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Inhibitive Effect of Leaf Extracts of *Duranta Erecta* on Mild Steel Corrosion in 1M Hydrochloric and 0.5M Sulphuric Acid Solution

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Abstract:

The inhibitive action as anticipated depended on the concentration of the inhibitor, period of immersion and temperature of the attacking acid. The results obtained from the study the acid extract of *Durenta erecta* leaf could bring out maximum inhibition of 98.6% in 1M HCL and 99.5% in 0.5M H_2SO_4 acid at room temperature. The absorption of the inhibitor on surface of mild steel was found to be Langmuir and Temkin adsorption isotherm which indicated the mono layer formation with heterogeneity in the surface of the electrode. Maximum efficiency of 96.8% in 1M HCl and 60.9% in 0.5M H_2SO_4 from icorr and Rp were obtained. Results from the polarization techniques such as Tafel and impedance spectroscopy could be comparable with the classical mass loss methods.

Keywords—**Mild Steel, Corrosion Inhibition, Electrochemical Analysis**

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INTRODUCTION

Mild steel is one of the most important widely used engineering materials particularly for the structure and automobile applications due to low cost and easy availability. MS suffers from severe corrosion in aggressive environment, which needs to be protected. Hence the study of corrosion inhibitor of MS in aqueous aggressive media is the subject of pronounced technological significance. Thus the investigation was carried out using mild steel. Corrosion behaviour of mild steel with varying parameters was discussed in effect of concentration of the inhibitor, influence of exposure time, temperature effect. Acid solutions are widely used in chemical laboratories and in several industrial processes such as pickling, acid cleaning, acid de-scaling and oil wet cleaning etc. among the commercially available acids hydrochloric acid and sulphuric acid are used in nearly all industries and is vital commodity in our national economy. Experiments were performed in 1M HCl and 0.5M H_2SO_4.

PREPARATION OF SAMPLE

Regular sample of area 1x5 cm^2 have been cut from a large sheet of mild steel. A hole was drilled in the specimen, mechanically polished, degreased, washed with de ionized water then thoroughly dried and kept in desiccators for weight loss tests. The mild steel specimens used in the following percentage elemental of composition Mo-0.021%,

S-0.019%, C- 0.089 %, Fe-99.58%, Mn-0.215%, P-0.017%.

PREPARATION OF THE INHIBITOR

Durenta erecta extract was prepared by refluxing 25g of leaves in 500ml of HCl and H_2SO_4 for three hours and kept overnight for cooling. The cooled extract was filtered and made up to 500ml with 1M HCl and 0.5M H_2SO_4 to get 5% extract of inhibitor. Phytochemical examinations were carried out for all the extracts as per the standard methods. The two methods mass loss methods & electrochemical measurements were done.

MASS LOSS METHODS

In the current study pre weighed coupons were immersed in triplicate with the help of glass hook into a beaker containing 100ml of 1 M HCl acid with and without inhibitor for a particular period of time. The coupons are then washed, dried and reweighed. The average mass loss of coupons was recorded. Varying the parameters such as concentration, time of immersion and temperature the experiments were conducted.

EFFECT OF CONCENTRATION OF THE INHIBITOR IN 1M HCL

The data showed that the corrosion rate of mild steel decreased with increase in concentration. The inhibition efficiency increased from 70.3% to 90.4% with 0.7% concentration of DEL extract. From the data, the maximum enhancement of inhibition was noted with 0.7% of the extract. The increase in inhibition efficiency with increase in concentration of the extract may be attributed to the increase in the number of molecular adsorbed over the mild steel surface. This blocks the active sites in which direct acid attack proceed there by effectively protecting the metal from corrosion. **[PandianBothi Raja *et al.*, 2009].**

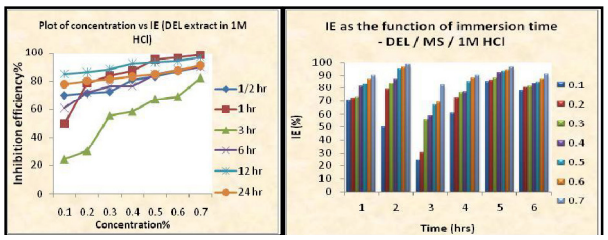


Fig 1.1Fig 1.2

From the results, it can be inferred that as the time of immersion increase, the inhibitor molecules gets coated on the surface of mild steel there by decreasing the mild steel dissolution effectively. A maximum of 98.6% of inhibition was obtained at 0.7% of extracts. In the present investigation it was also observed that the extract behaved as an excellent one at all periods of immersion. This proved the inhibitive nature of the adsorbed molecules on the surface of mild steel.

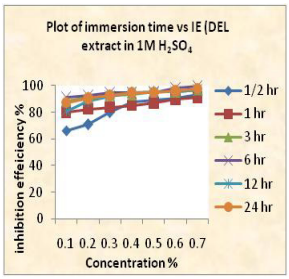
EFFECT OF TEMPERATURE

Temperature can influence the interaction between mild steel and the acid in the presence and absence of the inhibitors. To determine the activation energy and the energy of adsorption of the corrosion process, mass loss studies were conducted using DEL extract at various temperatures ranging from 303K to 353K. According to N.S Rawat and A.K Singh (1989), the above observation may be explained on the following basis adsorption and desorption of inhibitor molecules continuously occur at the metal surface and an equilibrium exists between these two processes at a particular temperature. With the increases of temperature the equilibrium between adsorption and desorption processes is shifted leading to a high desorption rate until equilibrium is again established at a different value of equilibrium constant. It explains the lower inhibition efficiency at higher temperatures.

EFFECT OF CONCENTRATION OF THE INHIBITOR IN 0.5M H_2SO_4

Figure 1.3 & 1.4, as the concentration of the inhibitor increased, the inhibition efficiency also

increased. This could be result of the fact that as the inhibitor increases, more surface of the metal was covered by the inhibitor molecular.**Dahmani*et al.,(2010)***reported that increase in inhibitor concentration led to a decrease in the concentration rate. A highest efficiency of 93.2% was obtained at 0.7 concentration of the extract.



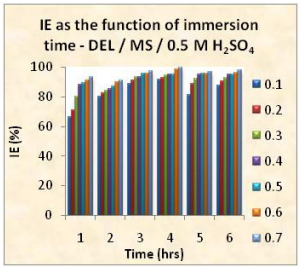
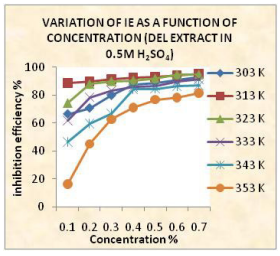


Fig 1.3 Fig1.4

IMPACT OF IMMERSION TIME

The influence of duration of immersion on the IE of MS system is given. When the immersion period increased, the inhibition efficiency decreased and the corrosion rate increased. This shows that the protective film formed on the metal surface, was broken by the corrosive environment and the film was dissolved.In the present study, results indicated the increase in IE with increase in time of immersion till 6h. At 6h, inhibition efficiency was maximum 99.5% and then decreased to 70.0% at ½ h. The best performance of the DEL extract was perceived at 313K of immersion period with the entire concentration of the inhibitor.



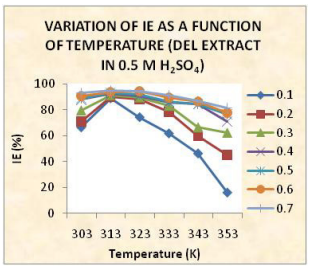
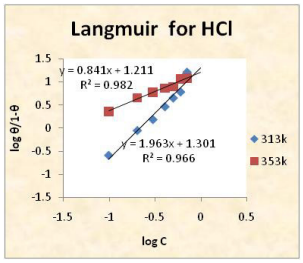


Fig.1.5

ADSORPTION BEHAVIOUR

The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metal has been deduced in terms of adsorption characteristic of the inhibitor. The inhibition data are used for constructing experimental adsorption isotherms. Adsorption isotherms provide a clue to the mode and mechanism of adsorption. It is assumed that the inhibition efficiency is comparable to the degree of surface coverage of the inhibitor on the metal surface.



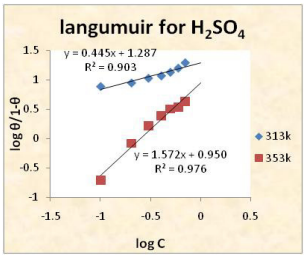
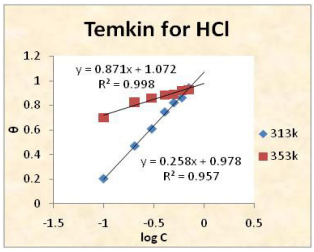


Fig 2



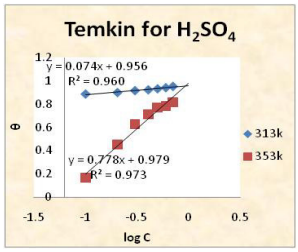


Fig 3

The surface coverage (θ) values for different concentration of the inhibitors in acid medium were evaluated from the mass loss data. Attempts were made to fit the data obtained from mass loss measurement into different adsorption isotherms like Langmuir and Temkin. An assumption of Langmuir adsorption isotherm relate concentration of inhibitor in the bulk electrolyte and the degree of surface coverage by the following equation,

Log [θ/1-θ] = log K + log C …….1

From the above equation, if the assumptions of Langmuir are obeyed, a plot log (θ/1-θ) Vs log C

should give a straight line. Langmuir plots for the corrosion reaction of mild steel in the presence of are shown in figure 2 & 3. The fact that the lines obtained were linear confirmed that Langmuir adsorption isotherm was applicable to the present study. It also confirmed the monolayer adsorption.

A straight line was obtained when the surface coverage was plotted against log C vs θ for the inhibitor. This shows that the adsorption of the inhibitor at the mild steel acidic solution interface obeys Temkin adsorption isotherm.

POTENTIODYNAMIC STUDIES

The anodic and cathodic polarization curves of MS electrode in 1M HCl and 0.5M H_2SO_4 medium in the absence and presence of various concentrations of DEL extracts in at 303K. The electrochemical polarization parameters for mild steel in 1M HCl and 0.5 M H_2SO_4 medium without and with different concentrations of DEL extract in 1M HCl and 0.5 M H_2SO_4.

The electrochemical parameters such as corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were calculated from the intersection of anodic and cathodicTafel slopes of the polarization curves depictedthat, the presence of DEL extract decreases both cathodic and anodic slopes with increasing concentration. That is DEL extract affected both the cathodic and anodic parts of the curves indicating that the extract influence the dissolution of MS and the hydrogen evolution processes, implying that DEL extract functioned as a mixed-type of inhibitor.

Corrosion current (Icorr) was found to decrease with increasing concentration, indicating the increased inhibition efficiency with the increase in the concentration of the inhibitors. This confirmed the inhibitive nature of the extract and also the adsorption of the plant extracts on metal surface.

The values of IE are found to be increasing with increase in concentration of inhibitors. A maximum of 96.8% and 60.4% of inhibition for DEL extract in 1M HCl and 0.5M H_2SO_4 was obtained with 0.7% concentration. No significant change in E_{corr} values in the presence of inhibitors was noticed indicating the mixed nature of the inhibitors. It was found that, the values of E_{corr}shifted toward more positive by increasing the concentrations of inhibitors. This is due to the dissolution of metal is retarded by the film formed on the metal surface. Generally, an inhibitor can be classified as cathodic or anodic type if the shift of corrosion potential (E_{corr}) in the presence of the inhibitor were more than 85 mV with respect to that in the absence of the inhibitors. From the results, the changes of E_{corr} are less than 85 mV for studied inhibitors, which indicate that inhibitors act as a mixed type inhibitors for the corrosion of MS in 1M HCland 0.5 M H_2SO_4 acid medium. (C.B. Pradeep Kumar, K.N. Mohana., 2014).

Rp values were found to increase with increasing concentration of the inhibitor in both acidic solutions. A maximum of 88.36% and 91.9 % efficiency was obtained for DEL extract in 1M HCl and 0.5M H_2SO_4 respectively.

The inhibition action of DEL extract in 1M HCl and 0.5M H_2SO_4 was attributed to adsorption and formation of barrier film on the metal surface that separates the metal surface from the corrosive medium.

IMPEDANCE SPECTROSCOPY

The impedance analysis of mild steel in 1M HCl and 0.5M H_2SO_4 shows one depressed capacitive loop (one time constant Bode-phase representation). All experimental plots have a depressed semicircular shape in the complex impedance plane, with the centre the real axis this behaviour is typical for solid metal electrodes that show frequency dispersion of the impedance data and has been attributed to roughness and other inhomogeneities of the solid surface.

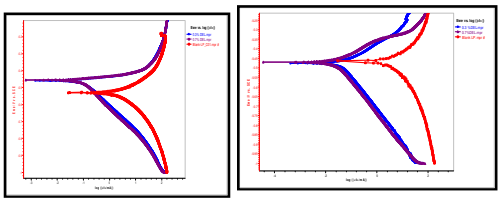
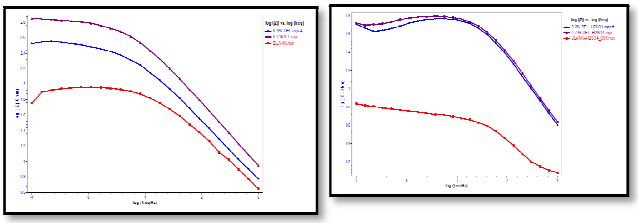
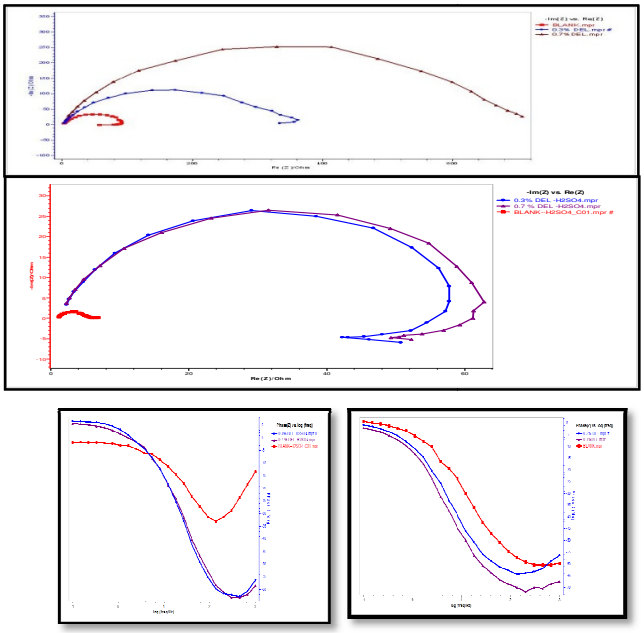


Fig 4



The Nyquist plot of the impedance behavior of mild steel in 1M HCl and 0.5 M H_2SO_4 in the presence of various concentrations of the inhibitor is shown. The impedance analysis of mild steel in 1M HCland 0.5 M H_2SO_4 shows one depressed capacitive loop (one time constant Bode-phase representation). All experimental plots have a depressed semicircular shape in the complex impedance plane, with the centre the real axis. A clean electrode without a passive film especially in the case of corroding electrode immersed in acid solutions gives rise to an impedance spectrum consisting of perfect semicircle. This behaviour is typical for solid metal electrodes that show frequency dispersion of the impedance data and has been attributed to roughness and inhomogeneties of the solid surface.



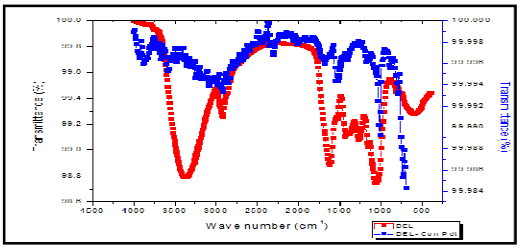
Impedance plots in Nyquist and Bode format for MS in 1M HCl& H_2So_4 (a-c) in the presence and absence of DEL extract

SURFACE ANALYSIS

FT- IR Spectral Analysis

In the presence of the inhibitor, IR spectrum of the corrosion product revealed that the –OH stretch (3379.23 cm^{-1}) was shifted from (3363.86 cm^{-1}).

From the spectra, it is observed that the C–H

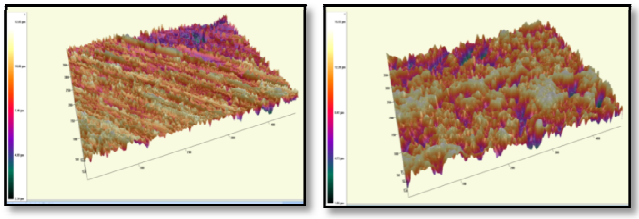


stretch of alkanes and C–C stretch (in–ring) of aromatics from the absorption bands at 2924.09 cm^{-1} and 2924.09 cm^{-1}. From the Figure (4.24) the IR spectrum of the phytochemical compounds adsorbed on the metal surface reveal the presence of functional group peaks whose absorption frequencies correspond to carbonyl groups at 1627.92cm^{-1} and 1689.64cm^{-1}.

Fig 6: IR spectrum of extract and corrosion products in 1M HCl

3D Laser profilometer

3D Laser Profilometer image analysis was performed to obtain the average roughness, Ra, (the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square roughness, Rq, (the average of the measured height deviations taken within the evaluation length and measured from the mean line). In Figure 7(a) the surface topography of non-corroded metal surface is shown. The value of Rq, Ra for the polished mild steel surface reference sample is 3.140 µm, 2.558 µm respectively.



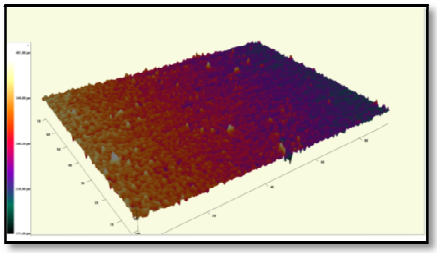


Fig 7: (a) Plain MS (b) MS in 1M HCl (c) 1M HCl +0.7% DEL

Scanning Electron Microscopy (SEM)

SEM morphologies of MS after immersing in 1M HCl for 3h in the absence and presence of DEL were shown in Fig 8 (a). Fig 8 (b), shows the general appearance of MS in HCl without DEL. No obvious corrosion products present on the sample. That is the corrosion attack in 1M HCl is more uniform in character and there is little tendency towards local enrichments of products on the surface. In addition, parallel features which can be associated with abrading scratches are also observed. Fig 8 (c) shows the SEM morphologies of MS in HCl in the presence of 0.7% DEL.

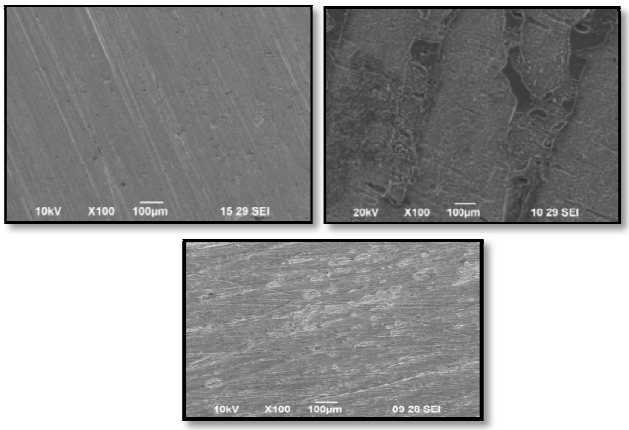


Fig 8: (a) Plain MS (b) Blank (MS in 1M HCl) (c) 1M HCl +0.7% DEL

UV- Visible Spectroscopy

UV-Visible spectroscopy provides a strong evidence for the formation of a metal complex (Quraishi*et al*, 2012). From Figure 9, a deviation is shown in absorbance values and their intensities.

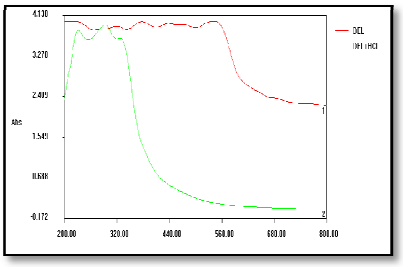


Fig9: UV analysis of DEL extract and 1M HCl+0.7% DEL

CONCLUSION

Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds and so they are environmentally friendly. In this direction, to arrive at inexpensive non-toxic ecofriendly inhibitors formation the present study **"Inhibitive effect of leaf extract of *Durenta erecta* on Mild Steel corrosion in 1M Hydrochloric and 0.5M Sulphuric acid solution"** leaves has been carried out by the classical mass loss measurements and polarization measurements.

The acid extracts of DEL could bring out a maximum inhibition of 98.6% in 1M HCl and 99.5% in 0.5M H_2SO_4 acid.

The extracts were temperature resistant in nature and the inhibition efficiency varied from 98.6%, at room temperature to 82.3% for DEL in1M HCl and 99.5%, at room temperature to 91.1% for 0.5M H_2SO_4 extract.

The inhibitors used in the current study followed Langmuir and Temkin adsorption isotherm which indicated the mono layer formation with heterogeneity in the surface of the electrode.

Thermodynamic parameters calculated could reveal the physisorption process, spontaneity of adsorption and there is interruption of solvent entropy. Thus a suitable mechanism could be predicted.

Increase in Rp and Rct values and decrease in I_{corr} and C_{dl} value confirm that DEL is adsorbed on the

mild steel surface and inhibition process is followed by monolayer adsorption.
Results from the polarization techniques such as Tafel and impedance spectroscopy could be comparable with the classical mass loss methods.
The eco-friendly inhibitors under study behaved as mixed type inhibitors.
Cost effective and non-toxic to the environment.

In the current investigation the *Durenta erecta* leaves extracts play a major role in reducing the metal dissolution as well as hydrogen evolution and protect the mild steel surface from corrosion.
Thus the *Durenta erecta* leaves extract has proved to be zero cost, eco-friendly and highly economical inhibitor.

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