Seed Extract of *Lablab purpureus* as Green Corrosion Inhibitor for Mild Steel in 1N Hydrochloric Acid Medium: An Experimental and Computational Investigations

[1]V.Kavitha, [2]Dr. N. Gunavathy

[1]Research Scholar, [2]DAssistant Professor

[1, 2] Department of chemistry,

[1, 2] Nirmala College for Women, Coimbatore. Tamil Nadu, India

Abstract: Corrosive effect of Seed extract of *Lablab purpureus* (LLP) was investigated using phytochemical screening, weight loss technique, surface morphological analysis and quantum chemical studies. Influence of bioactive compounds in LLP extract contributes for adsorption properties towards mild steel (MS). The maximum inhibition efficiency of LLP extract was 97.98 % in 1N HCl for immersion period of 5h at 2.5 % v/v. SEM analysis established formation of protective layer on mild steel surface. Inhibition efficiency was found to increase with increasing concentration of LLP extract at room temperature. Results from various studies show that LLP can serve as an efficient inhibitor for corrosion prevention of mild steel in 1N HCl medium. Inhibition action may be contributed by the products of hydrolysis of active constituents of seed extract.

***IndexTerms* - *Lablab purpureus*, weight loss method, quantum chemical studies, mild steel, corrosion Inhibitor**

I. INTRODUCTION

HCl is used in various industrial sectors for removal of undesired scales and rust. Application of inhibitors is one of the most practical process for protection against corrosion, especially in acidic medium. Different organic and inorganic compounds have been used for preventive measures. Though these compounds have exhibited good anticorrosive activity most of them are highly toxic to human life and the environment. Environmentally safe corrosion inhibitors in industries have been always a global concern and researchers track for toxic free agents to fulfill the needs of economy. Use of natural products as corrosion inhibitor are gaining more attention in order to protect the metal against corrosion in aggressive acid solution. In this current work, *Lablab purpureus* seed extract has been used as a corrosion inhibitor. *Lablab purpureus* L (Fig 1) belongs to Fabaceae family and commonly known as Dolichos bean, Hyacinth bean or Field bean and most ancient crops among cultivated plants.

II. MATERIALS AND METHODS

2.1 Preparation of LLP Seed Extract

Lablab purpureus seeds were collected from local market, Coimbatore, Tamilnadu, India. Seeds were cleaned; shade dried and ground into powder using a blender, sieved and fine powder was stored in air tight container. 25gm of dried seed powder was boiled in 500ml of 1N HCl in reflux condenser for 3 hours and was kept overnight for better extraction. Next day, extract was filtered and filtrate volume was made up to 500 ml using 1N HCl. Various concentrations were prepared from the stock solutions.

Fig 1. *Lablab Purpureus* Seeds and seed powder

2.2 Phytochemical Analysis

Standard procedures were employed to test presence of phytochemicals such as, terpenoids, phenols, flavonoids, steroids, tannins, saponins, and alkaloids in seed powder of Lablab purpureus (Harborne 1984; Kokate, 1999).

2.3 Mild Steel Preparation

Mild steel coupons were subjected to spark analysis to find percentage composition of elements present in material using ARL QUANTRIS optical emission spectrometer at SiTARC, Coimbatore. Results showed MS with the following composition. (Wt %) : C 0.045%, Ni 0.035%, Mo 0.018%, P 0.031%, Si 0.063%, S 0.017%, Mn 0.380% and rest was Fe.

2.4 Weight Loss Measurement

Mild steel samples were cut into small pieces of dimensions 5 × 1 × 0.2 cm and were abraded with a series of emery papers, washed with distilled water, degreased with acetone and dried. After weighing accurately, specimens in triplicate were immersed in test solutions for specified periods of immersion in absence and presence of LLP extract. After exposure at interval of time, specimens were removed, rinsed with water, dried in warm air then stored in a desiccator to remove moisture content and then reweighed. Experiments (Kavitha and Gunavathy, 2014) were performed with concentrations: 0.10 % v/v, 0.50 % v/v, 1.00 % v/v, 1.50 % v/v, 2.00 % v/v and 2.50 % v/v at time intervals: 1h, 3h, 5h, 7h, and 24h. Corrosion rate and inhibition efficiency was calculated using formula:

$$\text{Corrosion rate} = (87.6 \times W) / DAT \text{ (mm / y)} \quad (1)$$

Where, mm / y = millimeter per year, W = Loss in weight in milligrams, D = Metal density in g / cm^3 (7.86 g / cm^3), A = Area of sample (Sq cm), T = Time of exposure of metal surface (hours), 87.6 = Conversion factor value.

$$\text{Inhibition Efficiency } IE\,\% = \frac{WL - WL_{inh}}{CR} X\ 100 \quad (2)$$

Where, WL = Weight loss of mild steel in absence of inhibitor, WL_{inh} = Weight loss of mild steel in presence of inhibitor

2.5 Surface Morphological Analysis

Mild steel specimens used for surface morphology examination were immersed in 1N HCl in the absence and presence of LLP seed extract at room temperature for 5 hours at 2.5 % v/v. Nature of metal surface was analyzed by Scanning Electron Microscope (SEM) at Karunya University, Coimbatore.

2.6Computational Analysis

Theoretical quantum chemistry helps us to compute predictions of quantum theory, as atoms and molecules can only have discrete energies [Bouklah et al, 2005]. Quantum chemistry computer programs are used in computational chemistry to predict electronic properties of molecules. Molecular properties related to reactivity and selectivity of inhibitors like ionization potential (I), electron affinity (A), electronegativity (χ), global hardness (η) and softness (σ), were estimated according to Koopman's theorem (1933). MOPAC [Wan nik et al, 2011; Stewart, 1989] is a popular computer program used in computational chemistry. It has been designed to implement semi - empirical quantum chemistry algorithms.

III. RESULTS AND DISCUSSION

3.1 Phytochemical Screening

LLP seed extract (Table 1) was analyzed to detect presence of active functional groups using standard qualitative procedures. LLP extract showed presence of flavonoids, steroids, amino acids and carbohydrates. Plants are rich in primary and secondary metabolites with different viable functions. Presence of active constituents in extract contributes for inhibition efficiency of seed extract towards mild steel corrosion.

Table 1. Phytochemical Constituents in LLP Seed Extract

S. No	PHYTO COMPOUNDS	LLP
1.	Alkaloids	-
2.	Phenols	-
3.	Flavonoids	+
4.	Tannins	-
5.	Saponins	-
6.	Steroids	+
7.	Glycosides	-
8.	Reducing Sugar	-
9.	Amino Acids	+++
10.	Terpenoids	-
11.	Carbohydrates	++

Key: "+++" active compound copiously present, "++" active compound moderately present, "+" active compound present, "-" active compound absent.

3.2 Weight loss method

Weight loss technique was done for mild steel in 1N HCl with various concentrations of the extract ranging from 0.10 % v/v to 2.50 % v/v and corresponding values of inhibition efficiency and corrosion rate are tabulated. It was observed from Table 2 that corrosion rate decreased and inhibition efficiency increased with increase in concentration of LLP / 1N HCl.

Table 2. CR of Mild Steel and IE of LLP Extract in 1N HCl Acid at Various Concentration and Immersion Period

Conc. of extract (% v/v)	1 h		3 h		5 h		7 h		24 h	
	CR mm/y	IE %	CR mm/y	IE %	CR mm/y	IE %	CR mm/y	IE %	CR mm/y	IE %
BLANK	17.832		26.90		15.45		11.08		24.06	
0.10	2.229	87.50	2.75	89.78	1.54	90.04	1.18	89.37	2.68	88.85
0.50	1.895	89.37	2.19	91.85	1.23	92.06	0.89	91.95	2.45	89.81
1.00	1.560	91.25	1.82	93.23	0.89	94.23	0.75	93.25	2.35	90.22
1.50	1.337	92.50	1.63	93.92	0.78	94.95	0.67	93.97	2.02	91.59
2.00	1.226	93.12	1.37	94.89	0.74	95.24	0.61	94.54	1.72	92.86
2.50	1.003	94.38	1.23	95.44	0.31	97.98	0.38	96.55	1.32	94.52

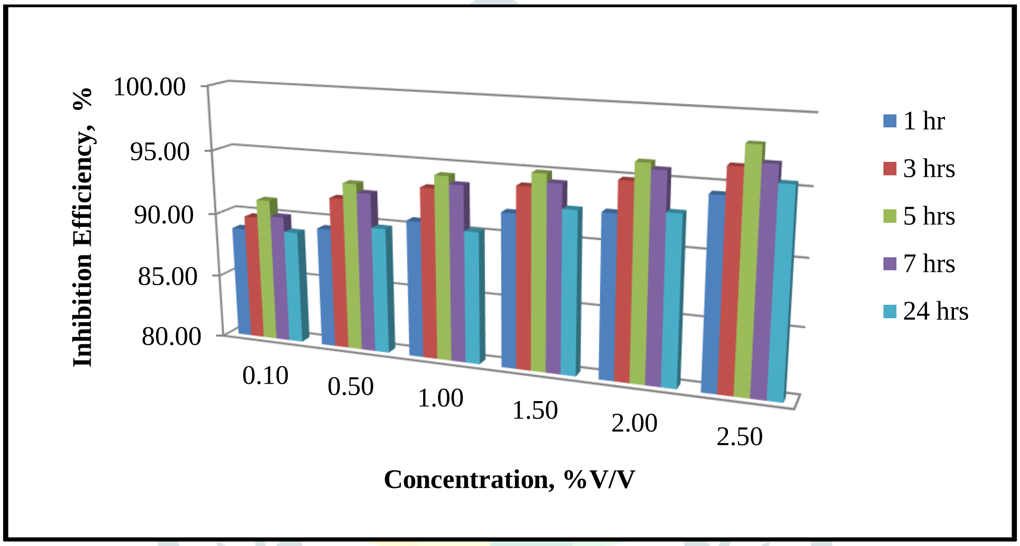

Fig 2. Influence of Concentration of LLP/1N HCl on IE % of Mild Steel

3.3 Surface Morphological Studies

Scanning Electron Microscopy (SEM) was employed to analyze mild steel surface examination exposed to medium without and with inhibitor. SEM photographs (Fig 3 and 4) of the mild steel specimens revealed the inhibitive layer sediment on surface produce a good protection to material. Inhibition was mainly due to formation of protective film by phytochemical active components present LLP seed extract / 1N HCl.

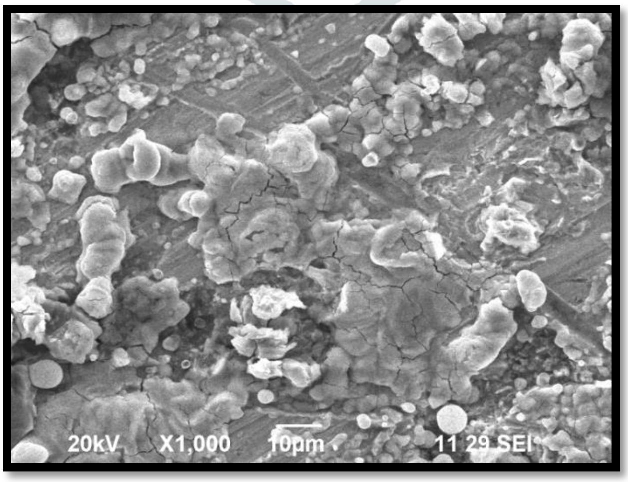

Fig 3. Mild Steel Exposed to 1N HCl Medium.

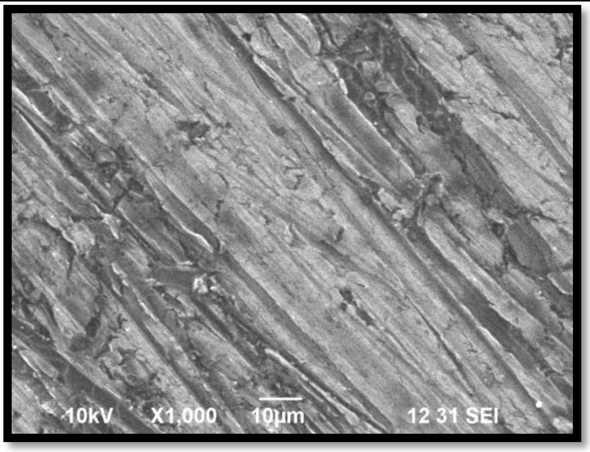

Fig 4. Mild Steel Exposed to IN HCl + 2.5 % LLP Seed Extract

3.4 Computational Analysis

Computational analysis are performed by application of quantum chemical calculations with implementation of Semi-empirical method Parameterized Model 3 (PM3). Structures of phytoconstituents of LLP seed extract were obtained from literature search; these structures were geometrically optimized with ArgusLab and electronic parameters of optimized stable molecules were calculated using MOPAC software. Output of MOPAC program reports values such as ionization potential, Eigen values, dipole moment etc. According to Koopmans theorem, ionization potential of a molecule is equal to negative of energy of highest occupied molecular orbital. Optimized structures of compounds studied are given in Figure 5 -7. Table 3 represents quantum chemical parameters for organic molecules present in LLP seed extract.3.3 Theoretical framework

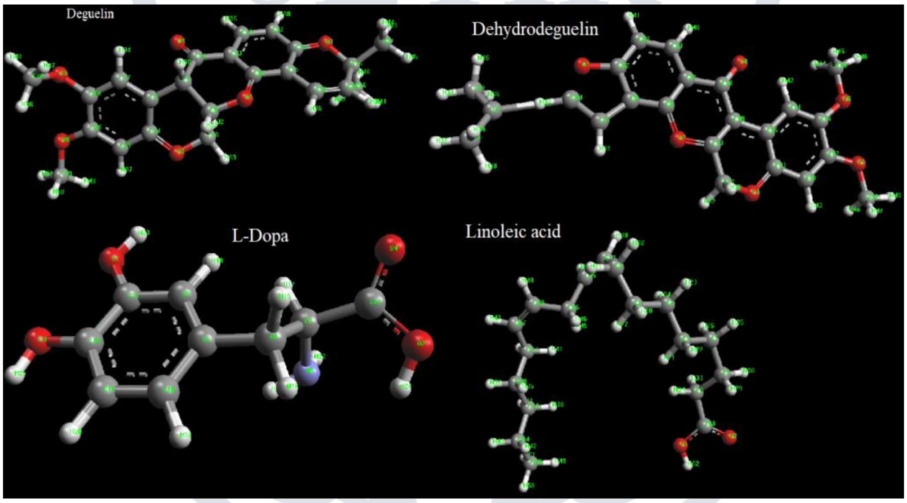

Fig 5. Molecular Structures of Deguelin, Dehydrodeguelin, L-Dopa and Linoleic acid

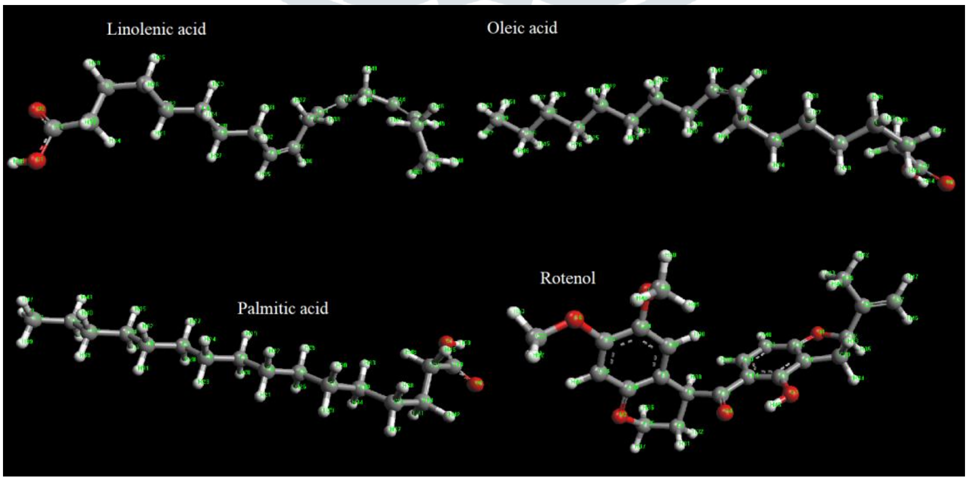

Fig 6. Molecular Structures of Linolenic acid, Oleic acid, Palmitic acid and Rotenol

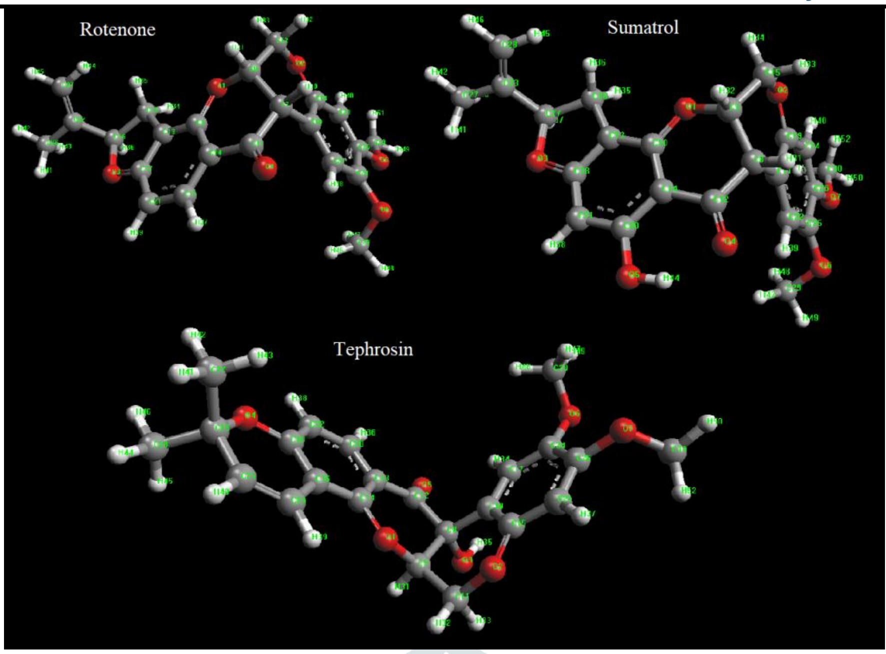

Fig 7. Molecular Structures of Rotenone, Sumatrol and Tephrosin

Energy of highest occupied molecular orbital (EHOMO) is a measurement to predict tendency of molecules to donate electrons. Therefore, higher values of EHOMO specify excellent tendency towards contribution of electron and thereby enhance adsorption of inhibitor on metal surface and demonstrate better inhibition efficiency [Hadisaputra et al, 2017]. ELUMO indicates ability of molecule to accept electrons [Zarrok et al., 2015]. Frontier molecular orbital diagrams of phytoconstituents of LLP seed extract are represented in Figures 8 - 13.

Energy of lowest unoccupied molecular orbitals indicates ability of molecule to accept electrons. Lower the value of ELUMO shows more probability of molecule to accept electrons. The higher energy gap (ΔE) may enhance corrosion inhibition efficiency. From results of quantum chemical analysis, it is evident that Dehydrodeguelin was the best inhibitor and has highest value of EHOMO -7.876 (eV) and would be better adsorbed on metal surface [Zarrok et al., 2015]. The energy gap (ΔE) provides information about overall reactivity of a molecule. As ΔE decreases, reactivity of molecule increases leading to increase in inhibition efficiency of molecule. Low values of ΔE gap will render good inhibition efficiencies since energy to remove an electron from last occupied orbital will be minimized [Herrag et al., 2012].

From quantum chemical study, tendency for (ΔE) values followed the order Dehydrodeguelin < Rotenol < Deguelin < Sumatrol < Rotenone < Tephrosin < L-Dopa < Linoleic acid < Linolenic acid < Oleic acid = Palmitic acid which suggests that inhibitor Dehydrodeguelin has highest reactivity in comparison to other compounds and would therefore likely interact strongly with metal surface [Herrag et al., 2012]. Since the contribution of phytochemicals of seed extract towards inhibition efficiency was mixed-type. Assessment of phytochemical helps us to focus on phytochemical individually.

Favorability of molecules that are susceptible to nucleophilic or electrophilic attack can be predicted with ESP-mapped density surface. ESP surface are useful for qualitative interpretations of chemical reactivity of molecules (Otuokere, 2017). Red-coloured surface shows region of high electron density and this region was prone for nucleophilic attack. White-colored surface are the methyl-rich region and these regions are susceptible to electrophilic attack.

Table 3. Quantum Chemical Parameters for Phytochemical of LLP Seed Extract

S. No.	Compounds	E_{HOMO} eV	E_{LUMO} eV	Energy gap eV
1	Deguelin	-8.281	-0.477	7.804
2	Dehydrodeguelin	-7.876	-1.178	6.698
3	Levodopa	-9.213	-0.208	9.005
4	Linoleic acid	-8.769	0.556	9.325
5	Linolenic acid	-8.785	0.545	9.330
6	Oleic acid	-8.766	0.562	9.328
7	Palmitic acid	-8.777	0.551	9.328
8	Rotenol	-8.391	-0.682	7.709
9	Rotenone	-8.292	-0.371	7.921
10	Sumatrol	-8.356	-0.445	7.911
11	Tephrosin	-8.707	-0.547	8.160

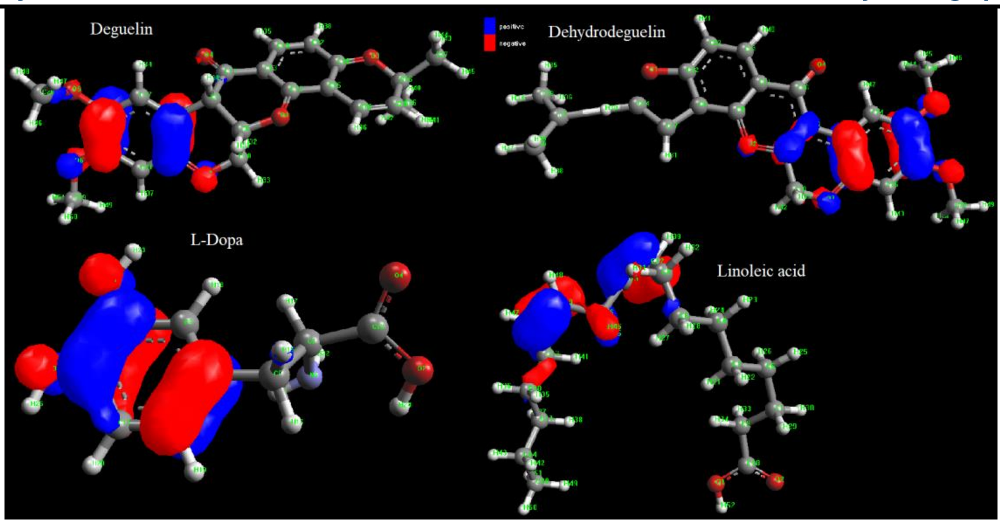

Fig 8. HOMO Orbitals of Deguelin, Dehydrodeguelin, L-Dopa and Linoleic acid

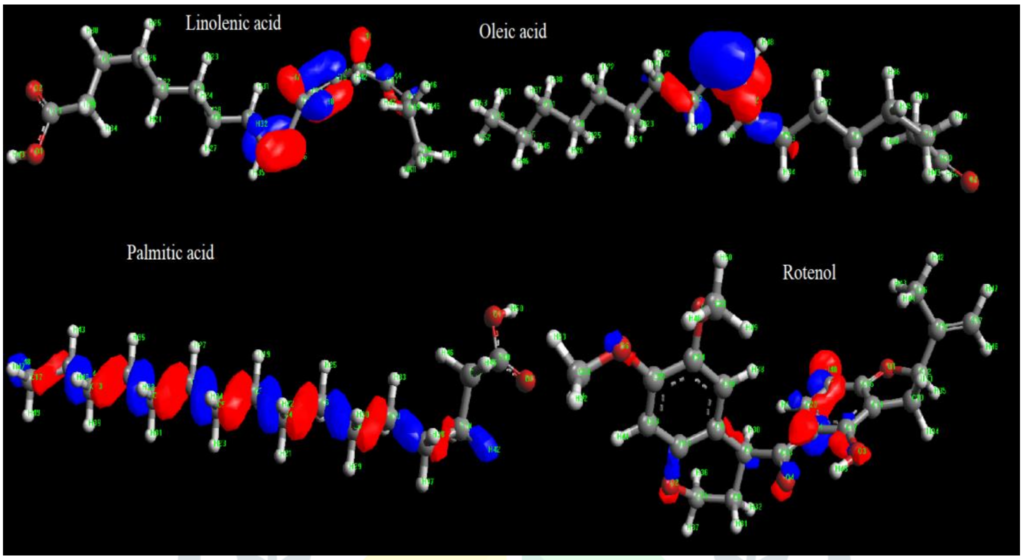

Fig 9. HOMO Orbitals of Linolenic acid, Oleic acid, Palmitic acid and Rotenol

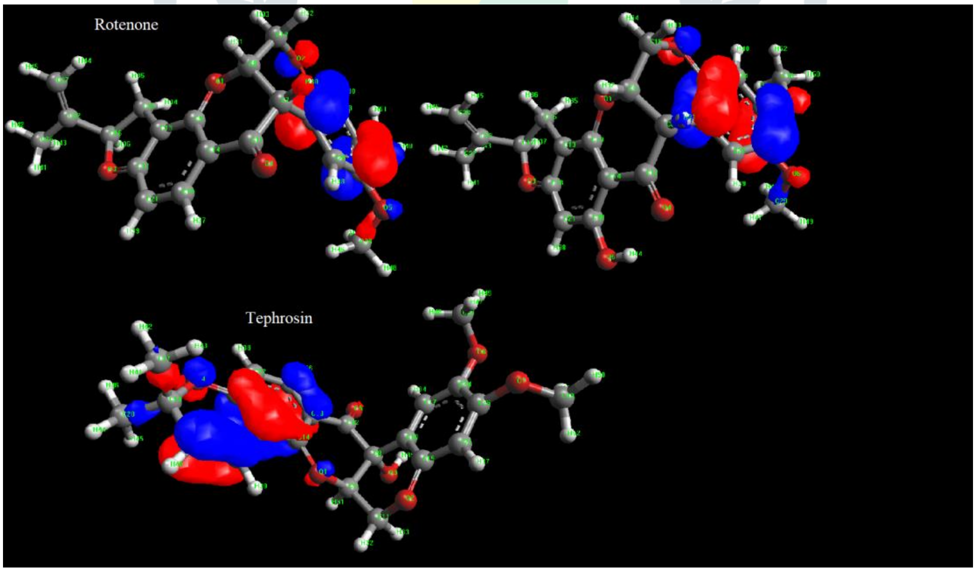

Fig 10. HOMO Orbitals of Rotenone, Sumatrol and Tephrosin

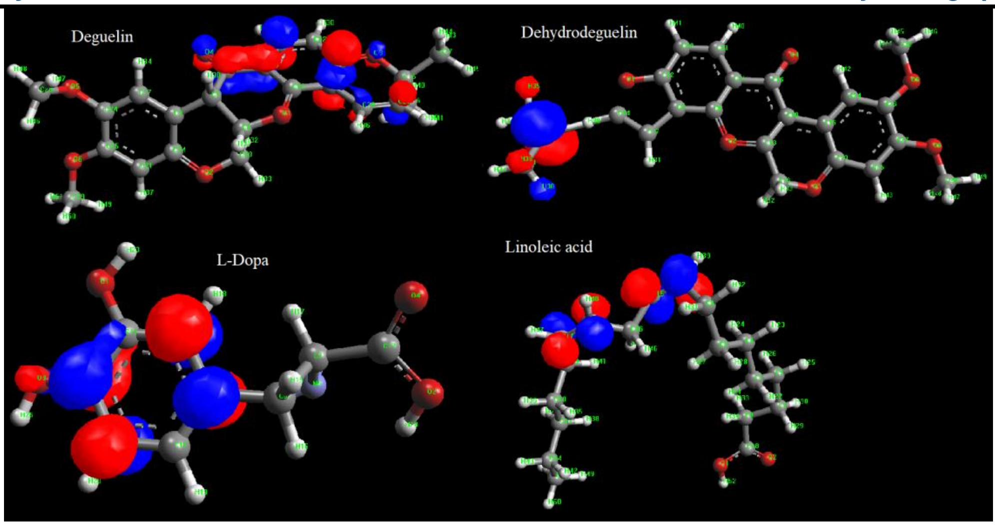

Fig 11. LUMO orbitals of Deguelin, Dehydrodeguelin, L-Dopa and Linoleic acid

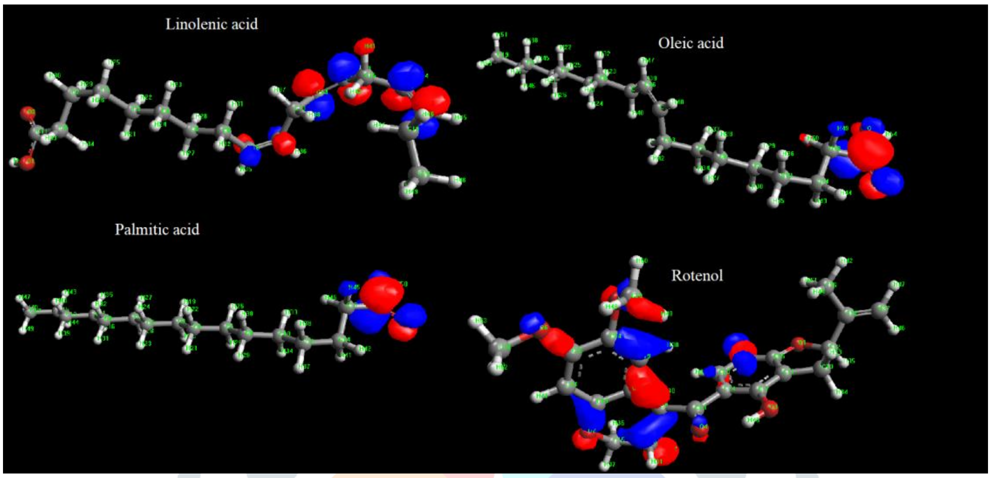

Fig 12. LUMO Orbitals of Linolenic acid, Oleic acid, Palmitic acid and Rotenol

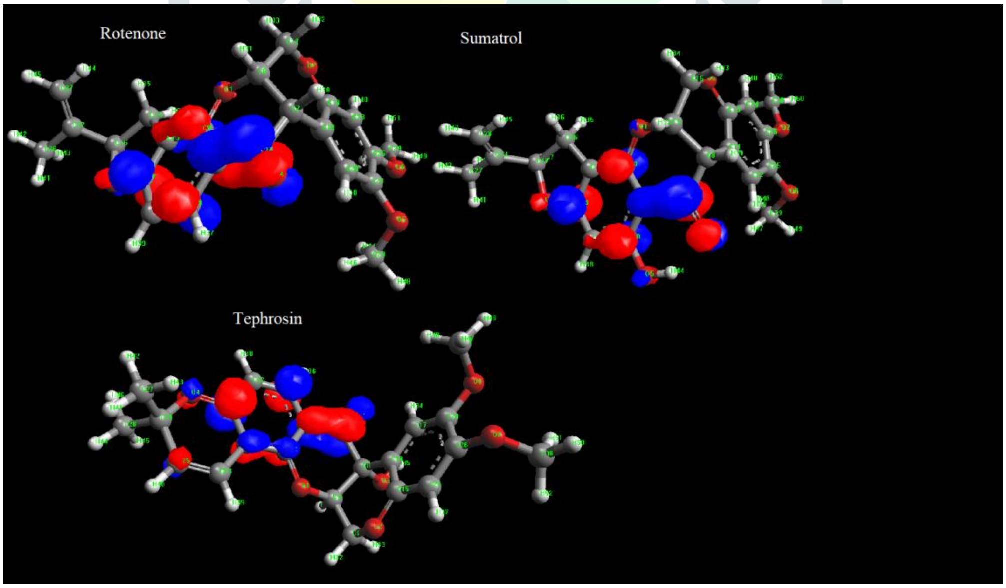

Fig 13. LUMO Orbitals of Rotenone, Sumatrol and Tephrosin

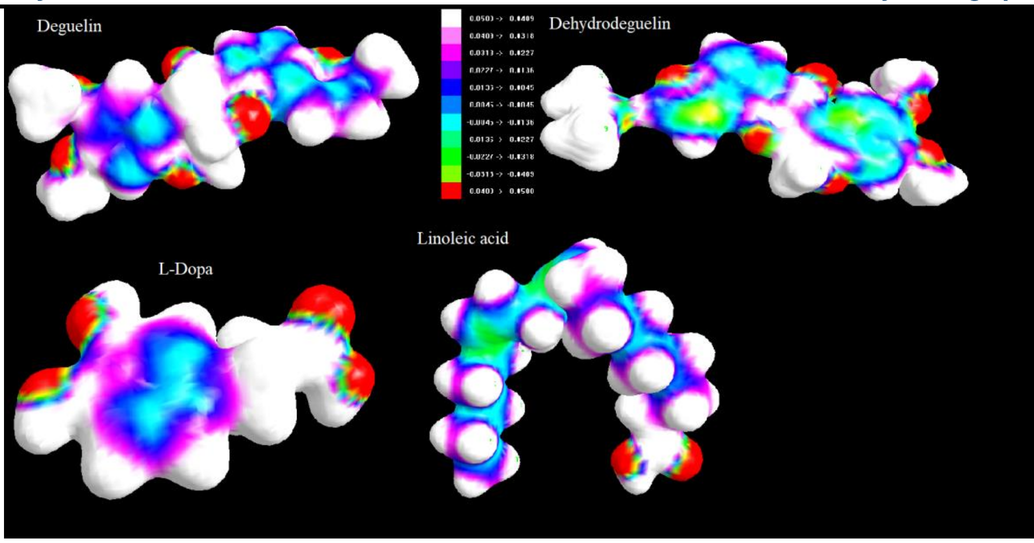

Fig 11. ESP of Deguelin, Dehydrodeguelin, L-Dopa and Linoleic acid

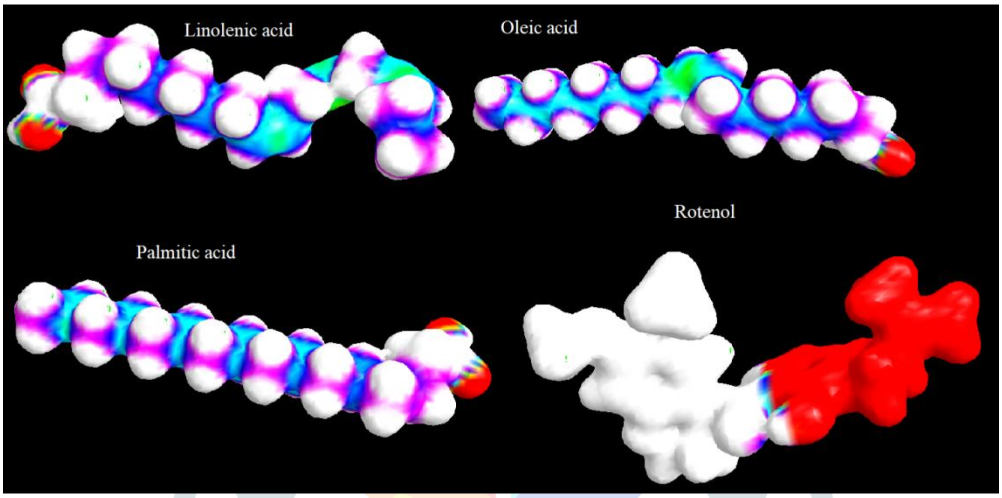

Fig 12. ESP of Linolenic acid, Oleic acid, Palmitic acid and Rotenol

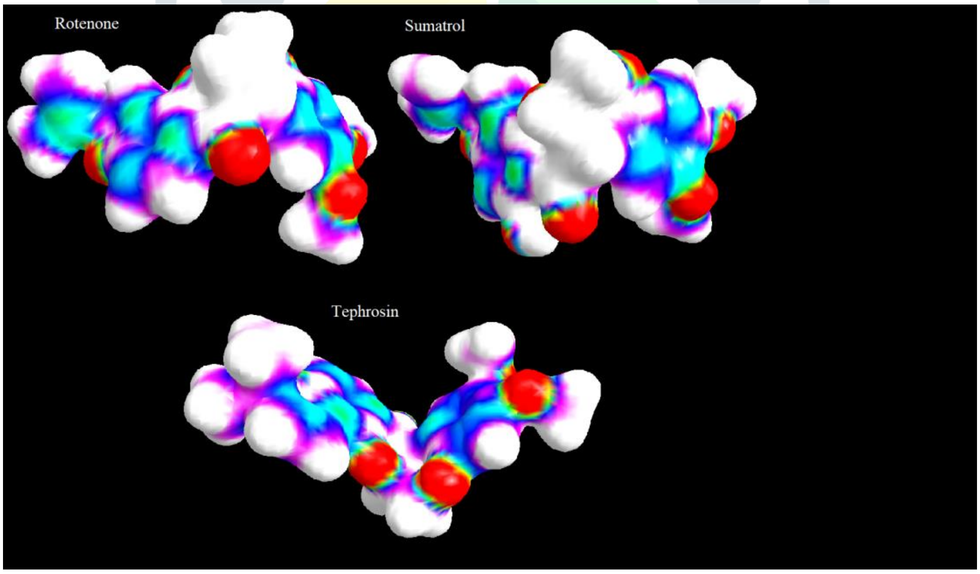

Fig 13. ESP of Rotenone, Sumatro and Tephrosin

CONCLUSION

LLP extract can acts as good and efficient corrosion inhibitor for MS in 1N HCl medium. Inhibition efficiency values increase with increasing concentrations of LLP seed extract. Surface examination studies revealed that phytochemical constituents of LLP extract adsorbed on surface of MS provide corrosion protection. Quantum chemical parameters such as molecular orbital analysis, HOMO-LUMO energy gap were carried out by PM7 which indicates active principles of LLP extract form a uniform film over mild steel surface, which effectively protects from corrosion environment.

References

1. J. B. Harborne, "Phytochemical Methods: A Guide to Modern Techniques of Plant Analysis", Chapman and Hall, London, 2rd Ed., 1984.
2. A. Kokate, "Phytochemical Methods", Phytotherapy Res., Vol.78, 126 – 129, 1999.
3. V. Kavitha and Dr. N. Gunavathy, 2014, "Evaluation of Daucus Carota aerial extract as corrosion inhibitor of mild steel in hydrochloric acid medium", International Journal of Research in Advent Technology, Vol. 2, pp 146-154.
4. M. Bouklah, A. Attayibat, S. Kertit, A. Ramdani, B. Hammouti, 2005, "Corrosion in Mild Steel", Applied Surface Science Journal, Vol. 242, pp 399 - 406.
5. T. Koopmans, 1933, "Uber die Zuordnung von Wellenfunktionen und Eigenwerten zu den einzelnen Elektronen eines Atoms", Physica, Vol. 1, pp104–113.
6. J. P. Stewart, 1989, "Optimization of parameters for semiempirical methods I. Method", Journal of Computational Chemistry, Vol. 10, pp 209 - 220.
7. Wan Nik, W. B. Ahmad, R. Rosliza, Prawoto, F. Zuklifi, 2011, "The Study of Temperature Effect on Mild Steel", International Journal of Engineering Science and Technology, Vol. 36, pp 6462 – 6471.
8. S. Hadisaputra, S. Hamdiani, A. A. Purwoko, 2017, "Corrosion Inhibition of Steel in Acidic Medium by Eugenol Derivatives: Insight from Density Functional Calculation", J Applied Chem. Sci., Vol. 4, pp 312-317.
9. H. Zarrok, M. Assouag, A. Zarrouk, H. Oudda, A. Hallaoui, R. Touzani, M. Allali, B. Hammouti, M. El Hezza , M, Bouachrine, 2015, "Quantum Chemical Study on the Corrosion Inhibition of Some Bipyrazoles", Research Journal of Pharmaceutical, Biological and Chemical Sciences, Vol 6, pp 1853-1860.
10. L. Herrag, M. Bouklah, N. S. Patel, B. M. Mistry, B. Hammouti, S. Elkadiri, M. Bouachrine, 2012, "Research on Chemical Intermediates", Journal of Chemical Science, Vol 38, pp 1669 – 1690.
11. I. E. Otuokere, 2017, "Electrostatic Potential-Mapped Electron Density Surface and Conformation Analysis of an Antidepressant, Mirtazapine", Acta Scientific Pharmaceutical Sciences,Vol. 1, pp 18 -22.