also electrochemical in nature. The anodic areas occur in the case of pitting as the result of localized breakdown on the surface. In case of crevice corrosion, the anodic areas generally occur because of differences in electrolyte composition. This form of corrosion is highly localized and general corrosion is frequently slight. Pitting corrosion may occur in any metal but the most common occurrences are in aluminum and stainless alloys in aqueous environments containing metal chlorides. Pitting is the most serious of these localized types of corrosion because it can occur very rapidly and may not be detected until failure occurs.

2.6.3 Stress – Corrosion Cracking:

Cracking often results from the combined effects of applied stress and chemical action without noticeable loss of metal through uniform corrosion. This form is generally occurred rapidly once action has started and is frequently not detected until failure occurs. It usually takes place by a fine pitting, with the cracks starting in a pit. The time required for cracking may vary from a few minutes to few years.

2.6.4 Hydrogen Blistering and Cracking:

Micro cracking and blistering with loss of ductility are often caused by the entrance and diffusion of atomic hydrogen. The most occurrence of this form of attack is in steel equipment containing hydrogen sulfide H₂S solution. The occurrence of the cracking phenomena increases with increase in hardness and is attributed to the inability of the steel to deform.

2.6.5 Intergranular Corrosion:

Localized electrochemical attack occurs along the grain boundaries of an alloy. This type of attack may penetrate completely through the metal section with essentially complete loss of strength.

2.6.6 Galvanic Corrosion:

When dissimilar metals are in electrolyte solution this causes an electrochemical attack for the less noble metal. The best example is the use of zinc to protect steel equipment. The galvanic corrosion does not depend only on the potential difference of the two metals but also upon the relative surface area involved.

2.6.7 Selective Corrosion:

Removal of a constituent of an alloy by corrosion without apparent loss in volume but with serious loss of strength is called "selective corrosion"; e.g. the zinc constituent present in brass alloys is selectively removed leaving only sponge copper in the original shape and volume of the un-corroded metal.

2.6.8 Erosion Corrosion:

Accelerated corrosion may result from erosion which removes normally protective films. It is most likely to occur in liquid systems that contain solids. Items, such as, agitator blades and pipe-line fittings are subjected to this form of corrosion. It can be minimized by changes in environment, by addition of an inhibitor to reduce corrosiveness of the solution or by the use of harder material.

2.6.9 Fretting Corrosion:

Corrosion between two surfaces resulting from the mechanical removal of a protective film is called fretting corrosion. This occurs at the interface of metals when they are fitted closely together. It is most common on machine parts with small relative motions and high unit loads.

2.6.10 High-Temperature Corrosion:

Chemical reaction of metals at elevated temperatures with one or more constituents of a gaseous environment often results in corrosion. The most common type is oxidation where metal oxides form by chemical reaction and losses occur in the form of scaling. Rate of metal loss under oxidizing conditions increases with increase in temperature due to loosening of scale and loss of its protective value.

2.6.11 Biological Corrosion:

Deterioration of steel or iron may occur directly or indirectly as a result of the metabolic activity of microorganisms. The anaerobic sulfate reducing bacteria are most frequently involved in this form of corrosion. They contribute to corrosion by affecting changes in surface film resistance, creation of corrosion environment or creation of a surface barrier so as to cause concentration cell corrosion. The most common occurrence is in clay or boggy soils.

2.7 The Major Harmful Effects of Corrosion:

1. Reduction of metal thickness leading to loss of mechanical strength and structural failure.
2. Hazards to people arising from structural failure (e.g. bridges, cars, aircrafts).
3. Loss of time in availability of profile-making industrial equipment.
4. Reduced value of goods due to deterioration in appearance.
5. Contamination of fluids in vessels and pipes (e.g. soap goes cloudy when small quantities of heavy metals are released by corrosion).
6. Perforation of vessel and pipes allowing escape of their content and possible harm to the surroundings, e.g. a leaky domestic radiator can cause expensive damage to decorations.
7. Loss of technically important surface properties of a metallic component, e.g. ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.
8. Mechanical damage to valves, pumps, etc. by solid corrosion products.
9. Added complexity and expense of equipment to resist the corrosion.

2.8 Conservation of the Metals:

There are different methods in use for combating corrosion (Green and Perry, 2007).

2.8.1 Select Proper Material:

Selecting material of construction for equipment which will be exposed to corrosive environment consideration should be given to the practical aspects and maintenance.

2.8.2 Proper Design:

Design consideration with respect to minimizing corrosion difficulties including the desirability, for free and complete drainage, elimination of crevices, and ease of cleaning and inspection.

2.8.3 Alter Environment:

Simple changes in environment make difference in corrosion of metals; oxygen is an important factor and its removal or addition may cause marked changes in corrosion. The treatment of boiler feed water to remove oxygen reduces the corrosiveness of water on steel.

2.8.4 Inhibitors:

The use of inhibitors as additives to corrosive environments to decrease the corrosion of metals is an important mean of combating corrosion.

2.8.5 Cathodic Protection:

By protecting the metal from the cathodes in the electrolyte involved.

2.8.6 Coating and Linings:

The use of non-metallic coatings and lining materials in combination with steel or other materials will continue to be an important type of construction for combating corrosion. Organic coatings of many kinds are used as lining in equipment such as tanks, piping, pumping lines and shipping containers and they are often an economical means of controlling corrosion without metal contamination.

In the next part of our review, we will focus on using inhibitors especially natural and non-poisoning inhibitors to reduce corrosion drawbacks.

3. CORROSION INHIBITORS

Corrosion inhibitors may be defined as a substance which when added in a small concentration to an environment effectively reduces the corrosion rate of a metal exposed to that environment. Inhibitors slow corrosion process by either:

1. Retarding either the anodic or cathodic reactions.
2. Reducing the movement or diffusion of ions to the metallic surface.
3. Increasing the electrical resistance of the metallic surface.

The scientific and technical corrosion literature has lists of numerous chemical compounds that exhibit inhibitive properties. Actually, few inhibitors were used in practice according to the desirable properties of an inhibitor for metal protection. There are several considerations when choosing an inhibitor; cost, toxicity, availability and environmental friendliness. A particular advantage of corrosion inhibitors is that are easily applied without causing any disrupting to the process. Inhibitors are used in a wide range of applications. The types of environment that can be modified include aqueous, partly aqueous and gaseous. Aqueous are often at near neutral pH range such as natural water, cooling water systems and in acidic range such as acid pickling to remove rolling scale as well as in the production and refinery of oil and gas. The major industries using corrosion inhibitors are the oils and gases exploration and production industry, the petroleum refining industry, the chemical industry, heavy industrial manufacturing industry, water treatment facilities and the product additive industries.

3.1 Types of Inhibitors:

There are several types of inhibitors available nowadays:

3.1.1 Volatile Inhibitors:

This type of inhibitors is also known as vapor phase inhibitors. When the inhibitor molecules in the vapor come into contact with the surface of a metal, the inhibitor adsorbs on the metal surface. The moisture then hydrolyses it; hence protective ions may be released. Amines and nitrites are used for inhibition of ferrous metal corrosion. Amines can be applied in volatile environment to prevent atmospheric corrosion. Amines are cationic type of inhibitors. They are often added to HCl-rich environments in the concentration of 0.2% in the form of mixture in polyhydric alcohols (glycol). In producing wells, long chain aliphatic diamines are employed. When the system involved is ferrous metal, neutralizing amines work by the mechanism that modifies the pH of the electrolyte and thus inhibiting rust formation (Revie, 2011, Roberge, 1999, Sharma and Eddy, 2011).

Nitrites can be used in a volatile form. In an open recirculating system, sodium nitrite is prone to chloride and sulphate induced localized attack. Nitrite loses its inhibitive effect when the pH is below 5.5-6.0. Nitrite is also used in inhibition for engine coolant for road vehicles and marine diesels. It has been found that nitrite is able to reduce corrosion in diluted seawater. In the oil and gas industry, nitrites in oil-soluble form have been applied to inhibit corrosion induced by the water settled at the bottom of the tank.

3.1.2 Passivating (Anodic) Inhibitors:

Passivating inhibitors are also known as anodic inhibitors. They have the ability to passivate the metal surface. There are two categories of passivating inhibitors, namely oxidizing anions and non-oxidizing anions. Oxidizing anions have the ability to passivate metal in the absence of oxygen; such as chromate, nitrite, and nitrate. However, the inhibitive effect of chromate is restricted because there is a possibility of localized attack if chloride and sulphate concentrations in the system rise to significant value. Non-oxidizing inhibitors such as phosphate, tungstate and molybdate require oxygen to

perform passivation. This kind of inhibitor is widely used and possesses higher efficiency than others. Phosphates precipitate a thin adherent film at cathodic sites on corroding metal surfaces and thus block oxygen from accessing the cathodic sites (Roberge, 1999).

3.1.3 Precipitation Inhibitors:

These inhibitors are often film-forming in nature, for instance silicates and phosphates. They are effective at blocking anodic and cathodic sites. They precipitate on the metal surface, forming a protective barrier. Hard water is rich in magnesium and calcium. When these salts precipitate on the metal surface, they establish a protection layer on the metal. The efficiency of Film-forming type of inhibitors depends on the pH value, the water composition and temperature (Roberge, 1999).

3.1.4 Cathodic Inhibitors:

Cathodic inhibitors reduce the rate of cathodic reaction namely oxygen reduction in near neutral environments and/or hydrogen evolution in acid solutions. These form species of inhibitor precipitate on cathodic sites and thus increase the surface impeding and lower the diffusion rate. The inhibiting action of cathodic inhibitors works by one of three mechanisms (Revie, 2011, Roberge, 1999):

- Cathodic poisons

In this case, the cathodic reduction process is suppressed, by impeding the hydrogen recombination. Typical types of cathodic poisons are arsenic and antimony.

- Cathodic precipitates

Compounds such as calcium, magnesium will precipitate as oxides to form a protective layer which acts as a barrier on the metal surface.

- Oxygen scavenger

This mechanism proceeds by the removal of oxygen in the system to reduce corrosion. The compounds of oxygen scavenger react with oxygen in the system.

3.1.5 Organic Inhibitors:

Organic inhibitors are forming a film over the corroded surface. They form a hydrophobic layer on the surface of the metal to prevent dissolution of metal. The efficiency of these inhibitors depends upon their chemical composition and their molecular structure as well as their affinity with the metal. They are used often when environmental issues are taken into account. The protection efficiency of organic inhibitors is attributed mainly to the presence of at least one polar group having atoms of N, and/or O, S, P,...etc. and acting as an active center for adsorption on the metallic surface (Roberge, 1999).

3.1.6 Inorganic Inhibitors:

The common inorganic inhibitors used are crystalline salts, for instance, sodium chromate and molybdate. The feature of inorganic inhibitors is the low protective values and their ability to form sparingly soluble compound around the metal surface (Revie, 2011).

3.2 Toxic Inhibitors:

The salts such as, Sodium Tungstate (Na_2WO_4), Vandates (NaVO_3), Nitrites (NaNO_2), Silicates ($\text{Na}_2\text{Si}_2\text{O}_5$), and chromates (NaCrO_4) were used to protect both ferrous and non-ferrous metals. The applications of nitrites and chromates are diminishing due to their toxic nature. For the environmental protection, molybdate salts or rare earth metals replaced chromates as corrosion inhibitors for open recirculating cooling water system, but these compounds are very expensive (Bofardi, 1995, Vukasovich and Van Riper, 1990). The phosphate salts were the commonly inorganic inhibitors used to give better inhibition efficiency in combination with zinc salt ($\text{zinc} \leq 2 \text{ mg / L}$) (Fontana, 1986, Gonzales, et al., 1995, Kalman, 1990, Manahan, 1999).

3.3 Friendly Inhibitors:

The current trend for inhibitor usage is towards more environmentally friendly green chemicals. For environmental protection, the scientific efforts have increased to study the inhibiting power of natural products like peels, seeds, fruit-

shells and leaves that contain different organic compounds, (e.g. amino acids, alkaloids, flavonoids, pigments, tannins,...etc.) which suppress the dissolution reaction of metals and prevent the environmental pollution (Favre and Landolt, 1993). Qurishi et al. (Qurishi, et al., 1999) have confirmed the use of aqueous extracts of some natural products which are widely available at low cost and non-toxic as corrosion inhibitors for metal dissolution.

El-Hosary et al. (El-Hosary, et al., 1990) have used aqueous extract of leaves, fruit-peels and seeds of some natural products as corrosion inhibitors for Fe, Cu, Al, Zn, ...etc. in different media. El-Dahan et al. (El Dahan, et al., 2006, El Dahan, et al., 2006) used alcoholic extract of *Atropa belladonna*, *Whithania somnifera*, *Achillea millefolium*, and *Medicago polymorpha* to inhibit the corrosion of copper and carbon steel in hydrochloric acid solution. Also, some authors used castor seed, tobacco leaves, black pepper, bignin (Favre and Landolt, 1993), *Azadirachta indica*, *Punica Granatum*, Date pits, and *Momordica* (Abo El Enin, 2006, El-Hosary, Saleh and El-Dahan, 1990, Gopi, et al., 2002, Qurishi, Farooqi and Saini, 1999). The corrosion protection properties of all these natural products were analyzed and their results showed that a reasonable corrosion protection could be obtained by natural products extracts.

3.4 Inhibitors Selection:

In this section, we present recommendations for selection of corrosion inhibitors (Faltermeier, 1999):

1. The solubility of the inhibitor in water or alcohol is an important factor. The solvent in which the inhibitor is applied should be inexpensive, non-toxic and not hazardous.
2. The corrosion inhibitor should form a complex with metal, resulting in a polymeric layer. The polymer layer acts as a barrier between the metal substance and its environment. The polymer structure should be thick, dense and without voids in order to stop further oxidation of metal.
3. The inhibitor-metal polymer film formed should not be soluble in water or organic solvents.
4. The corrosion inhibitors should be effective over the pH range from 2 to 8.
5. The best inhibitors would react in anodic and cathodic areas.
6. The visual appearance of the metal surface should not be altered by the application of the inhibitor.
7. The inhibitor should not be hazardous or harmful to the user.
8. The inhibitor should be readily available in a pure form through chemical suppliers.
9. The price of the inhibitor is a relative measure, but it should be still economical for large-scale applications.

3.5 Mechanism of the Corrosion Inhibition:

Corrosion inhibition of metals by organic compounds proceeds by adsorption of molecules and ions at the surface of metals (Nmai, 2004, Popova, et al., 2007, Tebbji, et al., 2005). Hence, the adsorption phenomenon is essential to understand the mechanism of corrosion inhibition (Benabdellah, et al., 2006, Chetouani, et al., 2006). The theoretical consideration for a correlation between the molecular structure of organic compounds and their ability to adsorb on the metal surface and hence to inhibit the corrosion process is aimed in a series of studies (Abdel-Gaber, et al., 2006, Müller, et al., 2000). Recently, it has been found that, the presence of heteroatom with unsaturated bonds in an organic compound causes inhibiting effect and reduces the metal dissolution. Protecting efficiency was also found to be improved with increasing the length of alkyl chain (Ai, et al., 2006, Sherif and Park, 2006). It was found that the ampholytic compounds adsorption depend on the nature of both hydrophilic and hydrophobic parts and their ability to form aggregates in solution. The highest corrosion inhibition of ampholytic compounds was observed when the lipophilic part was surrounded by 10-12 C-atoms (Vračar and Dražić, 2002).

The orientation of the adsorbed organic molecules at the metal surfaces is of a special interest, and dependent on pH values and/or electrode potentials. Some investigations on the corrosion inhibition of iron studied correlate molecular orbit interaction to the inhibition properties of the organic molecules. By comparing corrosion inhibition of iron by thiophenol, phenol and aniline, it was found that the best efficiency for thiophenol is due to the interaction between the sulphur lone pairs and vacant metallic orbit (Maayta and Al-Rawashdeh, 2004).

Among the alternative corrosion inhibitors, organic products containing one or more polar functions (with N,O and S atoms) have shown to be quite efficient to prevent corrosion, as well as heterocyclic compounds containing polar groups and π – electrons (Popova, et al., 2003). The polar function is usually regarded as the reaction centre for the adsorption

process establishment (Ferreira, et al., 2004). Different approaches have been applied to find correlation between the inhibitor properties and the electronic density, electron mobility, electron donor properties of different functional groups, position of the substituents and steric factors. Sulphur-containing compounds are generally more effective corrosion inhibitors for steel in acidic media because sulphur is better electron donor than nitrogen and therefore such compounds adsorb very well on the metal surface (Popova, et al., 2004). Phosphorous as heteroatom in homologous series of organic compound is easily polarizable and has lower electronegativity compared to other heteroatoms. Therefore, it is expected that phosphorous compounds should be most effective in retarding the dissolution of steel in acidic media (Morad, 2000). K. Bhrara (Bhrara and Singh, 2006) showed that benzyl triphenyl phosphonium bromide (BTPPB), Figure 2, retards corrosion of mild steel in 0.5M sulphuric acid very effectively at ordinary temperature. Corrosion efficiency of 99.3% has been reported.

At higher concentration, BTPPB molecules are not able to form a resistive layer whereas at lower concentration the resistive layer may be formed with the help of ions like Br^- , SO_4^{2-} present in the solution. It also has de-localized set of electrons which helps in the formation of complexes of the type $(\text{M-In})_{\text{ads}}$ [metal-inhibitor] $(\text{M-In-A})_{\text{ads}}$ where A is the anion present in the solution or is the anion of the additive that causes a synergistic effect.

For short period applications, researchers have developed a temporary corrosion protection which is designed to prevent the corrosion of metal surface of equipment during transport and storage. There are many types of temporary protection methods. Among them, the use of volatile corrosion inhibitors (VCIs) is an effective and convenient means (Subramania, et al., 2006). The VCIs is a group of anticorrosive chemicals, which extend their corrosion inhibiting properties to a metal surface by volatilization within an enclosed space. In spite of the fact that VCIs have been used for a long time for inhibiting atmospheric corrosion, the action mechanism of these compounds is not completely clear, it is believed that the major parameters responsible for their efficiency are vapour pressure and the interactions with the metal surface. The VCIs forms an adsorbed monolayer which prevents the penetration by corrosive agents such as water, erosive ions (Cl^- or SO_4^{2-}), etc. The adsorbed monolayer may change the rate of electrochemical reactions like the dissolution of metal or the reduction of oxygen. The metal surface almost consists of an irregular physical surface with grains of different size, orientation, grain boundaries and defects. Thus, the adsorption of VCIs on a metal surface may not be uniform and therefore, the corrosion rate may be determined by these defects such as the breakage of the VCI protection film.

Modern surface analysis techniques provide essential information about the interaction of corrosion inhibitors with metal surface such as X-ray photoelectron spectroscopy (XPS) and Atomic force microscopy (AFM). Zhang et al. (Zhang, et al., 2006) suggested based on XPS results that the bis-piperidinium methyl-urea (BPMU) molecule chelated with one Fe-atom form a complex film with two hexa – ring. Atomic force microscopy (AFM) techniques to study the surface of the electrode under real-time condition have shown the adsorption of BPMU to form a protective film of many BPMU molecular aggregates, as shown in Figure 3.

3.6 Application of eco-friendly corrosion inhibitors in chemical industries:

Acid solutions are widely used in chemical industries, the most of which are acid pickling, industrial acid cleaning, acid – descaling and oil well acidizing. The commonly used acids are hydrochloric acid and sulphuric acid (Asan, et al., 2006, Aytac, et al., 2005).

3.6.1. Corrosion inhibitors for Steel:

Tinned iron or Tinplate (Sn-Fe) is generally used for equipment and containers for a wide variety of products, from food cans to cleaners in form of aerosol. These diverse uses are due to its bright appearance, easy solderability, formability and adequate corrosion resistance for a wide range of environments.

In presence of chlorides or other halides, localized corrosion is occurring where the passivity breaks down at local points of the surface leaving the inner (Sn-Fe) layer exposed to corrosive media containing these aggressive ions. To avoid corrosion problems, recently, the researchers have been focussed on the use of rare-earth metals as green inhibitors. Among all the lanthanide compounds, cerium salts ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) have successfully been used as corrosion inhibitors on different metals and alloys. Arenas et al. (Arenas, et al., 2002) can be established the suitability of cerium salts as a green corrosion inhibitor for tinplate in aggressive media of chloride solution. The mechanism of slowing the pit growth is done where cerium acts as cathodic inhibitor precipitating in the damage zones of the Sn-layer blocking them and avoiding the progress of the attack.

- Morad et al. (Morad and El-Dean, 2006) synthesized the organic compound named 2,2 dithiobis (3-cyano-4,6-dimethylpyridine) as shown in Figure 4 and investigated it as corrosion inhibitor for mild steel in 1M, 3M and 5M H₂SO₄ solution at 35-50°C using polarization resistance and potentiostatic techniques.

The results showed excellent performance of the inhibitor 2,2 dithiobis, and its inhibition efficiency is not affected by increasing acid concentration or temperature. It behaves as anodic inhibitor in 1M H₂SO₄ solution as a mixed-type inhibitor in 3M and 5 M H₂SO₄ solutions at different temperature. Adsorption of 2,2 dithiobis compound on the anodic sites results in decrease of the anodic dissolution of iron.

- Abd El Haleem et al. (Abd El Haleem, et al., 2014) studied the corrosion inhibition of steel in saturated naturally aerated Ca(OH)₂ solutions contaminated by Cl⁻. Benzotriazole and its derivatives were used to suppress the corrosion, the authors suggested that Benzotriazole forms iron-chloro- benzotriazoles complexes which adsorb on the steel surface according to the langmuir's isotherm. Benzotriazoles have shown effective inhibition of the pitting corrosion of steel in Ca(OH)₂ solutions contaminated by Cl⁻.

- In many industrial operations, like pickling and acid cleaning, the choice of optimum working temperature and process duration is of particular importance. The effect of temperature in case of acidic corrosion, especially in hydrochloric and sulphuric acid was studied.

- Popova (Popova, 2007) studied the effect of temperature on mild steel corrosion in 1M HCl and 1M H₂SO₄ in the presence of a selected series of inhibitors of Azoles (I, BI, BNS and BTA), as shown in Figure 5. The experimental results proved that all compounds investigated have inhibition efficiency in both 1M HCl and in 1M H₂SO₄. The inhibition efficiency of BTA and BNS in 1M HCl increases with increasing temperature, while BI and I decrease their protective effect. In 1M H₂SO₄ at 60°C BTA and BNS keep a highly protective role when compared to their role in 1M HCl at the same temperature, while BI and I lose their inhibition properties at 60°C. The inhibition efficiency of BTA and BNS are most probably determined by predominating chemisorption of their molecules on the metal surface.

- Hot acid solutions are generally used for removing mill scales (oxide scales) from the metal surface in various industries at elevated temperature such as 60°C in HCl acid and up to 95°C in H₂SO₄ acid. To minimize the percentage metal loss during this process, various compounds as inhibitors are widely used such as acetylenic alcohols, indoles, etc. The literature reading has revealed that 2-mercaptobenzothiazole is an effective corrosion inhibitor up to 70°C (Al-Mayouf, et al., 2001, Frenier and Growcock, 1993). Quraishi et al. (Quraishi and Rawat, 2003) synthesized an organic inhibitor, namely tetraphenyl-dithia-octaaza-cyclotetradecane- hexaene (PTAT) Figure 6.

The polarization behaviour of mild steel in 20% H₂SO₄ in the absence and presence of different concentration of PTAT showed that the inhibition efficiency of the synthesized inhibitor is very high (98.8%) and the E_{corr} value in presence of PTAT shifts to the active direction indicated that PTAT is a predominantly cathodic inhibitor in 20% H₂SO₄.

- Acidization of oil well is one of the important stimulation techniques for enhancing oil production. It is brought about by using a kind of solution of 15-28% hydrochloric acid. To reduce the aggressive attacks of acid on tubing and casing materials, inhibitors were incorporated to acid solution during acidizing process (Quraishi and Jamal, 2001).

M.A..Quraishi et al. (Quraishi and Jamal, 2001), selected some compounds of oxadiazoles of fatty acids (as shown in Figure 7), as corrosion inhibitors of mild steel in 15% boiling HCl solution. From the weight loss measurements and the electrochemical studies of these inhibitors, it was found that the corrosion of mild steel in 15% boiling HCl solution containing oxidiazole of fatty acids can be inhibited due to the adsorption of these compounds on the steel surface through their lone pair of electrons and π -electrons of the heterocyclic ring.

- SX 316-steel is an improved version of SX 304-steel, with the addition of molybdenum and slightly higher nickel content. The resultant composition of SX 316-steel gives the steel much increased corrosion resistance in many aggressive environments. Because of its superior corrosion and oxidation resistance, good mechanical properties and fabricability, SX 316-steel is used in different applications in industry including tanks and storage vessels for corrosive liquids. Nevertheless, SX 316 steel could be attacked by highly concentrated acids during the cleaning pickling process. Therefore, the use of corrosion inhibitors in the cleaning and pickling solutions is very important to keep the surface of steel intact. The use of green compounds will add to the efforts which recently activated to protect our planet from the use of harmful chemicals (El-Etre, et al., 2005).

Such as the extract of Khillah seeds were tested by A.Y.El-Etre (El-Etre, 2006) as a corrosion inhibitor for general corrosion of SX 316 steel in HCl acid. Khillah or Bishop's flower (*Ammi Visnaga*) is an annual plant belongs to the family Umbelliferae. It is cultivated in many areas in the world such as Europe, Asia and Africa. Khillah seed contains small amount of volatile fatty oil, coumarins and furanochromones such as Khellin and Visnagin, as shown in Figure 8.

Among these compounds, the furanochromones have the highest concentrations in the aqueous extract of the seeds. Khillah seeds contain 10,000-40,000 ppm of furanochromones, most of them is Khellin (Duke, 2000). The results of weight loss measurement, potentiostatic polarization technique and the effect of temperature recorded that khillah extract acts as good inhibitor for SX 316 steel in HCl solution. The inhibition action of the extract was attributed to the presence of furanochromones (Khellin and Visnagin). The inhibition efficiency decreases with increasing temperature. Inhibition effect was performed via the adsorption of furanochromones on the steel surface. The adsorbed species formed insoluble complex compounds upon their interaction with the dissolved iron ions, as shown Figure 9.

- Li et al. (Li, et al., 2014) Phyllostachys nigra Munro leaves' extract (PMLE) to inhibit the corrosion of cold rolled steel and zinc in 0.2M citric acid solution in the temperature range of 20-50°C. The inhibition efficiency was studied using weight loss, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) methods. PMLE showed a good inhibition activity for both steel and zinc in citric acid, around 80 and 90% inhibition efficiency were reported for steel and zinc respectively.

- Eduok et al. (Eduok, et al., 2012) employed leaves and stem extracts of *Sida acuta* and iodine ions as corrosion inhibitors for mild steel in 1 M H₂SO₄. Using weight loss and hydrogen evolution methods at 30-60°C, the authors have reported a synergetic inhibition effect takes place when leaves and stem extracts of *Sida acuta* and iodine ions are added to 1 M H₂SO₄. The corrosion inhibition efficiency increases with increasing iodine ions and decreases with increasing temperature. By adding 0.5 g/l of leaves and stem extracts of *Sida acuta*, the inhibition efficiency increased to 85%. The inhibition efficiency increased to 91% when 5 mM of KI added to the solution while the inhibition efficiency fall down to 59.3% when the temperature is increased from 30 to 60°C.

- Al-Otaibi et al. (Al-Otaibi, et al., 2014) studied the corrosion inhibition of mild steel in 0.5M HCl using alcoholic extract of eight plants naturally growing in Saudi Arabia: *Lycium shawii*, *Teucrium oliverianum*, *Ochradenus baccatus*, *Anvillea garcinii*, *Cassia italica*, *Artemisia sieberi*, *Carthamus tinctorius*, and *Tripleurospermum auriculatum*. The open circuit potential (OCP), Tafel plots and A.C. impedance methods have confirmed that all the eight extracts inhibited the corrosion of mild steel in 0.5M HCl at room temperature. The eight extracts adsorb on the steel surface to form a mixed type inhibitor. The inhibition efficiency was: 76.1, 76.1, 84.4, 73.6, 25.4, 71.8, 61.8, and 71.6% for *Lycium shawii*, *Teucrium oliverianum*, *Ochradenus baccatus*, *Anvillea garcinii*, *Cassia italica*, *Artemisia sieberi*, *Carthamus tinctorius*, and *Tripleurospermum auriculatum* respectively.

- Water is the most commonly used cooling fluid to remove unwanted heat transfer surfaces. Open recirculating cooling water systems continuously reuse the water that passes through the heat transfer equipment. Water contains dissolved and suspended solids, dissolved and suspended organic matters, and dissolved gases (Puckorius and Cummunghan, 1997). The open recirculating system, with longer holding times at higher temperatures in the presence of higher dissolved solids concentrations results in more severe corrosion, scaling and microbiological growth. Many inhibitors have been used in cooling water systems in order to solve these problems. An inhibitor blended from citric acid, hydroxyl ethylidene diphosphonic acid (HEDP), acrylate copolymer, and isothiazolone with ratio 2:4:4:1 was investigated; as a corrosion inhibitor in cooling water system (Choi, et al., 2002). The weight loss and the corrosion rate exhibited a substantial reduction from 231.4 mg and 38.72 mpy without inhibitor to 9.2 mg and 1.54 mpy with inhibitor, respectively. The various microorganism used in this study were inhibited at 78ppm or below. The inhibition of corrosion can be attributed to the formation of protective film containing calcium phosphorous and iron. This inhibitor represents a new environmentally safe blend suitable for treating cooling water systems.

3.6.2 Corrosion inhibitors of Copper:

Copper is one of the common materials used in industry owing to its high electrical and thermal conductivities, mechanical workability, and its relatively noble properties. It is widely used in many applications such as electronic industries, and chemical industries, heat conductors, and heat exchangers. Thus, corrosion of copper and its inhibition in a wide variety of media, particularly when they contain chloride ions, have attracted attention of a number of investigators (Sherif, 2006). Recently, E.M.Sherif et al., (Sherif and Park, 2006), studied the inhibition of copper corrosion in 3.0%

NaCl by N-phenyl-1,4-phenylenediamine (NPPD). They found that NPPD is a good mixed-type inhibitor for copper corrosion by strong adsorbing on copper surface, and the inhibition efficiencies increase in the order of oxygenated > aerated > de-aerated solution. Figure 10 shows the 2-amino-5-ethyl-1,3,4-thiadiazole as an inhibitor for copper corrosion in de-aerated, aerated, and oxygenated 3.0% NaCl solution was tested (Sherif and Park, 2006).

2-amino-5-ethyl-1,3,4-thiadiazole has high inhibition efficiency for copper corrosion because it is a heterocyclic compound containing a variety of donor atoms (Otmačić and Stupnišek-Lisac, 2003). The compounds having such a structure are capable of inhibiting copper corrosion with a high efficiency.

- Copper is widely used in heating and cooling systems. Such systems are cleaned by acid-pickling processes, using hydrochloric acid. Dafali et al. (Dafali, et al., 2000) have studied the effect of 2-mercapto-1-methylimidazole (MMI), as shown in Figure 11, on the copper corrosion behaviour in aerated 3% NaCl solution using electrochemical polarization method. It was observed that MMI acts through the formation of a film on the surface of the copper. The inhibition action of MMI on Cu-corrosion in 1M HCl was tested by Benali et al. (Benali, et al., 2007) and Larabi et al. (Larabi, et al., 2006) using weight loss measurements and electrochemical polarization method. Imidazole and p-tolyl-3-methylimidazole were also included for comparison.

The conclusions drawn from those studies were (Benali, Larabi, Traisnel, Gengembre and Harek, 2007, Larabi, Benali, Mekelleche and Harek, 2006):

- MMI inhibits the corrosion of copper in 1 M HCl, the percentage of inhibition increases with increasing inhibitor concentration.
- The inhibition is attributed to chemical adsorption of S-atom of the inhibitor molecules on copper surface and blocking its active sites.
- The percentage of inhibition efficiency of tested compounds decreases in the order:

MMI (87.5%) > TMI (54%) > Im (33%)

- The non-toxic imidazole derivatives (Figure 12) have low inhibiting effect for copper corrosion in sulfuric acid. The introduction of the functional groups to the imidazole ring (Figure 12-a) has improved its inhibiting properties. The best protection (93%) was obtained by adding a phenyl ring to the imidazole structure (Figure 12-c) (Lee, 2003).

Due to the currently imposed environmental requirements for eco-friendly corrosion inhibitors, there is a growing interest in the use of natural products such as leaves or seeds extract. Azadirachta indica leaves extract (AI), were reported to contain several thousands of compounds, which have complicated molecular structure, large molecular weight and significant number of oxygen atoms incorporated in the structure (Valek and Martinez, 2007). Generally, compounds containing oxygen, nitrogen, or sulfur have a tendency to act as good inhibitors in acid media. Hence, the AI extract is expected to have great ability for inhibitory action thorough oxygen active center.

Valek and Martinez (Valek and Martinez, 2007) reported that AI extract has a significantly better inhibitive properties than 1,2,3-benzotriazole (BTAH) on copper in chloride medium. Investigation of copper corrosion inhibition by AI, BTAH and (2-acetamino-5-mercapto-1,3,4 thiadiazole), AAMTDA (Figure 13) in sulfuric acid was performed using electrochemical polarization and weight loss measurements. AI leaves extract has shown excellent corrosion inhibition of copper corrosion in sulfuric acid. While AAMTDA revealed better inhibitory properties, but its ecological aspects and costs are of question. BTAH exhibited lesser inhibition efficiency of copper dissolution. It can be concluded that AI proposed as good, ecologically acceptable candidate for acid copper corrosion inhibition.

- Wang et al. (Wang, et al., 2014) employed Domperidone to reduce the corrosion of copper in 3.5 wt.% NaCl solution. Several techniques were used to study the inhibition efficiency including: weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). SEM and AFM confirmed that Domperidone is anodic inhibitor which adsorbs on the surface according to the Langmuir's isotherm. The maximum corrosion inhibition efficiency reached 94.2%.

- Finsgar and Merl (Finsgar and Merl, 2014) and Finsgar (Finsgar, 2013) studied the corrosion inhibition of copper in 3 wt.% NaCl solution using 2-Mercaptobenzoxazole, as shown in Figure 14. 2-Mercaptobenzoxazole forms a complex with copper forming a layer of 1.4 nm which acts as a mixed type inhibitor. The maximum inhibition efficiency was achieved

after 180 days of copper immersion in 2-Mercaptobenzoxazole. The authors attributed the long period for maximum inhibition efficiency to the time needed for 2-Mercaptobenzoxazole to form a stable complex with copper.

- From an environmental point of view Fallavena et al. (Fallavena, et al., 2006) studied the efficiency of caffeine (1,3,7-trimethylxanthine). Figure 15 shows the non-toxic copper corrosion inhibitor, it is used in aqueous solutions with potassium nitrate as supporting electrolyte in the absence and presence of chloride as aggressive ion. Corrosion inhibition capability of caffeine was confirmed by weight loss and potentiometry measurements. All results confirmed the ability of caffeine to inhibit the corrosion process of copper in aqueous potassium nitrate solution even in the presence of dissolved potassium chloride as an aggressive ion.

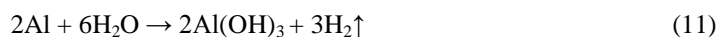
3.6.3 Corrosion inhibitor for Aluminum:

It is known that a strongly adherent passive film is developed on aluminum upon exposure to the atmosphere or aqueous solutions. This film is responsible for the corrosion resistance of aluminum in most environments. Hydrochloric acid solution is used for electrochemical etching of aluminum foil. A number of organic compounds have been described as aluminum corrosion inhibitors in hydrochloric acid solution. M.M. Hukovic et al. (Metikoš-Huković, et al., 2002) studied the inhibition properties of five substituted N-arylpyrroles on the corrosion of aluminum in 0.5 M hydrochloric acid solution:

- (A) 1-(2-methylphenyl)-2,5-dimethylpyrrole
- (B) 1-(2-fluorophenyl)-2,5-dimethylpyrrole
- (C) 1-(2-chlorophenyl)-2,5-dimethylpyrrole
- (D) 1-(2-iodophenyl)-2,5-dimethylpyrrole
- (E) 1-(2-fluorophenyl)-2,5-dimethylpyrrole-3-carbaldehyde

Using potentiodynamic and electrochemical measurements, it was found that the inhibition efficiency increased with increasing inhibitor concentration. The ability of N-arylpyrroles to inhibit hydrogen evolution was attributed to the adsorption of inhibitor molecules through their functional groups.

- For environmental protection, lanthanide compounds such as Ln Cl_3 have been used as corrosion inhibitors and as coating for AA5083 aluminum alloy. Aballe et al. (Aballe, et al., 2001) studied a mixture solutions of LaCl_3 and CeCl_3 in the corrosion protection of AA5083 (Al-Mg) alloy in NaCl solution. Ce/La binary solution showed a better performance than those containing solely LaCl_3 or CeCl_3 . The synergistic effect seems to exist when cerium and lanthamum ions act simultaneously as inhibitors. Lanthanide salts showed excellent performance as aluminum corrosion inhibitors which have a low toxicity, but they are very expensive.
- Aluminum pigments are used in metallic decorative topcoats whereas zinc pigments are used as anticorrosive pigments especially in primers. Both aluminum and zinc pigments react in aqueous alkaline media with the evolution of hydrogen



The evolution of hydrogen during these corrosion reactions may lead to dangerous pressure build up in containers. So, the investigation of non-toxic friendly corrosion inhibitors is necessary. Previous studies showed that corrosion inhibition of aluminum pigment in aqueous alkaline media by saccharides is possible (Müller, 2002, Müller and Fischer, 2006). The comparative investigation of the corrosion inhibiting effects of different saccharides on aluminum and zinc pigment in aqueous alkaline media was studied by Muller (Müller, 2002). Results have shown that hydrogen corrosion of aluminum pigment in aqueous alkaline media can be inhibited with addition of the reducing saccharides fructose and mannose as well as with addition of the reducing ascorbic acid.

- Researchers developed cheap and environmentally safe inhibitor for aluminum corrosion in the acidic solution. El-Etre (El-Etre, 2003) reported a successful use of vanillin as corrosion inhibitor for aluminum in high acidic solution. The aqueous extract of Opuntia plant stem was tested using weight loss and electrochemical measurements as corrosion inhibitor for aluminum in acidic solution. From the obtained results we can conclude that; Opuntia extract acts as good corrosion inhibitors for aluminum in acid solution and the inhibition efficiency increases with increasing extract

concentration. The Opuntia extract contains mainly polysaccharide, neutral carbohydrate-containing polymers and contains at least seven non-volatile acids (Haynes, 2012). The adsorption of these compounds leads to protect the metal surface from the aggressive attack of acidic media by synergistic effect.

- El-Dahan et al. (El Dahan, et al., 2006) employed the alcoholic extract of Capsicum annum, Citrus sinensis, Atropa belladonna, and achilla millefolium as inhibitors for aluminum corrosion in hydrochloric acid. The authors attributed the efficient inhibition of aluminum to the strong interaction between inhibitor molecule and Al surface.

4. CONCLUSION

- 1) Corrosion of industrial metals is one of the oldest problems that have ever challenged the industrial world.
- 2) There are several corrosion inhibition techniques.
- 3) Corrosion inhibitors, used in infinitesimal concentration could significantly retard the action of the corrosion elements.
- 4) The cost of corrosion is a measure of metal destroyed, the need for replacements, loss of time and deterioration of appearance.
- 5) Nowadays, most of the inhibitors used are long chain nitrogenous compounds.
- 6) Some of the standard organic inhibitors have had toxic effect on nature.
- 7) The extract of naturally occurring substances (such as; seeds, peels, fruit shells, leaves and stems of some plants) proved a good inhibition efficiency for metal corrosion in various media.
- 8) The natural extracts always contain many organic compounds (Amins, Alhaloids, Flavonoids, Tannins) which are improving the corrosion inhibition adsorption on the metal surface through synergistic effect.
- 9) The natural extracts named as eco-friendly corrosion inhibitor, because they are non-toxic compounds which are economical for large scale application.
- 10) The choice of corrosion inhibitor should be based on these consideration:
 - a) It could synthesize easily with high yield.
 - b) It could be prepared from relatively cheap materials.
 - c) It must possess multi-adsorption centers.
- 11) The higher inhibition efficiency is obtained by the presence of heteroatoms in molecule structure such as sulfur, nitrogen, and oxygen that make co-ordination bond with metal.
- 12) The inhibitors used must be chemically stable and provide high protective effect under the discussed condition;
- 13) The inhibition efficiency is a function of the system under consideration, for example water supply an inhibiting effect (IE) of 50% is adequate, while for pickling an inhibiting effect (IE) higher than 87% is required.

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