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A review: COMPARATIVE STUDY OF CORROSION INHIBITION OF METALS BY USING INHIBITORS AND INHIBITORS ASSEMBLED ON NANO PARTICLES IN ACIDIC MEDIA

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ABSTRACT:

There is an intensive effort underway to develop new plant origin corrosion inhibitors for metal subjected to various environmental conditions. These efforts have been motivated by the desire to replace toxic inhibitors used for mitigation of corrosion of various metals and alloys in aqueous solutions. Green inhibitors represent a class of interesting source of compounds currently being explored for use in metal corrosion protection in most systems, as possible replacement of toxic synthetic inhibitors. In this review article, research results on the use of eco-friendly corrosion inhibitors have been summarized. A general introduction to the topic of corrosion mitigation by inhibitors is presented followed by extensive literature survey on the use of natural inhibitors for corrosion control of metals and alloys in different corrosive media. This reports an overview of the consumption of green inhibitors to shield metals from corrosion as well as the current research on utilization of nanoparticles in inhibitors molecules. Nanoparticles has the large surface to volume ratio, due to large surface area it has tendency to form layer on the metal surfaces thereby, increasing the efficiency of the inhibitor by incorporating nanoparticles when compared with alone. Further, in most of the cases, the inhibition efficiency can be raised with the increase in temperature and time by treating green inhibitor with nanoparticles for the corrosion of metals in aggressive media.

1. Basic aspects of corrosion

Corrosion may be defined as a destructive phenomena, chemical or electrochemical, which can attack any metal or alloy through reaction by the surrounding environment and in extreme cases may cause structural failure. Corrosion can be also defined as the deterioration of material by reaction to its environment. The corrosion occurs because of the natural tendency for most metals to return to their natural state **[1-3]**.

The importance of corrosion studies is two folds. The first is economic, including the reduction of material losses resulting from the wasting away or sudden failure of piping, tanks, metal components of machines, ships, hulls, marine, structures…etc. Corrosion affects all area of the economy, from the integrated circuit to the bridge made of reinforced concrete. The cost of corrosion has been estimated to represent 4% of the gross national product. Even for all country like Switzerland, this number represents several billion Euros per year. The second is conservation, applied primarily to metal resources, the world’s supply of which is limited, and the wastage of which includes corresponding losses of energy and water resources accompanying the production and fabrication of metal structures **[4]**.

1.1 Factors that affect the rate of corrosion

Five factors do play an important role in determining corrosion rates **[5]**,

1. **Oxygen**: Like water, oxygen increases the rate of corrosion. Corrosion can take place in an oxygen-deficient environment, but the rate of the corrosion reaction (and destruction of the metal) is generally much slower. In immersed conditions, if an electrolyte is in contact with one area of metal containing more oxygen than the electrolyte in contact with another area of the metal, the higher oxygen-concentration area is cathodic relative to the remaining surface. An oxygen concentration cell then forms, which results in rapid corrosion.
2. **Temperature**: Corrosion reactions are electrochemical in nature and usually accelerate d with increasing temperature; therefore, corrosion proceeds faster in warmer environments than in cooler ones.
3. **Chemical Salts**: Chemical salts increase the rate of corrosion by increasing the efficiency (conductivity) of the electrolyte. The most common chemical salt is sodium chloride, a major element of seawater. Sodium chloride deposited on atmospherically exposed surfaces also acts as a hygroscopic material (i.e., it extracts moisture from the air), which then increases the corrosion in non-immersed areas.
4. **Humidity**: Humidity and time-of-wetness play a large role in promoting and accelerating corrosion rates. Time-of-wetness refers to the length of time an atmospherically exposed

substrate has sufficient moisture to support the corrosion process. The wetter the environment, the more corrosion is likely to occur.

Pollutants: Acid rain (a chemical by-product from manufacturing and processing plants), and chlorides (in coastal areas) promote corrosion. Acid gases, such as carbon dioxide, can also dissolve in a film of moisture in contact with the metal.

1.2 Forms of corrosion

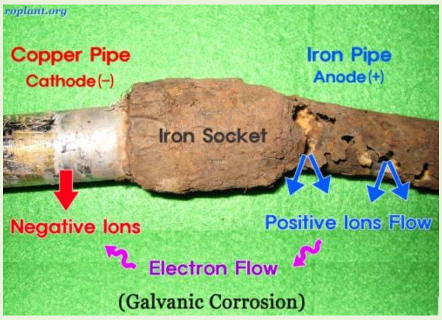
Different corrosion processes occur depending on the local environment of surface.

1. General corrosion or Uniform attack

This is the most common type in which the corrosion is uniform over the entire exposed surface. An example of this is water tank exposed to the atmosphere.

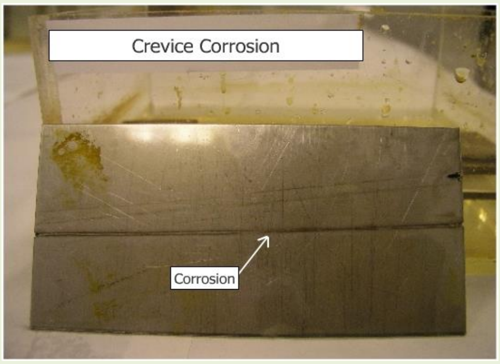
2. Galvanic corrosion

It is an accelerated electrochemical action due to two different metals being in electrical contact and exposed to an electrolyte. Heat exchanger failure in which aluminum tubes are supported by a perforated steel sheet is an example of this type of corrosion.



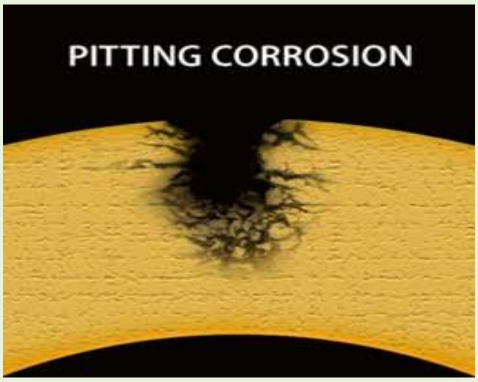
3. Crevice corrosion

This type of corrosion takes place when only one metal is in contact with different concentrations of the environment. Rectangular metal containers and reverted lap joints offer the possibility for this type of corrosion.



4. Pitting or Localized attack

It is one of the most destructive and insidious forms of corrosion. It is a highly localized corrosion; the attack is being limited to extremely small areas. An example is the corrosion of stainless steels in chloride solutions.



5. Stress corrosion

It is the spontaneous cracking resulting from the combined effect of prolonged stress and corrosive attack. Caustic embrittlement of boilers provides an example for this type of corrosion.

6. Erosion – corrosion

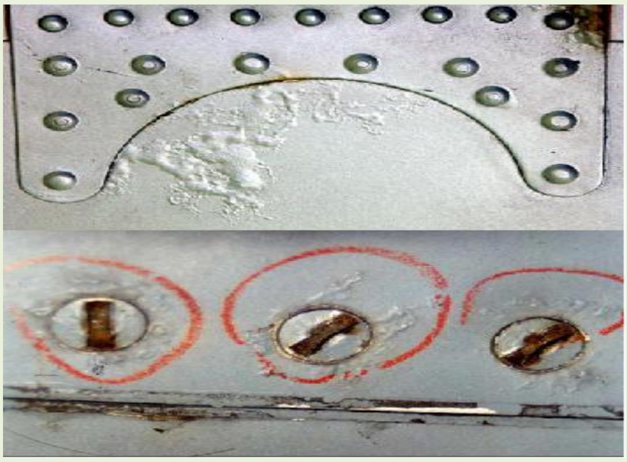
It is the acceleration in the rate of attack of a metal because of the relative movement between a corrosive fluid and the metal surface. Heat exchanger tubes with water movement undergo this type of corrosion.

7. Fretting corrosion

It is a case of deterioration resulting from repetitive rumbling at the interface between two surfaces in a corrosive environment. It is found in aircraft engine parts.

8. Filiform corrosion

It is a special type of rusting which occurs on certain metals under protective films like paints and is characterized by a thread like growth **[6]**.



1.3 Corrosion inhibitors

The protection of metals or alloys against corrosion can be achieved either by special treatment of the medium to depress its aggressiveness or by introducing into it small amounts of special substances called corrosion inhibitors. Inhibitors are classified according to their action (as anodic, cathodic and mixed inhibitors) and according to their mechanism of action (as hydrogen evolution, scavengers, vapour-phase and adsorption inhibitors).

(1) Anodic inhibitors:

Anodic inhibitors that cause a large shift in the corrosion potential are called passivating inhibitors. They are also called dangerous inhibitors because, if used in insufficient concentration, they cause pitting and sometimes an increase in corrosion rate. There are two types of passivating inhibitors: oxidizing anions such as chromate, nitrite, that can passivate steel in the absence of oxygen and the non oxidizing ions, such as phosphate, tungstate, and molybdate, which require the presence of oxygen in order to passivate steel. However, with careful control passivating inhibitors are frequently used because they are very effective in sufficient quantities **[7]**.

Passivation by inhibitors is more difficult at higher temperatures, higher salt concentration, lower pH, and lower dissolved oxygen concentrations. Nonoxidizing passivators require the presence of oxygen to cause passivation. They do not inhibit corrosion in the absence of oxygen. They apparently function by promoting the adsorption of oxygen on the anodes, thereby causing polarization onto the passive region. Nonoxidizing passivators are also dangerous when used in insufficient amount because the oxygen required for passivation is a good cathodic depolarizer.

(2) Cathodic inhibitors:

Cathodic inhibitors either slow the cathodic reaction itself, or they selectively precipitate on cathodic areas to increase circuit resistance and restrict diffusion of reducible species to the cathodes.

The cathodic reaction is often of reduction of hydrogen ions from hydrogen gas. Some cathodic inhibitors make the discharge of hydrogen gas more difficult, and they are said to increase the hydrogen overpotential. Compounds of arsenic and antimony are example of this type of inhibitors that are often used in acids or in systems where oxygen is excluded. Another possible cathodic reaction is the reduction of oxygen. The inhibitors for this cathodic reaction are different forms from those mentioned for the more acidic systems.

Other cathodic inhibitors use the increase in alkalinity at cathodic sites to precipitate insoluble compounds on the surface. The cathodic reaction, hydrogen ions, and / or oxygen reduction causes the environment immediately adjacent to the cathodes to become alkaline. Therefore, ions such as calcium, zinc, or magnesium may be precipitated as oxides to form a protective layer on the metal, many natural waters are self inhibiting due to the deposition of a scale on metals by precipitation of naturally occurring ions.

Inhibition by polarization of the cathodic reaction can be achieved in several ways. The three main categories of inhibitors that affect cathodic reactions are cathodic poisons, cathodic precipitates, and oxygen scavengers **[7]**.

(3) Mixed inhibitors:

About 80% of inhibitors are organic compounds that cannot be designated specifically as anodic or cathodic and are known as mixed inhibitors. The effectiveness of organic inhibitors is related to the extent to which they adsorb and cover the metal surface. Adsorption depends on the structure of the inhibitor, on the surface charge of the metal, and on the type of electrolyte. Mixed inhibitors protect the metal in three possible ways: physical adsorption, chemisorption and film formation. Physical (or electrostatic) adsorption is a result of electrostatic attraction between the inhibitor and the metal surface. When the metal surface is positively charged, adsorption of negatively charged (anionic) inhibitors is facilitated. Positively charged molecules acting in combination with a negatively charged intermediate can inhibit a positively charged metal. Anions, such as halide ions, in solution adsorb on the positively charged metal surface, and organic cations subsequently adsorb on the dipole. Corrosion of iron in sulphuric acid containing chloride ions is inhibited by quaternary ammonium cations through this synergistic effect. Physically adsorbed inhibitors interact rapidly, but they are also easily removed from the surface. Increase in temperature generally facilitates desorption of physically adsorbed inhibitor molecules. The most effective inhibitors are those that chemically adsorb (chemisorb), a process that involves charge sharing or charge transfer between the inhibitor molecules and the metal surface **[8]**.

2 Nanotechnology

Nanotechnology literally means “any technology that performed on a nanoscale” Nanotechnology literally means “any technology that performed on a nanoscale” **[9]**. Nanotechnology has proved to be a boon for semiconductor technology **[10]**, information technology **[11]**, cellular and molecular biology **[12]**, material technology **[13]**, bio-technology **[14]**, energy production and storage **[15,16]**, manufacturing **[17]**, instrumentation **[17]**, environmental application and security **[18]**, nanoelectronics **[19]**, medicine and health care **[20]**, genomics **[21]** robotics **[22]**, communications **[23]** etc. Nanoparticles are measured as a discovery of modern science because of its higher surface to volume ratio with decreasing in the size of the particles. Various transition metal oxides nanoparticles have attracted material science in many areas, ranging from bioengineering to automotive engineering. Many properties of nanometer-sized material proved superior than those of bulk materials **[24]** Nanoparticles draw much attention due to its broad range of high technology application such as in smart windows, electrochemical super capacitor, as a transparent p-type semiconducting layer with a wide band gap and as an antiferromagnetic thin film. It has been extensively used as sensors, anodes for ion batteries, electro chromic displays, drugs, and catalysts **[25]**.

3 Literature Review

El-Gaber et al. **[26]** studied the corrosion inhibition of zinc in 0.1M HCl in presence and absence of some hydrazide derivatives which have been investigated using mass-loss and polarization techniques. The obtained Results showed that the inhibition efficiency increased with increasing of the concentration of the additives and decreased with the increasing of temperature.

Fouda et al. **[27]** studied the inhibition of the corrosion of zinc in 0.4 M HCl by organic inhibitors which have been investigated at 30 °C using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) measurements. The obtained Results showed that these investigated compounds are good inhibitors and their inhibition efficiencies (%I) increase with the increasing of inhibitor concentration and with rising temperature.

Khulood Al-Saadie **[28]** studied the inhibition action of thiourea and guanidine on the corrosion behavior of zinc in 1M HCl which have been investigated using weight loss measurement and by following the zinc ions concentration in solution after several times by atomic absorption spectroscopy (AAS). The two inhibitors reduced the corrosion rate of zinc and the protection efficiency ranging between (10.6 -59.8) at low temperature (285, 299) K and the two inhibitors showed almost similar protection at (318, 328) K.

Shah et al. **[29]** investigated the performance of triethylenetetraminetribenzylidene (TTTB) and triethylenetetramine-trisalicylidene (TTTS) as corrosion inhibitors for zinc in hydrochloric acid. At lower concentrations, both inhibitors accelerate the attack but the corrosion inhibited at higher concentrations, e.g., 96– 100% with 1.0% concentration in 0.5 M and 1.0 M HCl. It has been found that the efficiency of TTTB decreases while the efficiency of TTTS remains almost constant (99.7%) up to 120 minutes at the temperature range 35– 65 ºC. The activation energies are higher in an inhibited than in plain acid with both inhibitors.

Lin Wang et al. **[30]** studied the inhibiting action of 2- mercapto benzimidazole on the corrosion of zinc in phosphoric acid (H_3PO_4) solution by using weight loss and polarization methods. This study revealed that the inhibitor is effective for the inhibition of zinc in H_3PO_4 solution and retards the anodic and cathodic corrosion reactions with emphasis on the former.

James and Akaranta **[31]** investigated the inhibition of the corrosion of zinc by acetone extract of red onion skin in hydrochloric acid solutions by using weight loss method. The results of the study revealed that different concentrations of the extract inhibit zinc corrosion. Inhibition efficiency of the extract was found to vary with concentration and temperature.

Shanbhag et al. **[32]** studied the corrosion inhibition characteristics of acetyl coumarine (AC), bromo acetyl coumarine (BAC) and thiazole derivatives (BTMQ and BTCQ) on the corrosion of zinc in 0.1 M HCl solution which were investigated by weight loss, potentiodynamic polarization and impedance techniques. The inhibition efficiency increased with increasing in inhibitor concentration up to 5×10^{-4} M, then gave almost the same inhibition efficiency.

Shylesha et al. **[33]** studied corrosion inhibition effect of 2- [4-(methylthio) phenyl] acetohydrazide (HYD) and 5-[4- (methylthio)benzyl]-4H-1,2,4-triazole-3- thiol (TRD) on zinc in 0.1 M HCl was studied by using mass loss, polarization and electrochemical impedance spectroscopy (EIS) techniques. Effect of concentration and temperature was evaluated by mass loss method. Results indicated that the compounds are efficient, mixed type but predominantly anodic in nature.

Yanardağet et al. **[34]** investigated the effect of benzotriazole (BTA), tolytriazole (TTA), benzo (c) cinnoline (E1), benzo (c) cinnoline 5-oxy (E2), 2,2-dinitro benzidyn (E4) and 2-Aminobenzo (c) cinnoline (E5), on the corrosion of pure zinc metal in four different aqueous solutions. The corrosion rates of the species were determined by electrochemical current density-potential curves.

Khulood AL-Saadie et al. **[35]** studied the corrosion behavior of Zn in 1 M HCl solution using various concentration of Urea range ($10^{-3} \rightarrow 5x10^{-3}$) M at temperature range (285-328) K was investigated. The corrosion inhibitive action of Urea on zinc metal was studied using weight loss measurement and analytical titration of the amounts of dissolved zinc in acidic solution in presence and absence of Urea , the results showed that Urea caused to protection efficiency reach to 88% when (50) mM Urea concentration used.

Vashi et al. **[36]** studied the corrosion behaviour for zinc in (HNO_3 + H_2SO_4) binary acid mixture containing ethanolamines. It has been found that corrosion rate increases with concentration of acid and temperature. At constant acid concentration, the inhibition efficiency of ethanolamine increases with the inhibitor concentration. Value of ΔGa increased and inhibition decreases with temperature. The mode of inhibition action appears to be chemisorption.

Vashi et al. **[37]** studied the corrosion of zinc in nitric acid containing nitro aniline at different acid concentration, inhibitor concentration and temperature. In acid, corrosion increases with increasing concentration of acid and with temperature. At constant acid concentration, the inhibition efficiency (I.E.) of nitro anilines increased with concentration. At constant inhibitor concentration, the I.E. increase with the concentration of acid.

Abdullah **[38]** studied the effect of some ethoxylated fatty alcohols, with different numbers of ethylene oxide units, on the corrosion of zinc in 0.5 M HCl using weight loss and polarization measurements. The inhibition efficiency has been found to increase with increasing concentration, number of ethylene oxide units per molecule and with decreasing the temperature.

Hong Ju and Yan Li **[39]** investigated the effect of Nicotinic acid as anon toxic corrosion inhibitor for hot dipped Zn and Zn-AL alloy coating on steels in diluted hydrochloric acid. The result of weight loss test and electrochemical measurement indicated that inhibition efficiency (%I) increases with inhibitor concentration, and the highest inhibition efficiency was up to 96.7%.

Hisham et al. **[40]** studied the effect of some organic additives as corrosion inhibitors for zinc in acetic acid media. The inhibition effect of some dialkylene dithiophosphate derivatives on the corrosion of zinc in 2M CH_3COOH solution has been investigated using weight loss, pH measurement and electrochemical measurements. The percentage inhibition efficiency was found to increase with increasing concentration of inhibitor and with decreasing temperature.

The adsorption of these inhibitors on the zinc surface obeys Langmuir isotherm. Some activated thermodynamic parameters were calculated. The variations of conductivity with time for different concentrations of these organic inhibitors revealed an inversely relationship.

Orubite et al. **[41]** explore the corrosion inhibition of zinc in hydrochloric acid by extract of Nypa Fruticans Wurmb was studied using weight loss techniques Maximum inhibition efficiency (and surface coverage) is obtained at an optimum concentration. However increase in temperature decreases the inhibition efficiency. The inhibition action of Nypa Fruticans Wurmb extract compared closely to that of 1,5-Diphenyl Carbazone (DPC).Optimum inhibition efficiency for zinc in the presence of Nypa Fruticans Wurmb extract is 36.43% and 40.70% with DPC. The phenomenon of physical adsorption has been proposed from the activation energy values (19.33kJ.mol^{-1} and 21.11kJ.mol^{-1}) with Nypa Fruticans Wurmb extract and DPC respectively. A first order kinetics has been deduced from the kinetic treatment of the results.

Ganesha et al. **[42]** investigate the zinc metal surface is chemically modified by newly synthesized Schiff's bases and its corrosion protection was investigated. The influence of increasing concentration of Schiff's bases on modification of zinc surface and immersion time in treatment bath are investigated and optimized for maximum corrosion protection efficiency. The electrochemical studies of treated zinc specimens are performed in aqueous acid solution using galvanostatic polarization technique. The treated zinc samples show good corrosion resistance. The recorded electrochemical data of chemically treated samples indicate a basic modification of the zinc surface. The protection efficiency of organic layer formed on zinc surface is tested by varying the acid concentration and temperature of the corrosive medium. The corrosion protection efficiency increases with the concentration of Schiff's bases and immersion time. This is due to a strong interaction between zinc and the organic molecules, which results in the formation of a protective layer. This layer prevents the contact of aggressive medium with the zinc surface. The surface modification is confirmed by the scanning electron microscopy images. The interaction between metal atoms and Schiff's bases is also established by IR studies.

Rajappa et al. **[43]** studied the surface treatment of zinc and its corrosion inhibition using a product formed in the reaction between benzaldehyde and thiosemicarbozide (BTSC). The corrosion behavior of chemically treated zinc surface was investigated in aqueous chloride-sulphate medium using galvanostatic polarization technique. Zinc samples treated in BTSC solution exhibited good corrosion resistance. The measured electrochemical data indicated a basic modification of the cathode reaction during corrosion of treated zinc. The corrosion protection may be explained on the basis of adsorption and formation of BTSC film on zinc surface. The film was binding strongly to the metal surface through nitrogen and sulphur atoms of the product. The formation of film on the zinc surface was established by surface analysis techniques such as scanning electron microscopy (SEM-EDS) and Fourier transform infrared spectroscopy (FTIR).

Emad et al. **[44]** studied the corrosion inhibition of zinc in 2.0 M HCl solutions at 30 ^{o}C using Furosemide as an inhibitor in concentrations of 100, 200, 300, 400 and 500 ppm. Furosemide exhibited excellent inhibition performance optimum concentration 300 ppm. In general, the acidic corrosion of Metals was reduced by the addition of an appropriate concentration, but our inhibitor has optimum concentration at 300 ppm. The inhibition efficiencies increased with inhibitor concentration until the optimum concentration, but were reduced proportionally with concentration higher than the optimum. The inhibition efficiencies obtained by using of weight loss method. Furosemide molecule showed that the highest %I.E. at optimum concentration of 300 ppm with the maximum θ. Based on the theoretical calculations, the low absolute reading of ΔE indicating that Furosemide molecule possessed a good %I.E. which in good agreement with the experimental study. Hence, further in depth study on surface morphology, influence of pH and etc parameters will carry out to explore the inhibition mechanism of Furosemide molecule.

Spinelli **[45]** studied the inhibitory action of Caffeic acid as a green corrosion inhibitor for mild steel. The inhibitor effect of the naturally occurring biological molecule caffeic acid on the corrosion of mild steel in 0.1 M H_2SO_4 was investigated by weight loss, potentiodynamic polarization, electrochemical impedance and Raman spectroscopy. The different techniques confirmed the adsorption of caffeic acid onto the mild steel surface and consequently the inhibition of the corrosion process. Caffeic acid acts by decreasing the available cathodic reaction area and modifying the activation energy of the anodic reaction.

The inhibition effect of Schiff base aniline-N-(p-methoxybenzylidene) (ANPMB) on the corrosion behavior of zinc in 0.5 M HCl was studied using galvanostatic polarization, electrochemical impedance spectroscopy (EIS) and weight loss method. The results showed that ANPMB is an excellent corrosion inhibitor for zinc in acidic medium. Inhibition efficiency increased with increase in the concentrations of ANPMB but decrease with rise in temperature. The adsorption of the inhibitor on the zinc surface is found to accord with Langmuir isotherm **[46]**.

Odoemelam et al. **[47]** studied inhibition of the corrosion of zinc in various concentrations (0.01 to 0.05 M) of H_2SO_4 was studied using weight loss and hydrogen evolution methods of monitoring corrosion. The results revealed that various concentrations of azithromycin (0.0001 to 0.0005 M) inhibited the corrosion of zinc in H_2SO_4 at different temperatures (303 to 333 K). The concentration of H_2SO_4 did not exert significant impact on the inhibition efficiency of azithromycin, but inhibition efficiencies were found to decrease with increase in the concentration of the inhibitor. Values of inhibition efficiency obtained from the weight loss measurements correlated strongly with those obtained from the hydrogen evolution measurements. The activation energies for the corrosion of zinc inhibited by azithromycin were higher than the values obtained for the blank. Thermodynamic data revealed that the adsorption of azithromycin on the surface of zinc was endothermic (values of enthalpies of adsorption were positive), spontaneous (values of free energies of adsorption were negative) and was consistent with the adsorption model of Langmuir.

The inhibiting action of aniline and its derivatives on the corrosion of copper in hydrochloric acid has been investigated by Henriquez et al. **[48]**, with emphasis on the role of substituents. With this purpose five different anilines were selected: aniline, p-chloroaniline, p-nitro aniline, p-methoxy, and p-methylaniline. A theoretical study using molecular mechanic and ab initio Hartree Fock methods, to model the adsorption of aniline on copper (100) showed results in good agreement with the experimental data. Aniline adsorbs parallel to the copper surface, showing no preference for a specific adsorption site. On the other hand, from ab initio Hartree Fock calculations, adsorption energy between 2 kcal/mol and 5 kcal/mol is obtained, which is close to the experimental value, confirming that the adsorption of aniline on the metal substrate is rather weak. In view of these results, the orientation of the aniline molecule with respect to the copper surface is considered to be the dominant effect. Mechanic molecular calculations were carried out using the Insight II, a comprehensive graphic molecular modeling program, to obtain configurations of minimum energy.

Titova **[49]** studied α-picoline and thiourea as corrosion inhibitors of zinc in hydrochloric acid. The inhibition efficiency of α-picoline decreases with increase in concentration of hydrochloric acid. Thiourea in general acts as stimulator of the corrosion of zinc in hydrochloric acid and this behavior increases with hydrochloric acid concentration.

Vahldieck **[50]** patented an inhibitor which is a by-product obtained in the synthesis of 2-methyl-5-ethyl pyridine from paraldehyde or other lower aliphatic aldehyde with ammonia. This inhibitor prevents corrosion of zinc in 7 to 10% hydrochloric acid at 80°C.

An Indian Patent by Rajgopalan et. al. **[51]** recommends the use of a mixture containing alkalihalide, a heterocyclic compound such as pyridine, quinoline or piperidine and a glucoside such as tannin or vegetable gum to inhibit the corrosion of zinc in hydrochloric acid.

Antropov and co-workers **[52]** investigated the inhibiting effect of thiourea derivatives (KPI-2 and KPI-4) on the corrosion of zinc in 0.1N to 1.0N hydrochloric acid saturated with hydrogen sulphide at 10°-90°C. Both these inhibitors inhibit the corrosion of zinc at room temperature as well as at elevated temperatures. The efficiency of the above inhibitors increases with the acid concentration. The inhibiting effect of these inhibitors increases with their surface activity on mercury as revealed by electro capillary measurements on mercury.

Subramanyan and Ramkrishnaih **[53]** studied the influence of alkaloids such as ephedrine, narcotine, papavarine, brucine and strychnine on the corrosion of zinc in hydrochloric and sulphuric acid. Of these alkaloids the efficiency of papaverine as an inhibitor was found to be highest both in hydrochloric and sulphuric acid. Papavarine brings about considerable cathodic polarization both in hydrochloric and sulphuric acid.

In sulphuric acid the corrosion potential of zinc shifts in positive direction in presence of above alkaloids; whereas in hydrochloric acid no significant change in corrosion potential was observed.

Clark **[54]** patented a synergistic mixture of an alkynylcycloalkanol (e.g.,ethynylcyclohexanol, propenylcyclohexanol, ethyenylcyclopentanol) and a N,Ndicycloalkylthiourea (e.g. N,N-dicyclohexylthiourea) to protect zinc from hydrochloric acid attack during cleaning corroded zinc surfaces.

Shams El Din **[55]** mentioned that thiourea at low concentrations inhibits the corrosion of zinc in hydrochloric acid but it accelerates the corrosion at high concentrations of thiourea. In non-oxidizing media, thiourea is reduced to SH– which accelerates corrosion.

Petrenko **[56]** studied benzotriazole as an inhibitor of iron corrosion and stimulant of zinc dissolution in the removal of a coating of zinc from galvanized iron. He showed that benzotriazole increases the dissolution rate of zinc coating on iron in hydrochloric and sulphuric acids and exposed iron is protected. The stripping solution for zinc removal contained 30 to 75 g/l hydrochloric acid and 2 to 20 g/l benzotriazole. The zinc layer is removed from the iron surface within 6 to 14 minutes. Stimulating effect on zinc dissolution in sulphuric acid became apparent only at 1g benzotriazole per liter.

Mellerowicz **[57]** stated that the corrosion of zinc and iron in hydrochloric acid is inhibited by a mixture containing diphenylamine and hexamethylenetetramine. 0.2 kg of hexamethylenetetramine in 5 kg of water and 0.2 kg of diphenylamine in methyl alcohol was added to 1m^3 18% hydrochloric acid. In this mixture steel is protected to an extent of 99% and zinc is protected to an extent of 80%.

Ethanolic extract of the *Ananas sativum* leaves was investigated for slowing the corrosion rate of aluminium corrosion in hydrochloric acid solution by weight loss and hydrogen evolution methods. It was found that the plant extract retarded the acid induced corrosion of aluminium **[58]**.

Obot et al. **[59]** studied the corrosion inhibitive effect of *Aningeria robusta* extract for aluminium in 2M HCl solution and the influence of potassium iodide additive on the inhibition efficiency using hydrogen evolution method at 30˚C and 60˚C. Inhibition efficiency followed the standard order of increment with increase in concentration of inhibitor. However, with increase in temperature inhibition efficiency was found to increase. On the other hand, inhibition efficiency synergistically increased on addition of potassium iodide but decreased with increase in temperature. The mechanism of chemical adsorption was proposed for the *Aningeria robusta* extract and physical adsorption for the extract-iodide mixture.

The inhibiting action of *Piper longum* seed extract was investigated as the corrosion inhibitor of aluminium in 1M NaOH solution. The results revealed that P. longum extract was an effective inhibitor **[60]**.

Inhibitive properties of *Melia azedarach L.* leaves and *Datura metel* were investigated to protect aluminium in 2M and 1M HCl solution medium respectively **[61,62]**. The study showed that both the inhibitors were highly efficient with inhibition efficiency of 86% and 90% for leaves and *Datura metel* respectively.

Fabienne et al. **[63]** studied that *Mansoa alliaceae* is a good inhibitor of corrosion for zinc in sodium chloride solution. The polarization study showed *Mansoa alliaceae* is a mixed-type inhibitor. The impedance study presented two phenomena included a charge-transfer and a passive layer. The two methods used to calculate the CPE parameters showed the same trend. The adsorption behavior of studied extract plant follows the Langmuir's adsorption isotherm theory. Phytochemical tests reveal the presence of many families like alkaloids, saponins, flavonoids, quinons, triterpens and coumarins. The study of the different families presents in the crude extract show that the families have the same behavior as the crude extract. Nevertheless, the inhibition behavior of the crude extract is due to the presence of flavonoids family in the crude extract.

Obot et al. **[64]** developed a simple, novel, green, sunlight mediated and economically feasible approach for the synthesis of silver nanoparticles (AgNPs) using a bio-derived product-honey. AgNPs was characterized using UV-Vis absorption spectrophotometer. An intense surface plasmon resonance band at 450 nm in the UV–visible spectrum clearly revealed the formation of the silver nanoparticles. The effect of the synthesized nanoparticles on the corrosion of mild steel in 0.5 M HCl was studied by electrochemical methods. The experimental results suggest that the silver nanoparticle from honey is an effective corrosion inhibitor for mild steel.

Chinweuba **[65]** Investigated corrosion efficiency of *Allium cepa* extract on the corrosion of mild steel and zinc in 2.0 M H_2SO_4 solution was carried out. The effectiveness of using *Allium cepa* extracts as corrosion inhibitor was characterized in terns of metal weight loss, corrosion rate and inhibition efficiency. The results showed that as the concentration of *Allium cepa* extract increases the rate of corrosion of the two metals decreases. The inhibition efficiency was also found to increase with increase in concentration of the extract. The inhibition efficiency increases up to a maximum of 97.7% for mild steel and 89.1% for zinc in 2.0M H_2SO_4 which was encouraging. The results confirmed that *Allium cepa* extract could serve as a good corrosion inhibitor for both metals in acidic media.

Ladha et al. **[66]** investigated effect of cumin extract as corrosion inhibitor for pure Aluminium in 1N HCl has been investigated by using Weight loss, Galvanostatic polarization and electrochemical impedance spectroscopy (EIS) techniques. The results obtained reveal that inhibition efficiency increases with increase in concentration of inhibitors but decreases with increase in temperature. The value of apparent activation energy shows that the cumin extract acts as a good inhibitor for pure Aluminium in acid medium. The values of free energy of adsorption and heat of adsorption show that the adsorption of cumin extract on Aluminium obeys mixed adsorption and exothermic in nature. Thermodynamic consideration shows that adsorption of cumin extract follows Langmuir Adsorption isotherm. The Galvanostatic polarization measurement indicates that the inhibitor is of mixed type. Electrochemical impedance study results are in good agreement with weight loss and Galvanostatic polarization studies.

The influence of a natural extract of fenugreek on the corrosion of steel in 1 M HCl has been studied by weight loss, polarisation and EIS measurements. Results obtained show that the natural substance inhibits the corrosion process. It acts on the cathodic domain without modifying the reduction mechanism. The inhibition efficiency increases with fenugreek concentration to attain 94% at extract of 10 g/L of fenugreek at temperatures between 308 and 353K. It is an efficient inhibitor. The effect of temperature on the corrosion behaviour of steel indicated that inhibition efficiency is temperatureindependent. The activation energy of adsorption is determined **[67]**.

The synthesized polymeric surfactant and its nanostructure with the prepared silver nanoparticles were examined as non-toxic corrosion inhibitors for carbon steel in 1 M HCl solution using weight loss and potentiodynamic polarization techniques. The results show that the value of the percentage inhibition efficiency (I.E %) obtained by poly 12-(3-amino phenoxy) dodecane-1-thiol surfactant self assembled on silver nanoparticles is better than that obtained by poly 12-(3-amino phenoxy) dodecane-1-thiol surfactant only. Polarization data indicate that the selected additives act as mixed type inhibitors. The slopes of the cathodic and anodic Tafel lines (bc and ba) are approximately constant and independent of the inhibitor concentration. The formation of a protective film was confirmed by the energy dispersive X-ray analysis (EDX) technique **[68]**.

Ayman et al. **[69]** prepared coated silver nanoparticles to protect carbon steel alloys from aqueous acidic corrosive media. In this respect, Ag nanoparticles colloid solutions were produced through reducing $AgNO_3$ separately with trisodium citrate in an aqueous solution or in the presence of stabilizer such as poly(ethylene glycol)thiol and poly(vinyl pyrrolidone). The morphology of the modified silver nanoparticles was investigated by TEM and DLS.UV-Vis absorption spectrum was used to study the effect of HCl on the stability of the dispersed silver nanoparticles. The corrosion inhibition efficiency of the poly (ethylene glycol) thiol, the self-assembled monolayers of Ag nanoparticles, was determined by polarization method and electrochemical impedance spectroscopy (EIS). Polarization curves indicated that the coated silver poly (ethylene glycol) thiol acted as a mixed type inhibitor. The data of inhibition efficiencies obtained measured by polarization measurements are in good agreement with those obtained with electrochemical impedance.

Ayman et al. **[70]** developed nontoxic effective corrosion inhibitors for metallic substrates are an issue of great importance for protection of metal alloys and components. Surface properties of new stabilized magnetic nanoparticle (MNP) colloids coated with Myrrh gum were investigated. The natural product Myrrh gum was used as capping agent to produce highly dispersed coated magnetite nanoparticles. The structure and morphology of the magnetic nanogel were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and ultrasizer. Drop shape analyzer was used to examine the surface properties of the produced magnetite nanoparticles. The corrosion inhibition efficiencies of aqueous solutions of Myrrh and Myrrh capped magnetite for steel in 1M HCl solution have been investigated at different concentrations of the inhibitor using potentiodynamic polarization and electrochemical impedance spectroscopy measurements. The results showed that corrosion resistance increased by increasing the inhibitor concentration and inhibition efficiencies up to 91% can be obtained. Polarization curves revealed that this compound acts as mixed type inhibitor The inhibition efficiency calculated from these techniques are in reasonably good agreement.

Tedim et al. **[71]** synthesized layered double hydroxides (LDHs) nanocontainers loaded with different corrosion inhibitors (vanadate, phosphate, and 2-mercaptobenzothiazolate) and the characterization of the resulting pigments by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The anticorrosion activity of these nanocontainers with respect to aluminium alloy AA2024 was investigated by electrochemical impedance spectroscopy (EIS). The bare metallic substrates were immersed in dispersions of nanocontainers in sodium chloride solution and tested to understand the inhibition mechanisms and efficiency. The nanocontainers were also incorporated into commercial coatings used for aeronautical applications to study the active corrosion protection properties in systems of industrial relevance. The results show that an enhancement of the active protection effect can be reached when nanocontainers loaded with different inhibitors are combined in the same protective coating system.

Xianming et al.**[72]** synthesized Homogeneous epoxy coatings containing nanoparticles of SiO_2, Zn, Fe_2O_3 and halloysite clay on steel substrates by room-temperature curing of a fully mixed epoxy slurry diluted by acetone The effect of incorporating various nanoparticles on the corrosion resistance of epoxy-coated steel was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy. The electrochemical monitoring of the coated steel over 28 days of immersion in both 0.3 wt.% and 3 wt.% NaCl solutions suggested the beneficial role of nanoparticles in significantly improving the corrosion resistance of the coated steel, with the Fe_2O_3 and halloysite clay nanoparticles being the best. The SiO_2 nanoparticles were found to significantly improve the microstructure of the coating matrix and thus enhanced both the anticorrosive performance and Young's modulus of the epoxy coating. In addition to enhancing the coating barrier performance, at least another mechanism was at work to account for the role of the nanoparticles in improving the anticorrosive performance of these epoxy coatings.

Vidhya et al. **[73]** investigated the leaf-extract of solanum nigrum by weight-loss method and potentio-dynamic polarization technique in carbon steel to study the corrosion inhibition. The antioxidant property of the leaf-extract was exploited for synthesis of gold nanoparticles (GNPs). Excellent results were obtained when the leaf-extract was used to reduce $AuCl_4$. The formation of GNPs was rapid and within a few hours $AuCl_4$ was reduced into fine GNPs as evidenced by the appearance of deep ruby red colloidal dispersion. The UV–visible spectral analysis revealed the reduction of $AuCl_4$ and showed a peak at ~545 nm originating from the surface plasmon resonance of GNPs. The GNPs were characterized using SEM with energy-dispersive X-ray spectroscopy, powder X-ray diffraction and zeta potential analysis.

Nnabuk et al. **[74]** studied the inhibitive and adsorption properties of ethanol extract of Hibiscus sabdariffa calyx by using gravimetric, gasometric, thermometric, and Fourier transform infrared methods of monitoring corrosion. The results obtained indicated that ethanol extract of Hibiscus sabdariffa calyx is a good adsorption inhibitor for the corrosion of mild steel in HCl solutions. The adsorption of the inhibitor on mild steel surface is spontaneous and supports the Langmuir adsorption model. From the calculated values of free energy of adsorption, the activation energy, and the variation of inhibition efficiency with temperature, it can be concluded that the initial mechanism for the adsorption of ethanol extract of Hibiscus sabdariffa calyx on mild steel surface is physical adsorption.

Roohangiz et al. **[75]** investigated the effect of the cerium concentration on the morphology and anticorrosion performance of cerium–silane hybrid coatings on hot dip galvanized (HDG) steel substrates. 3-glycidoxypropyltrimethoxysilane (GPTMS) and bisphenol A (BPA) were employed as precursors to prepare the sol–gel based silane coating. Cerium nitrate hexahydrate was added to the silane coatings as dopant in five different concentrations. Very low and very high cerium concentrations deteriorate the corrosion inhibition in the sol-gel matrix and consequently, there is an optimum concentration of cerium nitrate. Accelerated salt spray testing showed that corrosion near an artificial scratch is blocked efficiently by high cerium nitrate contents, whereas uniform corrosion is inhibited effectively with comparatively low ceria contents. Electrochemical studies indicate a general beneficial effect of the incorporation of cerium nitrate, although the performance of the coated substrate depends on the cerium nitrate content. The results of electrochemical impedance spectroscopy (EIS) and electrochemical polarization confirmed that the corrosion resistance of the coatings initially increases and then decreases as the cerium concentration goes up. Optimal corrosion resistance was obtained at a cerium concentration of 0.05 M.

Poonam et al. **[76]** investigated the corrosion inhibition efficiency of p-methoxybenzylidene-4,4'-dimorpholine (p-MBDM) and p-MBDM assembled on Nickelous Oxide Nanoparticles (NiONPs) by using three techniques: weight loss, electrochemical impedance spectroscopy (EIS) and galvanostatic polarization. For the first time, p-MBDM and p-MBDM assembled on NiONPs are used as efficient inhibitors for Mild Steel (MS) in 2N Hydrochloric acid (HCl) solution. From weight loss measurement, the results shows that inhibition efficiency increases with increase in inhibitor concentration. Moreover, with increase in temperature,

the inhibition efficiency increases for p-MBDM assembled on NiONPs whereas it decreases for p-MBDM only. EIS spectra demonstrate that the charge transfer resistance in case of p-MBDM assembled on NiONPs is comparatively more than that of p-MBDM. Analysis of polarization data indicates that both the inhibitors act as mixed type inhibitors. The present study reveals that p-MBDM assembled on NiONPs is more efficient than p-MBDM alone. Additionally, the characterization of synthesized products were performed by proton nuclear magnetic resonance (1H NMR), transmission electron microscopy (TEM), dynamic light scateering (DLS), fourier transform infrared (FTIR) spectrscopy, powder x-ray diffraction (PXRD), and mass spectrometer (ESI-MS). Surface morphology of MS surface was further carried out by scanning electron microscopy (SEM) and
atomic force microscopy (AFM).

Eddy et al. **[77]** studied inhibitive and adsorption properties of albomycin as a green inhibitor for the corrosion of zinc in H_2SO_4 solutions were studied using weight loss and hydrogen evolution methods. The results obtained, indicate that albomycin is a good adsorption inhibitor for the corrosion of zinc in H_2SO_4 solution. The inhibition potentials of albomycin for the corrosion of zinc in H_2SO_4 solutions are attributed to the adsorption of the inhibitor on the surface of zinc and its inhibition efficiency increases with increase in the concentration of the inhibitor but decreases with increasing temperature.

Sviatlana et al. **[78]** developed new effective anticorrosion pre-treatments for metallic substrates are an issue of primer importance for corrosion science due to the fact that chromates must be banned. Removal of hexavalent chromium from the industry opens a significant gap in the corrosion protection technologies. This work presents a new approach for design of self-healing anticorrosion pre-treatments for the 2024 aluminium alloy. A TiOx porous layer obtained by templating synthesis was used as nanostructured reservoir for an organic corrosion inhibitor. This provides active corrosion protection and self-healing ability of the coating system. The reservoir is composed by titania nanoparticles which are self assembled forming a cellular network that replicates the surface structure of the etched alloy. The nanoreservoir layer was coated with a sol–gel based thin hybrid film to provide additional barrier effect. Electrochemical impedance spectroscopy and the scanning vibrating electrode technique were used to study the anticorrosion behavior of the developed pre-treatments. The novel pre-treatments show enhanced corrosion protection when compared with undoped sol–gel films, or films doped directly introducing inhibitor in the sol–gel matrix. The pre-treatment formed by the nanostructured titania reservoir layer covered with the hybrid film demonstrates well-defined self-healing ability leading to effective long-term active corrosion protection. The nanostructured porous character of the titania layer provides a very high effective surface area for the adsorption of the inhibitor. The developed surface formed by the self-assembled layer offers also the good adhesion between the oxide and the sol–gel film due to the high contact area between the two phases. Moreover, employment of the nanoreservoir approach avoids negative effects of the inhibitor on the stability of the sol–gel matrix and improves the release of the inhibitor in the places where defects start to develop. The present work shows for the first time, the promising ability on the use of nanostructured porous oxide films doped with organic inhibitors as effective environmental-friendly corrosion protective pre-treatments for metallic substrates.

Abdulwahab et al. **[79]** investigated the inhibition action of Avogadro natural oil on corrosion of mild steel in one molar hydrochloric acid solution by gravimetric and potentiodynamic polarization techniques. The surface morphology of as-corroded samples was assessed with high resolution scanning transmission electron microscopy equipped with energy dispersive spectroscopy (HR-STEM/EDS). From the results, the presence of Avogadro natural oil in the metal–acidic interface decreased the corrosion rate with all the exposure times. The inhibition efficiency (%IE) increases with the concentration of the inhibitor considered. Results obtained from gravimetric measurements indicate that the natural oil exhibited higher efficiencies of 93.26 % after 384 h of exposure time and 98.26 % recorded in the potentiodynamic polarization method, both at 4.5 g/v inhibitor addition.

Ibrahim et al. **[80]** studied that the inhibitive effect of potato peel extract (PPE) toward the corrosion of mild steel in 2M HCl solution has been investigated by weight loss and electrochemical techniques. Potato peels' extract was found to provide excellent inhibitive characteristics for mild steel in 2M HCl. Under test conditions it provided inhibition efficiencies as high as 85-90% with various PPE concentrations. Nyquist plots from Impedance data showed that upon increasing the PPE concentration, the charge transfer resistance increased and the doubled layer capacitance decreased. It was demonstrated that the potato peels' extract follows the Langmuir adsorption isotherm. According to the conducted electrochemical tests, it was found that the PPE behaves as a mixed type inhibitor.

Quraishi et al. **[81]** studied that corrosion inhibition of mild steel in hydrochloric solution by Black pepper extract (Piper nigrum fem. Piperaceae). The inhibition efficiencies determined by potentiodynamic polarization, EIS, and mass loss methods are in good agreement. The results obtained revealed that Black pepper extract was a good corrosion inhibitor for mild steel in hydrochloric acid medium and maximum inhibition efficiency (98%) was found at 120 ppm at 35 ºC. Potentiodynamic polarization measurements show that the extract acts as mixed-type inhibitor. EIS measurements indicate that the presence of extract increases the charge transfer resistance and shows that the inhibitive performance depends on adsorption of the inhibitor molecules on the metal surface. The value of ΔG ads indicated that the adsorption of alkaloid molecules present in extract was a spontaneous process and was typical of chemisorptions. The adsorption model obeys the Langmuir adsorption isotherm at 35ºC. The results shows that the Black pepper extract which mainly contains alkaloid 'Piperine' could serve as an excellent green inhibitor for corrosion of mild steel in acid solutions.

Srivastava and Srivastava **[82]** investigated the inhibition effect of tobacco, black pepper, castor seed, Acacia gum and lignin and found to be good corrosion inhibitors for steel in acidic media. Tobacco, lignin and black pepper were also found to be effective inhibitors for aluminium in acid medium. Further research on castor seed, black pepper and lignin on carbon steel corrosion in 5% HCl solution obtained 60 – 70% inhibition efficiency.

Saleh et al. **[83]** carried out an intensive study on the inhibition effect of aqueous extract of Opuntia ficus indica, Aloe eru leaves and peels of orange, mango and pomegranate fruits on the corrosion of steel, aluminium, zinc and copper in both HCl and H_2SO_4 acid solutions using gravimetric and polarization measurement techniques. From their investigations, it was reported that the mango peel extract was the most effective corrosion inhibitor for Al and Zn whereas pomegranate fruit shells extract was most suitable for Cu. It was further reported that, all the extracts were more efficiently corrosion inhibitors in HCl solution as compared to H_2SO_4 solution.

El-Etre and El-Tantawy **[84]** reported the inhibitive action of Ficus extract towards general and pitting corrosion of carbon steel, nickel and zinc in different aqueous media. The study was performed using weight loss measurements, potentiostatic and potentiodynamic polarization techniques. It was found that the presence of Ficus extract in the corrosive media (acidic, neutral or alkaline) decreased the corrosion rates of the three tested metals significantly. The extract was reported to contain friedelin, epifriedelanol, nitidol (a triterpene, $C_{10}H_{50}O$) and a mixture of two sterols.

Toshiyasu et al. **[85]** studied to prevent corrosion, aluminum nanoparticles were coated with a polyurethane polymer. The coverage of the polyurethane polymer was controlled from 0 to 100%, which changed the corrosion rate of the nanoparticles quantitatively. The surface of the polymer coating was investigated by Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM), and the corrosion resistance of the nanoparticles was estimated by a wet/dry corrosion test on a Pt plate with a NaCl solution. Both the corrosion and H_2 evolution reaction rates were quantitatively reduced by the mass% of polymer coating. In the case of the 10 mass% coated sample, there was no corrosion of Al nanoparticles. This fact suggested that the electrochemical reaction was suppressed by the polymer coating. Moreover, the reaction rate of Al nanoparticles was suppressed in proportion to the coverage percentage of the coating. It was found that the corrosion rate of Al nanoparticles could be quantitatively suppressed by the coverage percentage of the polymer coating.

Roohangiz et al. **[86]** investigated the morphological and electrochemical behavior of hot-dip galvanized (HDG) steel substrates that were pre-treated with 3-glycidoxypropyltrimethoxysilane (GPTMS) and bisphenol A (BPA) modified with cerium ion-activated CeO_2 nanoparticles. The morphology of the coatings before and after the corrosion test was examined using atomic force microscopy (AFM) and scanning electron microscopy (SEM). The results indicated the formation of a comparatively smooth, nanostructured surface, with a small heterogeneity in the coating thickness. Microscopic observations also confirmed that the integral surface morphology of the silane coating filled with activated CeO_2 nanoparticles was maintained after short-term corrosion tests (144 h). The corrosion behavior of the sol–gel coatings was investigated using natural salt spray tests, electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization tests. The results showed that the presence of the nanoparticles reinforced the barrier properties of the silane films, and a synergy seemed to be created between the activated nanoparticles and the cerium ions, reducing the corrosion activity.

Zamblau et al. **[87]** studied composite coatings of copper incorporating Al_2O_3 nanoparticles electrodeposited on carbon steel were obtained and characterized. By using electrochemical methods such as open circuit potential (ocp) measurements, polarization curves and electrochemical impedance spectroscopy, the corrosion behavior of the Al_2O_3-copper nanocomposite coatings was examined. The corrosion parameters determined from the polarization curves recorded in Na_2SO_4 solution (pH 3) indicate that the corrosion process on copper-Al_2O_3 composite surface is slower than on pure copper. The impedance spectra recorded at the ocp showed in all cases an increase of the polarization resistance in time, which may be explained by the development of corrosion products on the electrode surface. Using a (2RC) equivalent electrical circuit, the process parameters were estimated by non-linear regression calculations with a Simplex method. The Al_2O_3 particles embedded in the electroplated copper increase the polarization resistance and decrease the corrosion rates as compared with electrodeposited pure copper.

Montemor et al. **[88]** investigated the electrochemical behaviour of galvanised steel substrates pre-treated with bis-[triethoxysilylpropyl] tetrasulfide silane (BTESPT) solutions modified with SiO_2 or CeO_2 nanoparticles activated with cerium ions. The electrochemical behaviour of the pre-treated substrates was evaluated via electrochemical impedance spectroscopy in order to assess the role of the nanoparticles in the silane film resistance and capacitance. The ability of the Ce-activated nanoparticles to mitigate corrosion activity at the microscale level in artificial induced defects was studied via scanning vibrating electrode technique (SVET). Complementary studies were performed using potentiodynamic polarisation. The results show that the presence of nanoparticles reinforces the barrier properties of the silane films and that a synergy seems to be created between the activated nanoparticles and the cerium ions, reducing the corrosion activity. The addition of CeO_2 nanoparticles was more effective than the addition of SiO_2 nanoparticles

Singh et al. **[89]** studied that Piroxicam was found to be a good inhibitor for mild steel corrosion in acid medium by electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and gravimetric methods. The mechanism of adsorption inhibition and type of adsorption isotherm were proposed from the trend of inhibition efficiency with temperature, Ea and ΔGo ads. The inhibition efficiency of piroxicam decreased with temperature, which leads to an increase in activation energy of the corrosion process. Potentiodynamic polarization curves revealed that piroxicam is a mixed-type inhibitor. The experimental data showed a frequency distribution and therefore a modeling element with frequency dispersion 14olariza, a constant phase element (CPE) has been used.

Vasudha et al. **[90]** studied that the acid extract of Terminalia catappa leaves show good inhibition efficiency of mild steel in 1N HCl medium as revealed by both weight loss and polarization, FTIR and scanning electron microscope studies . Inhibition efficiency increases with inhibitor concentration and reaches a maximum of 97% for 2% v/v inhibitor concentration. From the polarization studies the inhibitor is found to be of a mixed type inhibiting both anodic and cathodic corrosion reactions. The mechanism of inhibition may be due to the adsorption of the plant constituents on the metal surface.

Sanusi et al. **[91]** investigated the corrosion effect of mild steel in orange juice using a weight loss technique. Weight loss was measured at two day intervals for the determination of corrosion rate effect. Results show that the corrosiveness of sweet orange juice on mild steel was mainly a function of its acidity. Packed orange juice with preservative was most corrosive followed by natural orange juice and water, respectively.

Nwabanne et al. **[92]** investigated that inhibitive, thermodynamics and adsorptive properties of ethanol extract of vernonia amygdalina for the corrosion of mild steel in 0.4M HNO3 solutions by using weight loss technique. The inhibition efficiency of the extract decreased as temperature and time of immersion increased, but increased with increase in concentration of extract. The inhibition capacity of this extract is attributed to the presence of saponnin, tannin, alkaloid, anthraquinone, flavanoid, cardiac glycosides in the extract. The heat of adsorption obtained ranged from -48.84 to -51.06KJ mol-1 indicating that adsorption of the inhibitor on surface of mild steel was exothermic, spontaneous and follows the mechanism of physical adsorption. Langmuir, Temkin, Frumkin and Flory-Huggins adsorption isotherms were found to confirm the adsorption characteristics of the inhibitor.

Satapathy et al. **[93]** investigated the effect of Justicia gendarussa extract (JGPE) on mild steel, with dimensions of 1.0 x 4.0 x 0.2 cm in 1M HCl medium. Weight loss and electrochemical methods were used in the investigation at room temperature and at 50-70°C. The maximum inhibition efficiency was found to be around 93% using mixed inhibitor type. A concentration of 150 ppm was added to the studied solution in order to achieve this efficiency at room temperature. The inhibitor used was considered a mixed type inhibitor since there was a change in both the cathodic and anodic Tafel constants. It can also be seen that the resistance of the charge transfer is increasing as the inhibitor is added to the corrosive media. This indicates a decrease in the current transferred and the corrosion occurring. It was found that adsorption obeys Langmuir isotherm. An increase in the activation energy of the corrosion process in presence of the green inhibitor indicated a physical adsorption is occurring.

Dananjaya et al. **[94]** studied that Lawsone , 2-hydroxy-1,4-naphthoquinone, the main active ingredient of Henna (Lawsonia inermis) plant extracted and isolated which was found to be an effective inhibitor for corrosion of mild steel in 1M HCl, and inhibition efficiency increased with decreasing temperature. The corrosion inhibition of lawsone on the corrosion of mild steel in 1.0 M hydrochloric acid was studied using weight loss method. The adsorption of lawsone on the mild steel surface from 1 M HCl obeys the Langmuir adsorption isotherm and the adsorption is not activated.

Vimala et al. **[95]** studied that inhibition efficiency of acid extract of flowers of Cassia Auriculata (CAF) plant on the corrosion of mild steel in 1 M HCl by weight loss measurements and electrochemical studies .The inhibitive action of plant extract is discussed on the basis of adsorption of stable complex at the mild steel surface. The maximum inhibition efficiency of CAF is found to be 74.7% at 0.15(%v/v) of inhibitor from mass loss studies at 303K. Theoretical fitting of different isotherms, Langmuir, Temkin, Freundlich and the thermodynamic model, were tested to clarify the nature of adsorption. Potentiodynamic Polarisation curves revealed that this inhibitor act as a mixed type inhibitor and the inhibition efficiency of up to 74.7% can be obtained.

Patel et al. **[96]** studied that Extract of various plants (Wrightiatinctoria, Clerodendrumphlomidis, Ipomoeatriloba) leaves as corrosion inhibitor of mild steel in 0.5M H_2SO_4 using conventional weight loss, electrochemical polarization, electrochemical impedance spectroscopy and scanning electron microscopic studies . The results of all the experimental methods were in very good agreement of the corrosion of MS in stagnant 0.5 M H_2SO_4 solutions and its effective inhibition by each of the herbal extracts.

Gunavathy et al. **[97]** studied that The inhibition effect of unripe fruit peel extract of Musa acuminate (Cultivar variety – Nendran) (MNP) on corrosion of mild steel in 1 N HCl by using weight loss and electrochemical impedance spectroscopy (EIS) with various concentrations of the extract. The effect of temperature on the corrosion inhibition of mild steel in the temperature range of 30 °C – 80 °C was carried out. The result shows that MNP extract act as an effective inhibitor in the acid environment and is of mixed type inhibitor having efficiency as high as 96% at 2% inhibitor concentration. The inhibition efficiency of MNP extract increases with the increase of concentration but decreases with the increase in temperature. The inhibitor achieves its inhibition by physical adsorption of nutrients of the peel extract on the surface of the mild steel. The corrosion behavior of zinc metal in hydrochloric acid solution containing

Some organic solvents were studied by Mohamed **[98]** using galvanostatic polarization technique. It has been observed that studied organic solvents act as mixed type inhibitors. The inhibitor was assumed to occur via physical adsorption and Temkin's isotherm was obeyed. The inhibition efficiency of solvents increase in the order: glycerol >ethylene glycol > DMSO > dioxan. This order is not affected by variation in temperature in the range 55°C. Some thermodynamic parameters of adsorption have been calculated and discussed.

Petrenko **[99]** studied benzotriazole as an inhibitor of iron corrosion and stimulant of zinc dissolution in the removal of a coating of zinc from galvanized iron. He showed that benzotriazole increases the dissolution rate of zinc coating on iron in hydrochloric and sulphuric acids and exposed iron is protected. The stripping solution for zinc removal contained 30 to 75 g/l hydrochloric acid and 2 to 20 g/l benzotriazole. The zinc layer is removed from the iron surface within 6 to 14 minutes. Stimulating effect on zinc dissolution in sulphuric acid became apparent only at 1g benzotriazole per liter.

Halambek et al. **[100]** investigated natural oil extracted from *Lavandula angustifolia L.* as corrosion inhibitor of Al-3 Mg alloy in 3% NaCl solution using weight loss,polarization measurements and SEM technique. The oil dissolved in ethanol and used as 30% (v/v) solution, was found to retard the corrosion rate of Al-3 Mg alloy even at high temperatures. The inhibiting effect of lavender oil components on Al-3 Mg surface was attributed to the Langmuir's adsorption isotherm. It was found that the L. angustifolia L. oil provides a good protection to Al-3 Mg alloy against pitting corrosion in sodium chloride solution.

Gereng et al. **[101]** studied the corrosion inhibition of low carbon steel in 1 M HCl solution with different concentrations of Schinopsis lorentzii extract by using Tafel extrapolation, linear polarization, and electrochemical impedance spectroscopy (EIS). It was found that Schinopsis lorentzii extract acted as slightly cathodic inhibitor and inhibition efficiencies increased with the increase of extract concentration. The adsorption of the molecules of the extract on the low carbon steel surface was in accordance with the Temkin adsorption isotherm. The results showed that Schinopsis lorentzii extract could serve as a corrosion inhibitor of the low carbon steel in hydrochloric acid environment.

Loto et al. **[102]** investigated the effect of C. Papaya (pawpaw) leaves and C. Sinensis (tea) extracts as an organic „green" inhibitor on the corrosion of α β (duplex) brass (65-35% Cu-Zn alloy) in 1M HNO_3 (nitric acid) was studied at ambient temperature. Weight loss/corrosion rate and potential measurement techniques were used for the experimental work. The tea extract was obtained from the green tea leaves. The results obtained showed effective corrosion inhibition of the extracts on the brass test specimens in the 1M nitric acid used. The different combined extracts concentrations also gave good corrosion inhibition performance. They also exhibited effective corrosion reactions synergism. The test specimen (duplex brass) gave some appreciable corrosion resistance in the test environment.

Ambrish et al. **[103]** investigated the stem extract of *Bacopa monnieri* as corrosion inhibitor of aluminium in 0.5 M NaOH solution using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) methods, and weight loss measurements. The results revealed that *Bacopa monnieri* stem extract was an effective inhibitor, and the inhibition efficiencies obtained from polarization and weight loss experiments were in good agreement. Using the potentiodynamic polarization technique, the extract proved to be a mixed-type inhibitor for aluminium in alkaline solution by suppressing both anodic and cathodic reactions on the metal surface. The Langmuir adsorption isotherm model fitted results obtained from the weight loss.

Popoola et al. **[104]** studied the corrosion inhibition efficiency of *Nicotiana tobacum* (tobacco leaves) on the corrosion performance of zinc electrodeposited mild steel in 2 M HCl by using weight loss and gasometrical principle. The zinc electroplated mild steel coupon of 45 mm by 20 mm was immersed in HCl, in the presence of *N. tobacum* of varying extract concentration of 25, 55, 75 and 100 cm^3 at 50°C elevated temperature in 56 min. Increasing rate of hydrogen gas during the chemical reaction was examined. Inhibition feasibility was explained by formation of insoluble complex absorbing adhesion on the surface metal. However, results obtained indicate that, percentage of extract concentration increase as the number of H_2 gas generated. Extract in acid medium retard corrosion degradation of the deposited mild steel and forcefully reduce corrosion rate. Micro structural examination through OPM, AFM and XRD revealed the morphology and evaluation performance of *N. tobacum.*

Umoren et al. **[105]** studied corrosion inhibition of aluminium in 1 M HCl by coconut coir dust extract (CCDE) by using weight loss and hydrogen evolution techniques at 30 and 60 ^{0}C. It was found that the studied extract exhibits a very good performance as inhibitor for aluminium corrosion in 1 M HCl. Results show that the inhibition efficiency increases with increasing temperature and concentration of the extract. Inhibitive effect was afforded by adsorption of the extracts' components which was found to accord with Langmuir adsorption isotherm. Inhibition mechanism is deduced from the temperature dependence of the inhibition efficiency and was further corroborated by the values of activation parameters obtained from the experimental data.

The inhibitive effect of fenugreek (*Trigonell foenum graecum*) seeds extract on the corrosion of zinc in aqueous solution of 0.5 M sulphuric acid were investigated by Abdel-Gaber **[106]** at 30, 35, 40 and 45°C using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Potentiodynamic polarization curves indicated that the fenugreek seeds extract behaves as an anodic type inhibitor. EIS measurements showed that the dissolution process occurs under activation control. Inhibition was found to increase with increasing concentration of the fenugreek seeds extract but decreases with increasing temperature. The associated activation parameters were determined and the results showed that the fenugreek seeds extract could serve as an effective inhibitor for the corrosion of zinc in sulphuric acid media at higher temperature. The influence of exposure time on the performance of fenugreek seeds extract was investigated. Results showed that the extract performed well after an induction period that is required to release zinc ions in solution in stoichiometric ratio necessary to form stable adsorbed complex with the chemical constituents of the extract.

The effect of the extract of *Aloe vera* leaves on the corrosion of zinc in 2.0 M HCl solution was studied by Abiola **[107]** using weight loss technique. *Aloe vera* extract inhibited the corrosion of zinc in 2.0 M HCl solution and the inhibition efficiency increased with increasing concentration of the extract but decreased with increasing temperature. The adsorption of the inhibitor molecules on zinc surface was in accordance with Langmuir adsorption isotherm. A first- order kinetics relationship with respect to zinc was obtained with and without the extract from the kinetics treatment of the data.

El-Hosary et al **[108]** studied the effect of *Hibiscus subdariffa* (Karkade) extract on the dissolution of Al and Zn in NaOH using the thermometric, the weight-loss and the galvanostatic polarization techniques. The extent of corrosion inhibition as measured by the three techniques is comparable. The results indicated that the additive acts by way of adsorption on both cathodic and anodic corrosion areas. Curves representing the variation of the reaction number (R.N.) in thermometric experiments, and the decrease in weight as a function of the concentration of the additive, are invariably sigmoid in nature. When present in enough amounts, the additive decreases the dissolution rate by as much as 85 per cent of the value recorded in its absence. The two main constituents of the aqueous extracts of *Hibiscus subdariffa,* namely the organic acids and the colouring materials were separated and tested independently for surface activity. Both constituents were effective in retarding the dissolution of the two metals; but the activity of the colouring portion was considerably higher than that of the organic acids.

CONCLUSION:

The diverse set of research summarized and discussed indicates on going intensive research being carried out to tackle the problem of metal corrosion. Although it is realized that the preceding discussions are not infinitive the literature provided in this review reveal concerted efforts directed at the search for more green inhibitors as alternatives to the fossil origin toxic corrosion inhibitors. One main drawback is even with the growing interest in the search for green inhibitors the amount of research being undertaken is not significant compared to the effect of corrosion to the economy given the current consumption of metals and alloys. However, regardless of the drawback mentioned, this review has shown that the use of green corrosion inhibitors is the way forward in the search for safer and environmentally secure protection against metal corrosion. The use of green inhibitors also has the potential of being cost effective due to the renewability of its resources. Furthermore, high inhibition efficiency can be achieved by consuming very less concentration of inhibitor using self-assembled nanoparticles which today proves a great advantage in corrosion science. These Nano-inhibitors can also be studied by cyclic voltammetry, UV-visible spectrophotometric, Fourier Transform Infrared Spectroscopy (FT-IR), Energy Dispersive X-ray Analysis (EDAX), Atomic Force Microscopy (AFM) and order of activity can be verified theoretically by using quantum chemical facility.

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