CORROSION INHIBITOR OF MILD STEEL IN 1M SULFURIC ACID (H2SO4) SOLUTION USING MORINGA LEAF AND SEED EXTRACTS.

[1]Okpala, K. O., [2]Nwanekezie, M. N. and [3]C.A Obiajuru.

[1]Department of Chemical Engineering, Federal University of Technology, P.M.B. 1526, Owerri, Imo State, Nigeria.
[2,3]Department of Chemical Engineering, Chukwuemeka Odumegwu Ojukwu University, P.M.B. 02, Uli, Anambra State, Nigeria.
E-mail: Chibuzo_bright@yahoo.com.

ABSTRACT

The inhibitive effect of Moringa leaf (LE) and Moringa seed (SE) on mild steel corrosion in 1M H2SO4 solution was investigated using standard weight loss at 32ºC and 60ºC.The analysis of the experimental results revealed that the leaves and seeds extract establish their inhibitive action through adsorption of phytochemical component molecules on the metal surface. The FTIR analysis of leaf and seed extracts and corrosion product shows the variation of the peak numbers and the nature of the shifts indicate that there is synergy among the functional groups of the Moringa leaf and Moringa seed extracts in the corrosion inhibition process. Potentiodynamics polarization shows that the extracts inhibited both cathodic and anodic reactions and acted as mixed-type inhibitor. Moreover, the inhibitive action of the plants extract demonstrates that the adsorption of plants extract is spontaneous and the physical adsorptions are found in accord with Langmuir isotherm. Thermodynamic parameters governing the adsorption process were calculated and discussed.

Keywords: Corrosion Inhibitor, Adsorption Isotherm, MoringaOleifera (leaf and seed), Physiosorption.

1.0 INTRODUCTION

Corrosion of materials has continued to receive interest in the technological world as its effect on the structural integrity of materials has been a question for sometimes. Metallic materials are still the most widely used group of materials particularly in mechanical engineering and the transportation industry. In addition, metals are commonly used in electronic and increasingly also, in the construction industry (Buchweishaija, 2009a). However, the usefulness of metals and alloys is constrained by one common problem known as corrosion. Hence, it has been studied extensively since the industrial revolution in the late eighteenth century (Sato, 2012). Corrosion is a naturally occurring phenomenon defined as deterioration of metal surfaces caused by the reaction with the surrounding environmental conditions (Buchweishaija, 2009a). corrosion is a fast process and accompanied by number of reactants that change the composition and properties of both metal surface and local environment (Landolt,2007), for example, formation of oxides, diffusion of metal cations into the coating matrix, local pH changes and electrode potential. Corrosion can cause disastrous damage to metals and alloy structure causing economic consequences in terms of repair, replacement, product losses, safety and environmental pollution. Due to these harmful effects corrosion is an undesirable phenomenon that ought to be prevented.

Scientists are persistent in seeking better and more efficient ways of combating the corrosion of metals. There are several ways of preventing corrosion and the rates which it can propagate with a view of improving lifetime of metallic and alloy materials (Buchiweishaija, 2009a). Hunag and Chen (2012) highlighted the measures in preventing and control of corrosion as follow; use of resistant metal and alloys, cathodic and Anodic protection, use of protective coatings (Stack, 2012) and addition of corrosion inhibitors to the corrosion environment (Papavina Sam, 2000).

Among the methods of corrosion control, the use of inhibitors is very popular (Raya et al., 2008). Corrosion inhibitors are substances which when added in small concentrations to corrosive media or medium decrease or prevent the reaction of metal with the media (Perez and Nestor, 2004). Inhibitors are added to many systems namely cooling systems, Refinery units, chemical oil and gas production units, boiler etc. Corrosion inhibitors are one of the acceptable practices used to reduce and / or prevent corrosion due to ease of application. Most of the effective inhibitors used are heterocyclic

compounds containing oxygen, sulfur and nitrogen as heteroatoms (Kumara et al., 2014) and multiple bonds in their molecules through which they are absorbed on the metal surface (Orubite and Oforka, 2004). It has been observed that adsorption depends mainly on certain physio-chemical properties of the inhibitor group such as functional groups, electron density at the donor atom, pie (π) – orbital character and the electronic structure of the molecule. To be effective, an inhibitor must also transfer water from the metal surface, interact with anodic and cathodic reaction sites to retard the oxidation and reduction of corrosion reactions and prevent transportation of water and corrosion – active species on the metal surface (Maqsood, 2011).

Despite these promising findings about possible corrosion inhibitors, most of these substances (chemical or synthetic inhibitors) not only expensive but also toxic and non-biodegradable thus, causing corrosion problems (Raja et al., 2008). The known hazardous effects of synthetic organic inhibitors which have been in use such as damage to organ or system (kidney, liver) or disturbing a biochemical process or disturbing an enzymes system at some site in the body (Popova et al., 2007; Li et al., 2009) and the need to develop cheap, non-toxic and eco-friendly inhibitors have now made researchers to focus on the use of natural products from plants (Umeron et al., 2008; Umeron and Ebenso, 2008; El Etre 2008). Plant extracts are recognized as sources of naturally occurring compounds that are generally referred to as a green compounds or green inhibitors because of the complex molecular structures and having a variety of physical, chemical and biological properties (Buchweishaija, 2009a). Plant extract have become important because they are environmentally acceptable, inexpensive, readily available, renewable sources of material, biodegradable and ecologically acceptable. Plant extracts are organic in nature and some of the constituents including tanning, amino-acids, alkaloids and pigments are known to exhibit inhibiting action in plant extracts and they can be extracted by simple procedures with low cost which prompt the growing trend in the use of plant extracts as corrosion inhibitors for metals and alloys in various corrosive media.

2.0 MATERIALS AND METHOD
2.1 Mild Steel preparation
The mild steel coupon used for this study was mechanically cut to form square of dimension 2cm x 2cm x 0.17cm coupons. The surfaces of each coupon were then polished using emery paper and degreased by washing with ethanol. The washed samples are then rinsed with acetone, removed and allowed to dry in air before use. All reagents used for the study are analytical grade and distilled water was used for their preparation.

2.2 Preparation of the Moringa Leaf extract
The procedure for the preparation of the leaf extracts is similar to that reported by Okafor et al., (2008). Moringa leaves obtained by drying, completely shade dried at room temperature and ground to powder form and soaked in a solution of ethanol for 24hours filtered using a filter paper. The filtrate so obtained was then subjected to evaporator (in order to leave the filtrate free of ethanol) using a rotary evaporator set at 75^0C. the stock solution of the extract so obtained was used in preparing different concentration by dissolving 0.l - 0.5g/L using IM H_2SO_4 (Acidic) as solvent at different temperature for use in weight loss in analysis.

2.3 Preparation of Moringa Seed Extract
Moringa seeds obtained by drying completely (shade drying) at room temperature were peeled to remove the outer shell. The whitish seeds obtained were then pulverized using a mortar and pestle and soaked in a solution of ethanol for 48hours in accordance with method used by Abdulrahman, (2012). After 48hours, the solution was filtered using a filter paper. The filtrate so obtained was then subjected to evaporation (in order to leave the filtrate free of the ethanol) using a rotary evaporator set at 75^0C. The stock solution of the extract so obtained were used in preparing different concentrations of the test solution by dissolving 0.1- 0.5g/L of the extract in IM H_2SO_4 (acidic) for use in weight loss analysis.

2.4 Loss Method
The mild steel samples were first weighed to determine their initial weights using digital weighing balance and were labeled and recorded accordingly, with time being noted, coupon samples were dipped into each of the beakers containing the different concentrations of the test solution at 32^0C and 60^0C with and without the presence of aqueous Moringa leaf

and seed extracts. The temperature was controlled using a water bath. Tests were conducted with different concentrations of inhibitor. At the end of the tests, the specimen were carefully washed in absolute ethanol having used nitric acid to quench further corrosion from taking place and rinsed with acetone and dried in air. Triplicate experiments were performed in each case and the mean values recorded. Weight loss was determined by gravimetric tests (taken as the difference in the weight of the mild steel coupons samples before and after immersion in different test solutions) using a digital weighing balance and the corrosion rate values were evaluated using equation 1

$$CR = 0.59WL/DAT \ \ (g/mm^2hr) \tag{1}$$

The inhibition efficiency (IE %) and the degree of surface coverage (θ) values were obtained using equation 2 and 3.

$$IE\% = 1- (P_{inh}/P_{blank}) \times 100/1 \tag{2}$$

$$\theta = 1 - P_{inh}/P_{blank} \tag{3}$$

3.0 RESULTS AND DISCUSSION

Figure 1 and 2 showed the degree of protection which varies for different extracts with unstable sensitivity to the inhibitor concentration. Increase in inhibitor concentration resulted in decrease in corrosion rate in acidic (H_2SO_4) medium at different temperature of 305K and 333K. Also, increase in inhibitor concentration of the two extracts (Moringa leaf and seed) increases the inhibition efficiency in acidic (H_2SO_4) media. The increase in inhibition efficiency reflects the strong adsorption of constituent present in the Moringa leaf and Moringa seed extracts on mild steel surface resulting in a more protective layer formed at the mild steel / sulfuric acid solution interface. Thus,MoringaOleifera leaf and seed extracts effectively inhibits mild steel corrosion in IM (H_2SO_4) solution.
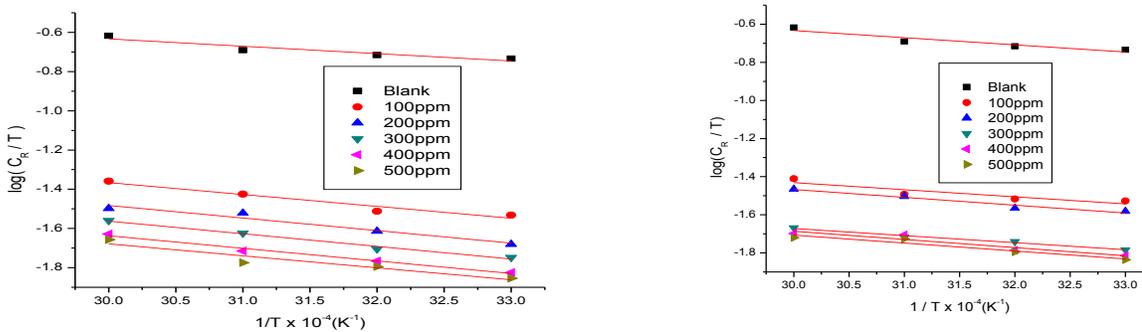

Figure 1 and 2: Plot of log C_R/T against 1/T for LE and SE in 1M H_2SO_4

3.1 Effect of Temperature

Effect of temperature on the corrosion rate was described using Arrhenius equation;

$$C_R = Ae^{-Ea/RT} \tag{4}$$

Where C_R is the corrosion rate of the mild steel, A is the pre-exponential factor, Eais the activation energy, R is the gas constant.

Equation (4) can be linearized to form Equation (5).

$$\text{Log } C_R = {}^{-Ea}/_{2.303RT} + \log A \tag{5}$$

Considering the corrosion rates of the metal at T_1 and T_2 as CR_1 and CR_2, thenEquation (5) can be expressed by Equation (6)

$$\log \left({}^{CR_2}/_{CR_1}\right) = \left({}^{Ea}/_{2.303R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{6}$$

$$logC_R / T = (log R / Nh + \Delta S_{ads} / 2.303R) - \Delta H_{ads} / 2.303R \qquad (7)$$

Where R is molar gas constant; N is Avogadro's constant; h is Planck's constant.
The heat of adsorption Qads (kJmol-1) was calculated using Equation (8).

$$Qads = 2.303\,R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \text{ x } \frac{T_2.T_1}{T_2-T_1} \qquad (8)$$

Where R is the gas constant, θ_1 and θ_2 are the degree of surface coverage attemperatures T_1 and T_2, respectively.

Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies in the presence of inhibitors as seen in table 1 and 2 gives some insight into the possible mechanism of inhibitor adsorption. A decrease in inhibition efficiency with rise in temperature, with analogous increase in corrosion activation energy in the presence of inhibitor compared to its absence is frequently interpreted as being suggestive of formation of an adsorption film of physical (electrostatic) nature. The effect, corresponding to an increase in inhibition efficiency with rise in temperature and lower activation energy in the presence of inhibitor, suggests a chemisorption mechanism (Oguzie, 2007; Nnanna et al., 2010; Eddy et al., 2008). From the foregoing trends for the Moringa leaf suggest a predominant effect of physiosorption of the inhibiting species in acidic (H_2SO_4) environment was obtained. Also, the extracts of Moringa seed suggest a predominant effect of a mix reaction in acidic (H_2SO_4). Also the values of ΔS_{ads} is large and negative in Moringa leaf and Moringa seed extract in acidic medium indicating that decrease in disordering takes place on going from the reactant to the adsorbed species and the shift towards a negative value of entropies implies that the activation complex in the rate – determining step represent association rather than dissociation while ΔH_{ads} with negative signs in both extracts in acidic medium indicates the exothermic nature of the dissolution process that is, physiosorption or chemisorption of the inhibitors. Since exothermic adsorption process signifies either physiosorption or chemisorption while endothermic adsorption process signifies chemisorption only (Durnie et al., 2001).
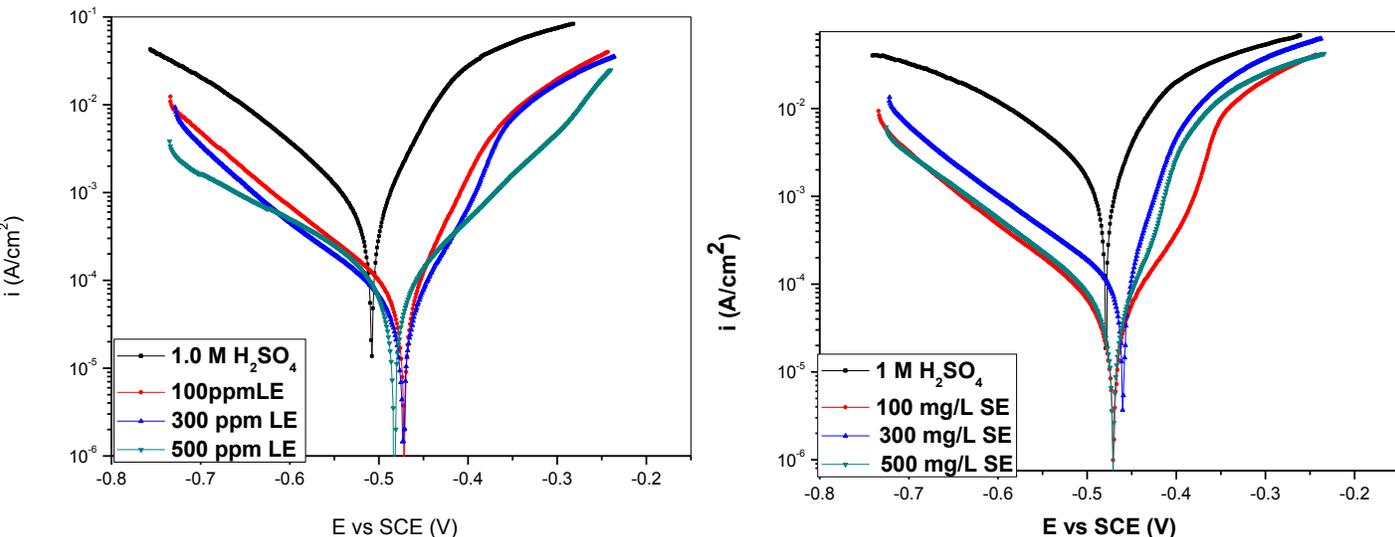
3.2 Electrochemical Results

Figure 3: Potentiodynamic Polarization curves of mild steel in 1 M H_2SO_4 in the absence and presence of various

concentrations of LE and SE.

In 1M H_2SO_4 environment (Figure 1), the effect of Moringa leaf extract (LE) on E_{corr} was not significant though a slight shift was observed towards the anodic direction. Also, a reduction in the cathodic and anodic half reactions was observed with predominant cathodic effect. The result for Moringa seed extract (SE), in 1 M H_2SO_4 environment are presented in Figure 1, no shift of E_{corr} was observed towards the anodic direction. It is generally accepted that if the displacement in E_{corr} is greater than 85 mV, we could classify the inhibitor as anodic or cathodic and if the displacement is less than 85 mV the inhibitor may be seen as a mixed type [Ahamad*et al,* 2010]. Results indicate that the maximum displacement in E_{corr} value in acidic environment are less than 85 mV, therefore, Moringa leaf extract (LE) and seed extract (SE) are regarded as mixed-type inhibitors. Though, Moringa leaf extract (LE) functions as a mixed-type inhibitor with predominant cathodic effect in 1 M H_2SO_4.

FTIR RESULT

A comparison of the FTIR spectra of Moringa leaf extract (LE) and seed extract (SE) powder and that of the protective layer formed on the mild steel surface are presented in parts a and b of Figure2.
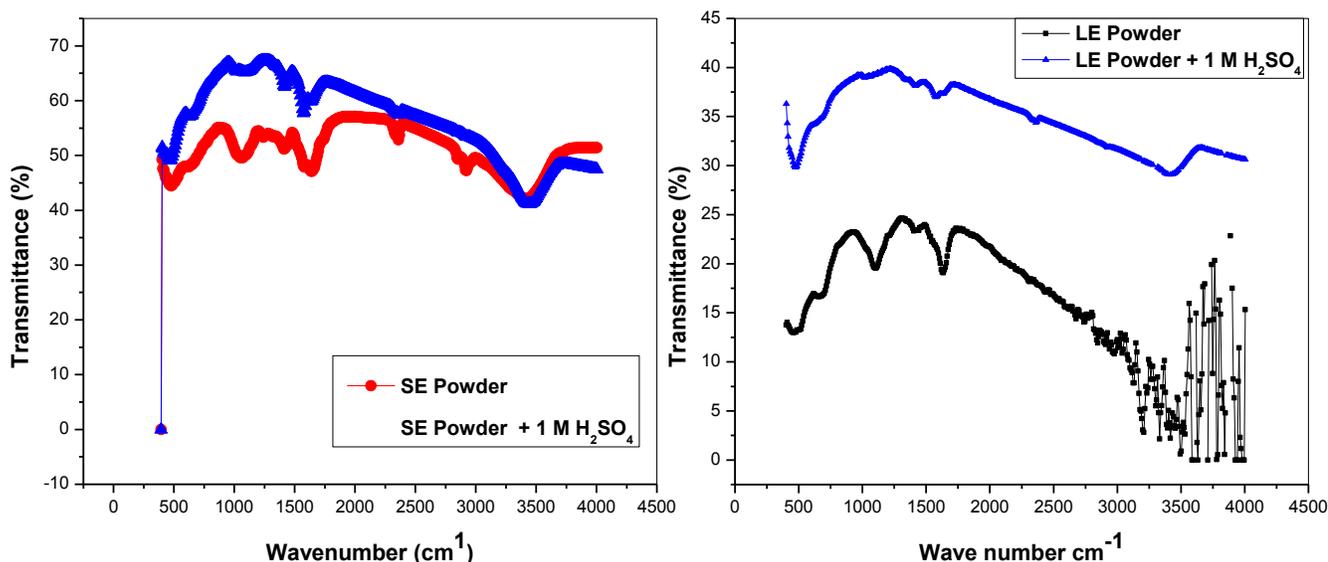

Figure 2: FTIR Spectra of: (a) SE powder and its corrosion products in aggressive environment (1 M H_2SO_4) (b) LE powder and its corrosion products in aggressive solution (1 M H_2SO_4).

Close scrutiny of the spectra reveals the presence of some peaks in 1.0 M H_2SO_4; which could be ascribed to the existence of functional groups. Almost all the peaks in leaf extract (LE) (Fig.2a) and seed extract (SE) (Fig.2b) powder were also observed in the protective layer adsorbed on the metal surface, confirming the existence of these active groups in the inhibitor film. Some of the peaks deviated, while some vanished. In 1.0 M H_2SO_4 there is a shift from 1723 to 1696 cm^{-1} due to the C=O stretching the bands associated with O-H/N-H (Singh *et al,* 2010) at 3209 shifts to 3320 cm^{-1}, the bands associated with C-N at 1002 vanished. The shift of C=C and C-O stretching frequencies from 1650 to 1636 cm^{-1} and from 1243 to 1083 cm^{-1}, respectively suggests the adsorption of leaf extract (LE) and seed extract (SE) molecules on the corroding metal surface.

3.3 Adsorption Considerations and Adsorption Isotherms

The data obtained for the degree of surface coverage were used to test for theapplicability of different adsorption isotherms (Langmuir, Frumkin, Temkin and Flory-Huggins isotherms).

Langmuir isotherm can be expressed as

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{9}$$

Where C is the concentration of the inhibitor, K is the adsorption equilibriumconstant and θ is the degree of surface coverage. In logarithmic form, Equation (9) can beexpressed into Equation (10).

$$\log \frac{C}{\theta} = \log C - \log K \tag{10}$$

The free energy of adsorption (ΔGads) was calculated according to Equation below

$$\Delta G_{ads} = -RT \text{ In } (55.5 \text{ K}) \tag{11}$$

In the situation where it is suspected that the inhibition of metal corrosion occurred as a result of the adsorption of molecules of plant extracts onto the metal surface. It is instructive to investigate the possible adsorption mode by testing the experimental data obtained with several adsorption isotherms. The predominant adsorption mode will be dependent on factors such as the extract compositions, chemical changes to the extract and the nature of the surface charge on metal. A negative surface charge will favor the adsorption of cations whereas anion adsorption is favored by a positive surface coverage. The ability of SO_4^{2-} ion in Sulfuric acid to be strongly adsorbed on the metal surface and hence facilitate physical adsorption of inhibitor cations is an important consideration. Several adsorption isotherms were tested for fit with the experimental data; incidentally, the Langmuir adsorption isotherm gave the best fit with the experimental data. The slopes obtained from the graph which is just about unity and this shows that the adsorption sites on the metal surface are uniformly distributed and energetically identical and that is maximum number of adsorbed molecules do not interact with one another. The negative values of ΔG$_{ads}$ obtained means that the adsorption process was spontaneous and the values of ΔGads obtained characterize the physisorption model of adsorption.

CONCLUSION

From the above discussion, it is quite obvious that natural plant extracts (Moringa Leaf and Moringa seed) are effective green corrosion inhibitors against mild steel in acidic and alkaline medium.

(i)   MoringaOleifera leaf and seed extract is a good inhibitor for mild steel corrosion in 1M H_2SO_4solution. Inhibition efficiency increases with increasing leaf and seed extracts concentration and the values obtained from different methods employed are in reasonable agreement.

(ii)   The electrochemical impedance study showed that corrosion inhibition of mild steel in IM H_2SO_4takes place by adsorption process.

(iii)   Polarization curve measurements indicate that Moringa Leaf and seed acted as a mixed type inhibitor.

(iv)   The increasing value of CPE exponent, that is, the phase shift (n) with increasing inhibitor concentration indicated that surface roughness decreased with increasing inhibitor concentration which is also seen in the scanning electron microscopy.

(v)   The adsorption of Moringa leaf and seed extracts in IM H_2SO_4on mild steel obey Langmuir adsorption isotherm since it is the isotherm that gave the best fit for the experimental data.

REFERENCES

Bentis, F., Traisnel, M. and Lagrenee, M. (2000), *The inhibition action of 3, 6 – bis(2-methoxyphenyl)-1,2-dihydro 1,2,4,5-tetrazine on the corrosion of mild steel in acidic media. Corrosion science*, Vol. 42, pp. 127 – 146.

Buchiweishaija, J. and Mhinzi, G. S. (2008), *Natural products as a source of environmentally friendly corrosion inhibitors: the case of gum exudates from Acacia seyal var. seyal, P*ortugulia Electrochimica Acta, Vol. 26(3), pp. 257-265.

Durnie, R., DeMarco, B., Kinsella, A. and Jefferson, A. (2001), *A Study of Adsorption properties of commercial carbon dioxide corrosion inhibitor formulation*, Journals of Electrochemistry, Vol. 31, pp. 1221 – 1226.

Eddy, N. O., Odoemelam, S. A. and Odiongenyi, A.O. (2009), *Ethanol extract of Musa species peels as a green corrosion inhibitor for mild steel: kinetics, adsorption and thermodynamic considerations,* Electronic Journal of Enviornmental Agriculatural and Food Chemistry, Vol. 8, No.4, pp. 243-255.

EL-Etre, A.Y. (2008), *Inhibition of carbon steel corrosion in acidic solution using the aqueous extract of zallouh root,* Material of chemistry and Physical Science, Vol. 108, pp. 278 - 285.

Guan, N. M., Xueming, L. and Fei, L. (2004), *Synergistic inhibition between o –phenanthroline and Chloride ion on cold rolled steel corrosion in phosphoric acid,* Materials Chemistry and Physics, Vol. 86, pp. 59 – 68.

Hunag, A. and Chen, L. (2012), *Microstructural, trobiological and electrochemical corrosion studies on reactive DC magnetron sputtered zirconium nitride films witzr interlayer on steel,* Metals and Materials International, Vol. 18(6), pp. 951-964.

Kumara, S., Daveb, P. and Shah, N. K. (2014), *Experimental studies on the inhibition effect of audine –N-(P- Methoxy benzyl-otene) Schiff base on zinc corrosion in hydrochloric acid,* International Research Journal of Chemistry (IRSC), pp. 2321-2330.

Landolt, D. (2007), *Corrosion and Surface chemistry of metals,* EPFL Press London, pp. 224-245.

LI X., Dend S., FU H., MU G. (2009). *Inhibition effect of 6-benzylammopurine on the corrosion of cold rolled steel in H_2SO_4 Solution,* Corrosion Science Journal 51, pp620.

Maqsood, K. (2011), *The Inhibitory Effect of Ethanolic Extract Moringaoleifera Leaf on the Corrosion of mild steel in 5M and 1M hydrochloric acid HCl,* Journal of Science and Engineering, Vol. 40(8), pp. 436-455.

Oguzie, E. E., (2007), *Corrosion Inhibition of Aluminum in Acidic and Alkaline Media, Sansevieriatrifasciataextract,* Corrosion Science, Vol. 49, No. 3, pp. 1527-1539.

Orubite, K. O., and Oforka, M. C. (2004), *Inhibition of the Corrosion of Mild Steel in Hydrochloric acid solution by the extracts of leaves of Nypafruiticanwumib,* Material Letter Vol. 58(11),pp. 1768-1772.

Papavinasam, S. (2000), *Corrosion inhibitors uhlig's Corrosion Handbook,* pp1091-1092.

Perez, S. K. and Nestor, S. M. (2004), *Electrochemistry and Corrosion Science,* Kluwer Academic Publisher, Mexico, pp. 102-112.

Popova, A., Christor, M. and Zwetanora, A.,(2007).*Effect of the molecular structure on the inhibitor properties of azoles on mild steel corrosion in IM HCl,* Corrosion Science Journal, Vol. 49, pp. 21 – 31.

Raja P.B., and Sellturaman M.G., (2008).*Natural products as corrosion inhibitor for metals in corrosive media,* A Review of Material Letters, Vol.62(1), pp. 113-116.

Sato N., (2012).*Rahman spectroscopy of thin corrosion films on iron at 100 to 150^0C in Air,* Journal of Science and Engineering, Vol. 42(8), pp. 476-481.

Stack M.M., (2002). *Micro-abrasion resistance of thermodynamically treated steels in aqueous solutions: mechanisms, maps, material selection,*Trobiological int. 21, pp141 – 149.

Umoren, S., Ebenso, E.E., (2008).*Studies of the anti-corrosive effect of Rapiahookeri exudates gum-halide mixtures for aluminum corrosion in acidic medium*, Pigment Resin Technology, Vol. 37(3), pp. 173.

Umoren, S., Obot I., Ebenso E., and Okafor P. (2008).*Eco-friendly inhibitors from naturally occurring exudates gums for aluminum corrosion inhibition in Acidic medium,* Port Electrochemical Acta, Vol. 26, pp. 267-282.