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INHIBITIVE EFFECT OF *Mussaenda frondosa* LEAVES EXTRACT ON MILD STEEL CORROSION-STATISTICAL AND THEORETICAL VIEW

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ABSTRACT
The statistical and theoretical view on mild steel (MS) corrosion in a sulphuric acid medium in the presence of leaves extract of *Mussaenda frondosa* (MF) were studied by electrochemical impedance spectroscopy and potentiodynamic polarization techniques. The nature of the inhibitor was defined by the polarization studies. The semicircle curves observed in electrochemical impedance spectroscopy indicated that the corrosion of mild steel is controlled by the charge transfer process. The corrosion inhibition performances enhanced by the addition of MF extract and increase with increase in the concentration of the MF extract. GCMS is used to gather the important phytochemical constituents in the MF extract. The adsorption of MF on the metal surface is confirmed by SEM images. DFT was performed in order to confirm the adsorption of the constituents in MF extract on MS.
Keywords: Mild steel; Adsorption; Corrosion; Potentiodynamic polarization; GC-MS; SEM.

INTRODUCTION

Mild steel (MS) is the extensively used materials in engineering mainly for the automobile and structural applications. Moreover, MS easily undergo rusting in the acidic and humid atmosphere and the rate of corrosion tend to become high[1,2]. Application of inhibitors on controlling metal corrosion that is in contact with an aggressive environment is an accepted practice. Many organic compounds have been used as corrosion inhibitor[3]. The compounds especially with hetero atoms such as nitrogen, sulphur and oxygen showed a better inhibition performance. But these compounds are toxic to living components and expensive too[4,5]. In order to overcome these problems 'Green Inhibitors' are in use. Plant extracts have become important because they are readily available, environmentally acceptable. They phyto ingredients in the plant extracts 3 have very greater inhibition efficiency and they are also cheap and safe inhibitors of corrosion of metals[6]. Hence in the present work, an effort has been made to use leaves extract of *Mussaenda frondosa* as a corrosion inhibitor for mild steel in H_2SO_4 medium using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP).

EXPERIMENTAL

Materials and Methods

The ethanol extract of MF dried leaves extract was collected, filtered from the soxhlet apparatus after 6 hours. The extract was concentrated by evaporation on a water bath (at 60^{o} C) until most of the ethanol is evaporated. Desired concentrations of inhibitor were prepared by dilution of crude extract of MF with ethanol. The electrochemical measurements were carried out using CH- Instrument Model-608D in a typical three-electrode system consisting of the MS specimen as working electrode , a platinum electrode as a counter electrode and saturated calomel electrode as a reference electrode. Electrochemical

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measurements were performed in a glass cell with mild steel, taken as the working electrode with an exposed area of 1cm^2. Before each experiment electrode was polished and degreased as per ASTM procedure[7]. GC-MS technique was carried out on a SHIMADZU QP-2010 Plus Gas Chromatograph-Mass Spectrometer comprising an AOC-20i autosampler and gas chromatograph interfaced to a mass spectrometer. The adsorbed layer coated over the MS surface was authenticated by SEM. The statistical significance is measured by analysis of variance (ANOVA).

RESULTS AND DISCUSSION

The EIS is an effective tool to characterize the film coverage on the electrode, which measures double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}). The impedance responses are pictorially given in the form of Nyquist plots. The corrosion resistance of MS in 0.5 M H_2SO_4 in the absence and presence of MF extract was estimated and the respective Nyquist plots are presented in the Fig.-1. The data obtained from these figures are tabulated in the Table-1. The added MF extract in the test solution tends to change in impedance response behavior of MS. The impedance behavior of MS enhanced by the adsorption of MF molecules on the metal surface owing to increasing the surface coverage.[8,9] These results inferred that increase in IE. Adsorbed the constituents present in MF extract molecules form protective films which inhibit corrosion and protect the metal surface. From the table, it is evident that on increasing concentrations of MF extract enhance the R_{ct} values considerably and also reduce the C_{dl} values. The increase in the resistance values tends to enhance the IE is due to the gradual displacement of H_2O by the inhibitor molecules. In the presence of MF extract to that of the blank solution may tend to decrease the dielectric constant or increase the width of the double layer resulting decreases C_{dl} values. Hence adsorptions of MF molecules on the metal surface leads to form the protective layer over the MS surface.[10]

Table-1: Polarisation and Impedance Data on MS Corrosion by Changing Concentrations of MF Extract in 0.5 M H_2SO_4

MF Conc. (g/L)	I_{corr}x10^{-3} (Amp/cm^2)	b_a (mV)	b_c (mV)	-E_{corr} (mV dec^{-1})	IE (%)	R_{ct} (Ω cm^2)	C_{dl} (F cm^{-2})	IE (%)
0	2. 9920	165.837	199.92	521.3	-	14.24	0.00004869	-
0.05	1.8130	147.929	201.05	512.1	39.4	33.38	0.00004760	57.3
0.10	1. 0190	131.096	183.65	506.5	66.0	64.19	0.00004230	77.8
0.15	0.7250	124.084	173.73	504.4	75.7	79.52	0.00004105	82.0
0.20	0.5663	117.495	167.31	502.3	81.0	92.79	0.00003757	84.6
0.25	0.3898	110.338	151.49	502.3	87.0	111.1	0.00003325	87.1

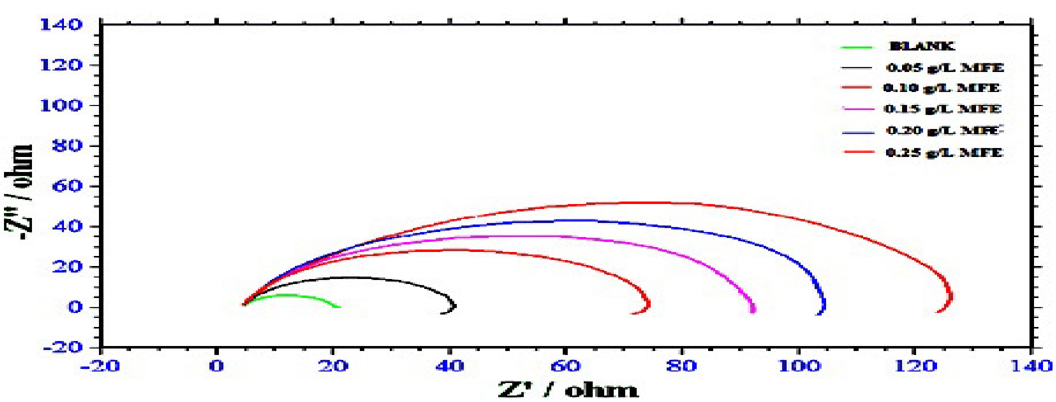

Fig.-1: Nyquist plots on MS Corrosion by Changing Concentrations of MF Extract in 0.5 M H_2SO_4

Figure-2 shows the positive and negative polarization curves of mild steel in 0.5 M H_2SO_4 in addition and without MF 0.05-0.25 (g/L) and the corresponding polarization parameter are tabulated in Table-1. Careful scrutiny of Fig.-2 depicts that the added MF extract alters the cathodic curves anodic curves to lesser values of current density leading to diminishing corrosion by adsorption of MF on the electrode surface.[11] Hence the ethanol extract of MF leaves could be categories as mixed type. The corrosion potential shifted positive direction compared to that of blank inferring that the MF chiefly controls the reaction at the anode site.[12] This is due to the fact that organic compounds get adsorbed at the active sites of MS and form a shielding layer over the electrode. The deposit developed by a weak force of interaction between the metal and the components of MF and the I_{corr} values decreases due to the blockage of anodic reaction.[13,14]

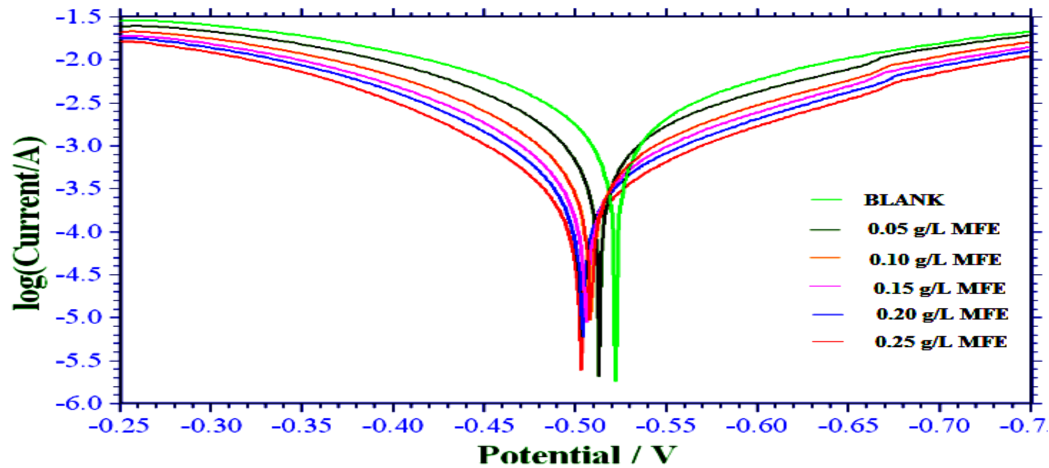

Fig.-2: Tafel Plots on MS Corrosion by Changing Concentrations of *MF* Extract in 0.5 M H_2SO_4

GCMS

On comparing the GC retention indices of the constituents with respect to the retention time and on comparing with mass spectra libraries from Wiley and NIST, the constituents there in the MF extract were quantified. From the chromatogram (Fig.-3.) that it is well clear that out of 32 individual constituents four are prominent and they are listed in the Table-2.

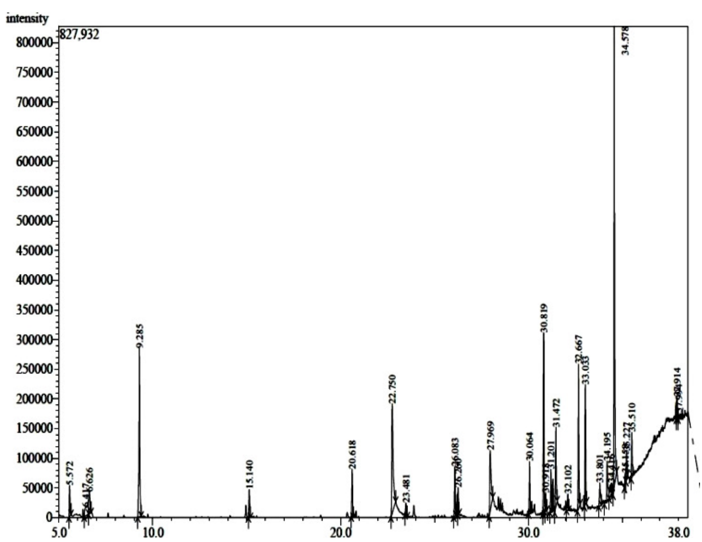

Fig.-3: Chromatogram of *MF* Extract

Table-2: GC MS Analysis of *MF* Extract

Compound name	Molecular Formula
Styrene (CP 1)	C_8H_8
Dibutyl-phthalate (CP 2)	$C_{16}H_{22}O_4$
Isopropyl 2-phenyl-4,5-dihydro-1,3-oxazole-4-carboxylate (CP3)	$C_{13}H_{15}NO_3$
Benzamide,N-[1,2,3,4-tetrahydro-2-(3-nitrophenyl)-4-oxo-3-quinazolinyl] (CP4)	$C_{21}H_{16}N_4O_4$

SEM

Surface analysis of MS was calculated by scanning electron microscopy after 6 h immersion in the presence and absence of MF extract in 0.5 M H_2SO_4. Fig.-4A represents the photograph found for polished metal not including any aggressive solution while Fig.-4B showed strongly damaged MS surface due to the formation of corrosion products after in 0.5 M H_2SO_4 solutions. SEM micrographs of MS after in the presence of 0.25g/L MF extract in 0.5 M H_2SO_4 is shown in Fig.-4C. Comparisons of figures show that there are no pits and fractures are observed in the micrographs in the inhibited MS. Thus it is clearly seen that the occurrence of good shielding layer over the MS surface which is responsible for corrosion inhibition.

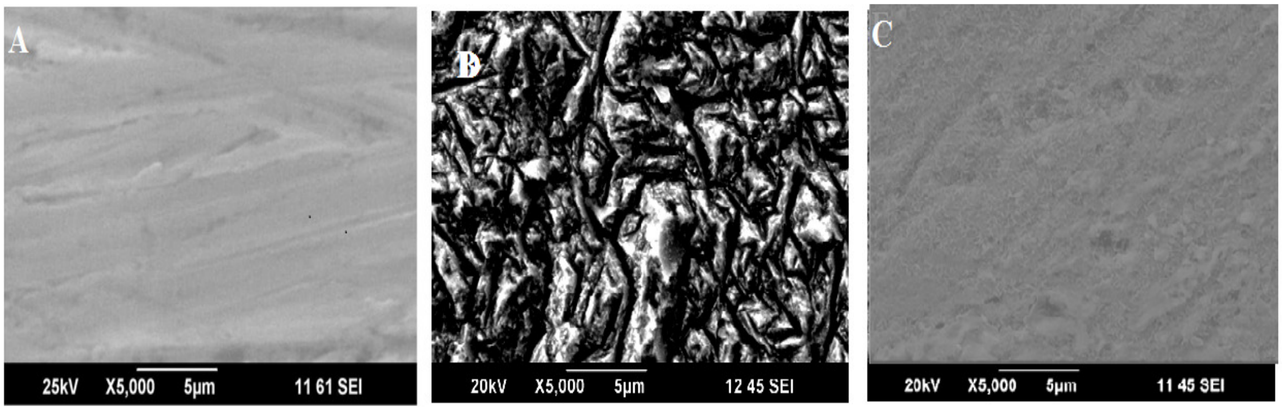

Fig.-4: SEM Micrograph of (A) Polished MS, (B)Uninhibited MS, (C) Inhibited MS in 0.5 M H_2SO_4

ANOVA

The values of IE calculated from PDP and EIS methods including and excluding MF extracts in 0.5 M sulphuric acid as a function of the concentration of MF are given in Table-3. The table was rearranged into a matrix array. Matrix array is helpful for statistical analysis. The analysis of variance was employed on the data given in tables and the parameters like mean square (MS), degrees of freedom (Df), the sum of the squares,(SS), P, F and $F_{critical}$ values were found out and listed in Table-3. From the tables it is clear that the calculated F-values are higher than the $F_{critical}$ values for the given degree of freedom and the p values are less than 0.01 at p=0.01 .The results indicate the concentrations of MF extract have a significant role in the corrosion mitigation process and it is also clear that the interaction between the exposure time and the concentration of inhibitors are statistically significant and hence the null hypothesis s rejected.[15,16]

Table-3: Statistical Results for the IE and Concentration of *MF* Extract in 0.5 M H_2SO_4 at p=0.01

System	Source of Variance	SS	Df	MS	F -value	P- value	$F_{critical}$
MF in 0.5 M H_2SO_4	Concentration	7312.662	5	1462.532	3.8960454	0.032059	3.3258345
	IE	15194.81	2	7597.406	20.238756	0.000305	4.102821
	Error	3753.89	10	375.389			
	Total	26261.36	17				

Quantum Chemical Calculations

To link the inhibition efficiencies and the constituents in MF extract, performed quantum chemical calculations using density functional theory (DFT) and the respective parameters were calculated. The structural aspect of the components of MF extract such as Styrene (CP 1), Dibutyl-phthalate (CP 2),Isopropyl 2-phenyl-4,5-dihydro-1,3-oxazole-4-carboxylate (CP3), Benzamide,N-[1,2,3,4-tetrahydro-2-(3-nitrophenyl)-4-oxo-3-quinazolinyl] (CP4) and the performance of adsorption was used to identify the mechanism of inhibition. Table-4 listed the data obtained from DFT calculations values. The optimized structures, occupied and unoccupied molecular orbital structures of the investigated compounds are given in Fig.-5. The centers of adsorption of the CP1, CP2 and CP3 and the interaction with an electrode are predicted by FMO theory.[17] The distance between the occupied and unoccupied molecular orbital of the compound is also an important factor that should be considered.

However, the greater the energy value of occupied molecular orbital greater the tendency to donate the electrons to an empty orbital of the Fe is greater tends to retard corrosion. However, the lower the unoccupied energy facilitates the gain of electrons from the metal surface and leading to lower the distance between LUMO–HOMO and improved the efficiency of inhibitor. A molecule having lower ΔE is easily polarized and they are coupled with greater activity of the chemical constituents. Thus the molecules get adsorbed over the electrode surface at a greater extent. In the present case, the change energy values track the order of CP3 < CP1 < CP4 < CP1, suggesting that CP3 has the greater affinity towards electrode in the acidic medium on comparing with other constituents and tend to interact stoutly with the electrode surface and prevent further deterioration of metal surface. From this parameter, it is evident that the CP3 shows better efficiency than others.

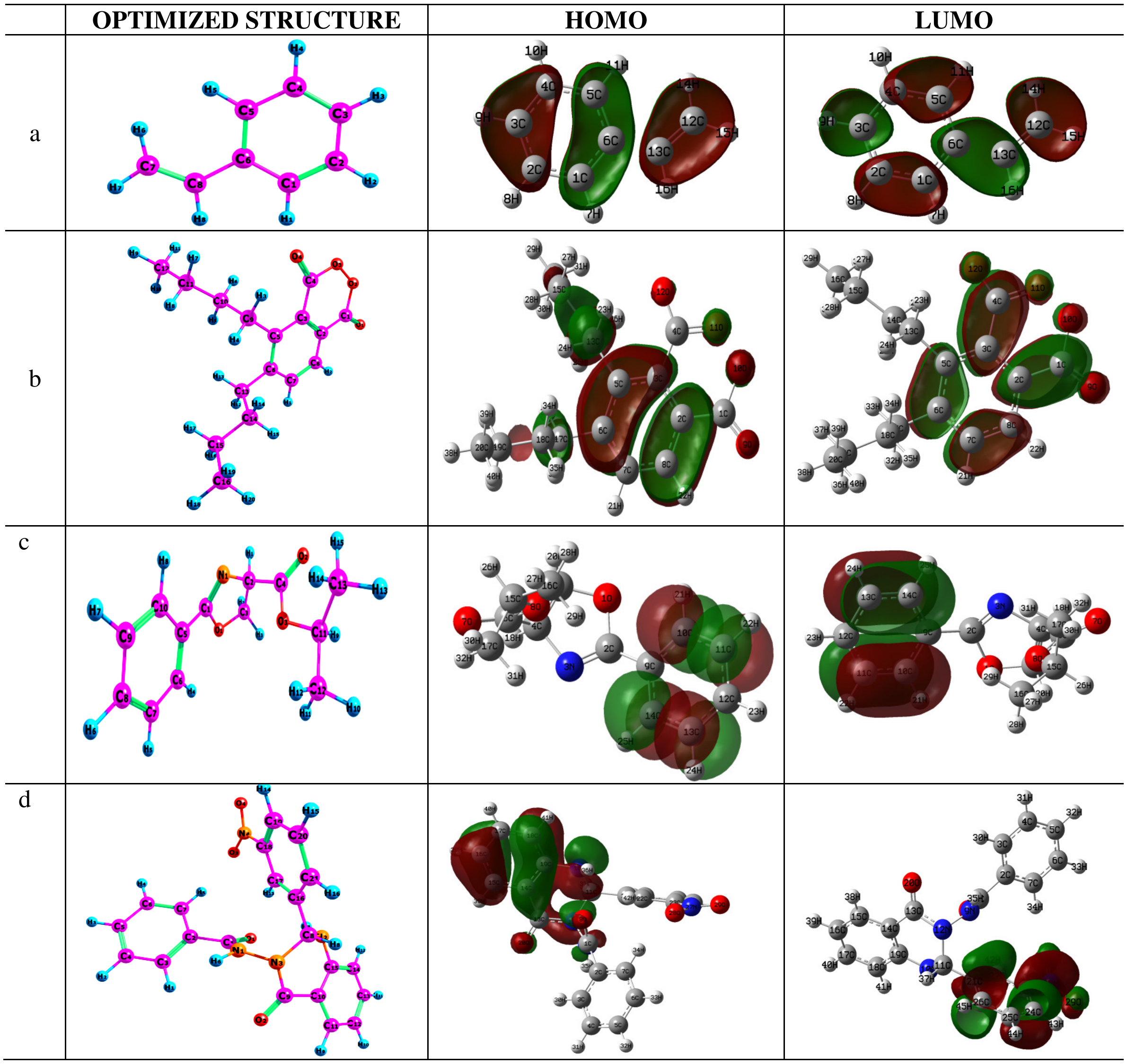

Fig.-5: Optimized, Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital of (a) CP1, (b) CP2, (c) CP3 and (d) CP4

Table-4: Calculated Quantum- Chemical Parameters

Compound	E_{HOMO}	E_{LUMO}	ΔE
CP1	-6.1402	-0.7938	5.3465
CP2	-10.240	-1.5910	8.6485
CP3	-6.1720	-3.7273	2.4447
CP4	-9.4645	-1.5176	7.9469

CONCLUSION

The MF extract brings down corrosion considerably in both the acids. Effective concentration was found to be 0.25 (g/L) for MF at room temperature in 0.5 M H_2SO_4. The negligible shift in E_{corr} values infers that extract of MF extract act as mixed nature. Enhancement of the charge transfer resistance values and fall of corrosion current and double layer capacitance values proved that the MF extract is cover mild steel surface with a layer of protective coating and inhibits further corrosion. GC-MS studies revealed that MF extract contains 32 components out of these 4 are prominent. The considerable development in surface topology in the presence of inhibited MS was confirmed by micrograph obtained from SEM. ANOVA studies explained the concentrations of MF extract have a significant role in the corrosion mitigation process and it is also clear that the interaction between the exposure time and the concentration of inhibitors are statistically significant. The obtained quantum chemical parameters indicate the Isopropyl 2-phenyl-4,5-dihydro-1,3-oxazole-4-carboxylate (CP3) effectively control the acid corrosion by the formation of an even film over the MS electrode surface.

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