Bauhinia acuminata leaf extract as corrosion inhibitor for Mild Steel in 1N hydrochloric acid medium: an experimental and computational investigation

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ABSTRACT *Eco friendly corrosion inhibitor can prevent use of expensive and harmful synthetic inhibitor. Plant extract contain many ingredients which are environmentally friendly, non-toxic and readily available. Plant components contain several organic compounds and possess ability to get adsorbed onto the metal surface through polar atoms and form a protective film. Influence of Bauhinia acuminata leaf (BAL) extract on corrosion of mild steel in 1N HCl was studied using weight loss method, FTIR, surface examination analysis and computational analysis. Data so obtained were used to explain effectiveness of inhibitor when present in different concentrations. Surface examination studies help to understand changes that occur on surface layer with respect to BAL extract concentration. Analysis revealed that BAL acts as an efficient inhibitor and shows good inhibition efficiency.*

Keywords: *Bauhinia acuminata, weight loss measurements, FTIR, surface examination studies, computational analysis.*

I. INTRODUCTION

In industrial environments, steel is affected by different corrosion attacks because of acids like sulphuric acid and hydrochloric acid during various industrial processes (acid pickling, chemical cleaning, oil well acidification) [1]. Naturally occurring molecules exhibit a strong affinity for metal surfaces and help toward the development of environmentally friendly corrosion inhibitors. Presently various plant extracts, containing mixture of compounds having oxygen, sulphur and nitrogen elements, are employed as green corrosion inhibitors from acidic solution. Generally, plant extracts are non-hazardous, friendly, cheap, readily available, and renewable sources [2].

Aim of the present work was to investigate *Bauhinia acuminata* leaf extract **(**BAL**)** in order to find a naturally occurring, cheap and environmentally safe substance that could be used for inhibition purposes.

II. MATERIALS AND METHODS

A. Collection of *Bauhinia acuminata* and plant extract preparation

Bauhinia acuminata leaves (Figure 1) were collected from house garden in Palakkad, Kerala, India, cleaned, shade dried and ground into powder using a blender, sieved and fine powder was stored in air tight container. 25gm of dried leaf powder was boiled in 500ml of 1N HCl with reflux condenser for 3 hours and was kept overnight. The following day, extract was filtered and filtrate volume was made up to 500ml using respective acid. Extract was taken as 5% stock solution and from this; other concentrations were prepared (Figure 2).

Fig.1. Leaves of *Bauhinia acuminata*

Fig.2.Various Concentration of BAL Extract

B. Phytochemical analysis

Standard procedures were employed to test the presence of phytochemicals such as, terpenoids, phenols, flavonoids, steroids, tannins, saponins, and alkaloids in leaf powder of *Bauhinia acuminate* [3] [4].

C. Metal preparation

Mild steel coupons of size 5 × 1 × 0.2 cm were cut from a large sheet of mild steel obtained from local steel vendor, Coimbatore, India. A small hole of about 1.0 mm diameter near 1.5 cm side end for suspending. Coupons were degreased with acetone, pickled in conc. HCl and washed with distilled water and coupons were polished with 400, 600 grade of emery papers, cleaned, dried and stored in desiccator to avoid adsorption of moisture [5].

D. Weight loss measurements

Mild steel specimens were immersed in beaker containing 100ml acid solution without and with different concentrations of BAL using glass hooks for a predetermined time period at room temperature. Analyses were performed in triplicate for reproducibility. Weight loss measurements were carried out using a SHIMADZU model AY 220. Test specimens were removed and washed with de-ionized water, dried and reweighed. Experiments were performed for various parameters such as:

- Concentration variation (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)
- Different time intervals (1h, 3h, 5h, 7h, and 24h)

From the initial and final mass of specimens, weight loss was calculated, and corrosion rate (in mpy) [6] [7] was computed from the following equation:

$$\text{Corrosion rate, CR} = \frac{87.5\ \text{W}}{\text{DAT}} \qquad (1)$$

Where W is weight loss (mg) of the coupons, D is density of the coupon (7.8 g/cm^3), A is surface area of coupon (cm^3), and T is immersion time (h). Inhibition efficiency of mild steel was then calculated [8]. The percentage inhibition efficiency (IE %) of the inhibitor in terms of concentration has been calculated from expression,

$$\text{IE \%} = \frac{\text{Weight loss without inhibitor} - \text{Weight loss with inhibitor}}{\text{weight loss without inhibitor}} \times 100 \qquad (2)$$

E. Surface morphology

Surface analysis studies of mild steel specimens were done in order to study that occurrence during corrosion of mild steel in presence and absence of inhibitor in acid medium. Nature of metal surface was analyzed by Scanning Electron Microscope (SEM), and Fourier Transforms Infrared (FTIR) spectroscopic studies.

F. Computational analysis

Theoretical quantum chemistry mainly involves computational chemistry, which help us to calculate predictions of quantum theory as atoms and molecules can only have discrete energies [9]. Quantum chemistry computer programs are used in computational chemistry to implement methods of quantum chemistry. 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 [10]. MOPAC [11] is a popular computer program used in computational chemistry. It is designed to implement semi - empirical quantum chemistry algorithms.

III. RESULTS AND DISCUSSIONS

A. Phytochemical analysis

Extracts were subjected to phytochemical analysis to detect presence of biomolecules using standard qualitative procedures. Carbohydrates, tannins, and coumarins were copiously present in the *Bauhinia acuminata* leaf extract (Table 1). *Bauhinia acuminata* leaf extract showed moderate presence of saponins and terpenoid. *Bauhinia acuminata* extract showed presence of reducing sugar, alkaloids and quinones. Existence of primary bioactive metabolites of commercial importance could acts as precursors for synthesis of secondary metabolites.

Table.1. Phytochemical constituents present in BAL extract

PHYTO COMPOUND	BAL	PHYTO COMPOUND	BAL
Carbohydrates	+	Terpenoids	+
Reducing sugar	+	Phlobatannins	-
Alkaloids	+	Coumarins	+

Saponins	+	Cycloglycoside	-
Tannins	+	Quinones	+
Flavonoids	-		

B. Weight loss Measurements – Effect of Concentration

Table 2 shows values of inhibition efficiency obtained from weight loss measurements of mild steel for various concentrations of BAL in 1N HCl at room temperature after varied time period of immersion. Mild steel was found to corrode in 1N HCl acid solution. This was evidenced by decrease in corrosion rate with addition of plant extract to acids. It was found that inhibition efficiency increased with increase in concentration from 0.1 to 2.5% v/v and with increase in time due to adsorption of plant compound on to surface of metal and contribute protective layer (Figure 3) .

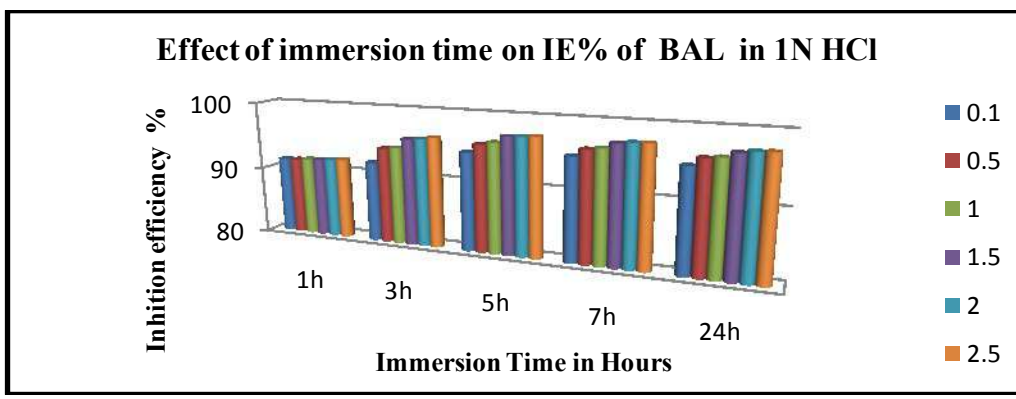

Fig.3. Influence of Immersion Time on IE % of in 1N HCl / BAL Extract

Table 2. Inhibition efficiency (IE) and corrosion rate (CR) of BAL/1N HCl against mild steel at various concentrations and different immersion period

Conc. of extract (%v/v)	1h		3h		5h		7h		24h	
	CR mm/y	IE (%)	CR mm/y	IE (%)	CR mm/y	IE (%)	CR mm/y	IE (%)	CR mm/y	IE (%)
BLANK	0.0459	-	0.0363	-	0.3271	-	0.2570	-	0.7511	-
0.10	0.0878	91.28	0.0029	91.79	0.0179	94.43	0.0129	94.98	0.0382	94.91
0.50	0.0039	91.32	0.0021	94.04	0.0138	95.70	0.0100	96.10	0.2970	96.04
1.00	0.0039	91.50	0.0020	94.32	0.0127	96.11	0.0092	96.39	0.0277	97.30
1.50	0.0038	91.61	0.0015	95.70	0.0094	97.12	0.0071	97.20	0.0220	97.01
2.00	0.0037	91.74	0.0014	95.91	0.0090	97.20	0.0066	97.41	0.0200	97.33
2.50	0.0037	91.85	0.0013	96.21	0.0086	97.32	0.0064	97.50	0.0190	97.40

C. Scanning Electron Microscopy (SEM)

The surface morphological characteristics of the uninhibited mild steel in 1N HCl and inhibited mild steel using BAL in 1N HCl analyzed at an accelerating voltage using SEM photographs of the mild steel specimens after immersion in 1N HCl for three hours at room temperature without and with inhibitor containing optimum concentration of (2.5 % v/v) plant extract are presented in Figure 4 and 5. Inhibition action due to formation of protective film by the phytochemical components present in plant extract on mild steel surface results in decrease in contact between metal and destructive medium and effectively exhibit excellent inhibition effect.

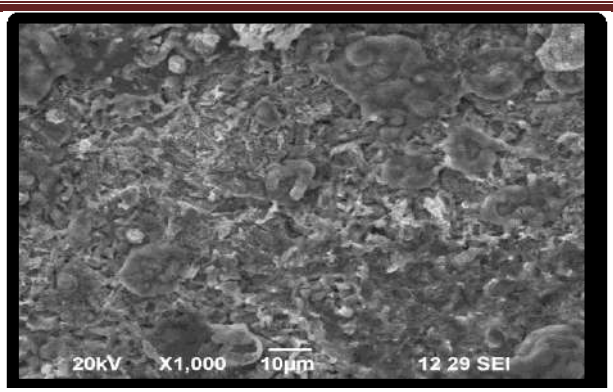

Fig.4. Photograph of Mild Steel exposed to IN HCl (Blank)

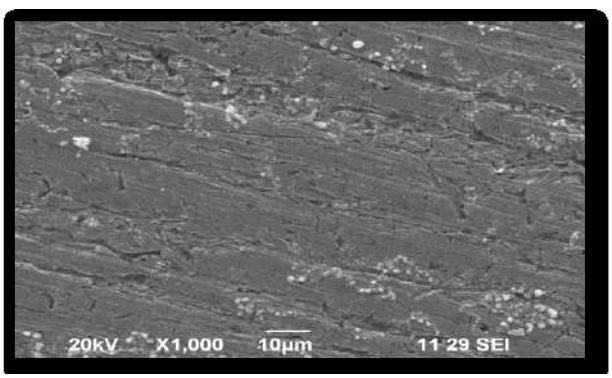

Fig.5. Photograph of Mild Steel exposed to IN HCl + 2.5% BAL

D. Quantum Chemical Calculations

Structures of phytoconstituents of *Bauhinia acuminata* leaf extract were first optimized and simulations were conducted to calculate electronic parameters. Quantum chemical calculations were done using Semi-empirical method Parameterized Model 3 (PM3). The output of MOPAC program reports values such as ionization potential, Eigen values, dipole moment etc. According to Koopmans theorem ionization potential is negative of Eigen value of highest occupied molecular orbital (HOMO). Optimized structures of compounds studied are given in Figure 6 and 7. Table 3 represents quantum chemical parameters for organic molecules present in *Bauhinia acuminata* leaf extract.

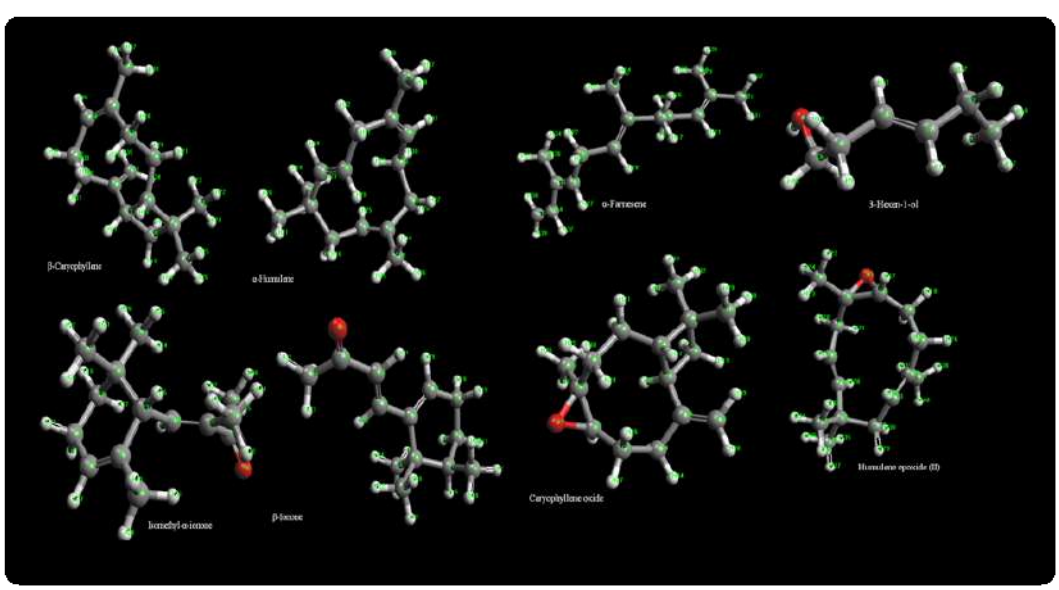

Fig.6. Structure of β-Caryophyllene, α-Hummulene, Isomethyl-α-ionone, β-Ionone, α-Farnesene, 3-Hexene-1-ol, Caryophyllene oxide, Hummulene epoxide

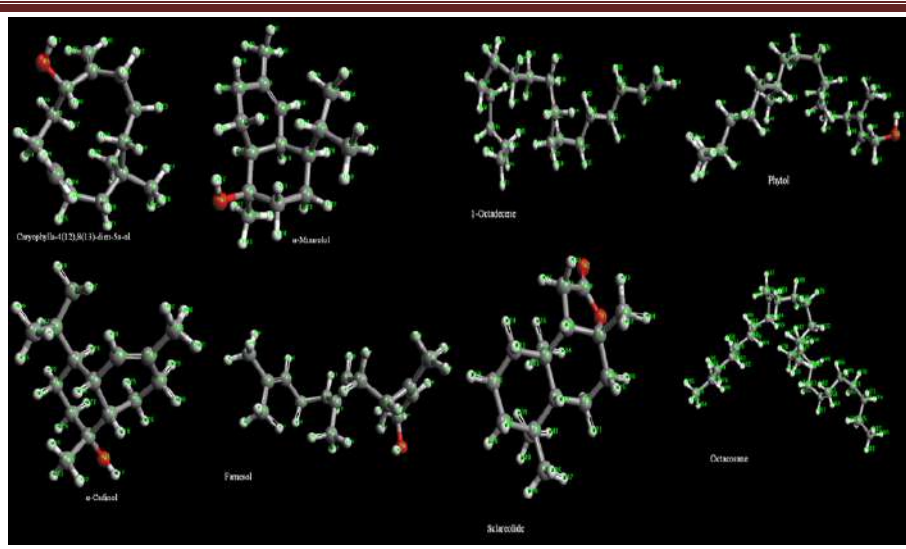

Fig.7. Structure of Caryophylla-4(12), 8(13)-dien-5a-ol, α-Murrolol, α-Cadinol, Farnesol, 1-Octadecene, Phytol, Sclareolide, Octacosane

Energy of highest occupied molecular orbital (E_{HOMO}) measures tendency of molecule to donate electrons. Therefore, higher values of E_{HOMO} indicate good tendency towards contribution of electron, enhance adsorption of inhibitor on metal surface and demonstrate better inhibition efficiency [12]. E_{LUMO} indicates ability of molecule to accept electrons [13]. Frontier molecular orbital diagrams of phytoconstituents of *Bauhinia acuminata* leaf extract are represented in Figures 8 - 11.

The energy of lowest unoccupied molecular orbitals indicates ability of molecule to accept electrons. The lower value of E_{LUMO} more probability of molecule to accept electrons. The higher energy gap (ΔE) may enhance corrosion inhibition efficiency. From the results of the quantum chemical calculations, it is evident that 1-Octadecene which is the best inhibitor has the highest value of E_{HOMO}-5.509 (eV) and would be better adsorbed on metal surface [13].

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 [14].

In quantum chemical study, tendency for (ΔE) values follows order 1-Octadecene < Isomethyl-α-ionone < β-Ionone < Humulene epoxide (II) < Sclareolide < α-Muurolol < α-Cadinol < α-Humulene < Caryophyllene oxide < Farnesol < Phytol < β-Caryophyllene < α-Farnesene < Caryophylla-4(12), 8(13) – dien-5a-ol < 3 – Hexen – 1-ol < Octacosane which suggests that inhibitor 1-octadecene has highest reactivity in comparison to other compounds and would therefore likely interact strongly with metal surface [14].

Table 3. Quantum Chemical Parameters for Organic Molecules of *Bauhinia acuminata*

S.No.	Compounds	E_{HOMO} eV	E_{LUMO} eV	Energy gap (ΔE) eV
1	β–Caryophyllene	-9.266	0.522	9.788
2	α–Humulene	-9.135	1.133	10.268
3	Isomethyl –α–ionone	-8.273	0.399	8.672
4	β–Ionone	-8.337	0.331	8.668
5	α–Farnesene	-9.358	0.796	10.154
6	3 – Hexen – 1–ol	-10.166	1.138	11.304
7	Caryophyllene oxide	-9.166	1.190	10.356
8	Humulene epoxide (II)	-8.581	0.727	9.308

9	Caryophylla-4(12),8(13)-dien-5a-ol	-9.591	1.256	10.847
10	α–Muurolol	-9.051	1.452	10.503
11	α–Cadinol	-9.113	1.393	10.506
12	Farnesol	-9.174	1.236	10.410
13	1-Octadecene	-5.509	-2.123	3.386
14	Phytol	-9.177	1.399	10.576
15	Sclareolide	-8.695	0.984	9.679
16	Octacosane	-10.678	3.904	14.582

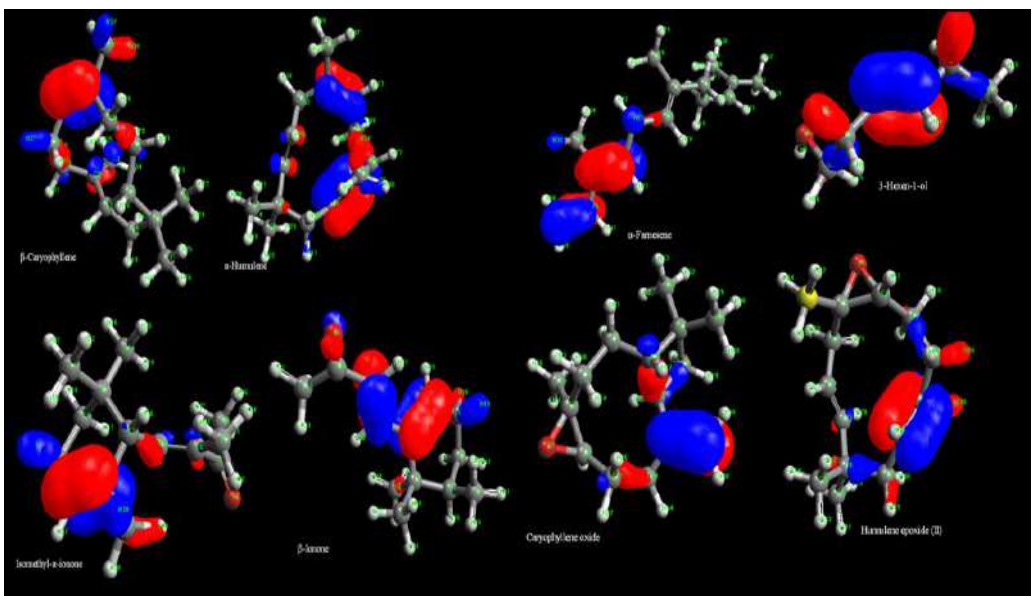

Fig.8. HOMO orbitals of β Caryophyllene, α-Hummulene, Isomethyl-α-ionone, β- Ionone, α-Farnese, 3- Hexen 1-ol, Caryophyllene oxide, Hummulene epoxide

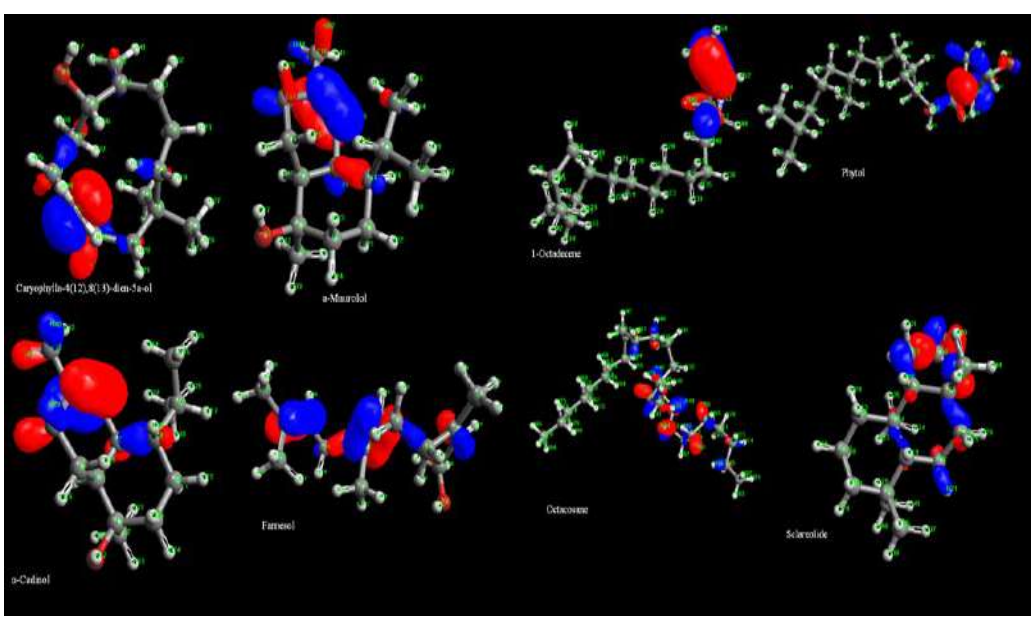

Fig.9. HOMO orbitals of Caryophylla-4(12), 8(13) – dien-5a-ol, α-Muurolol, α-Cadinol, Farnesol, 1-Octadecene, Phytol, Octacosane, Sclareolide

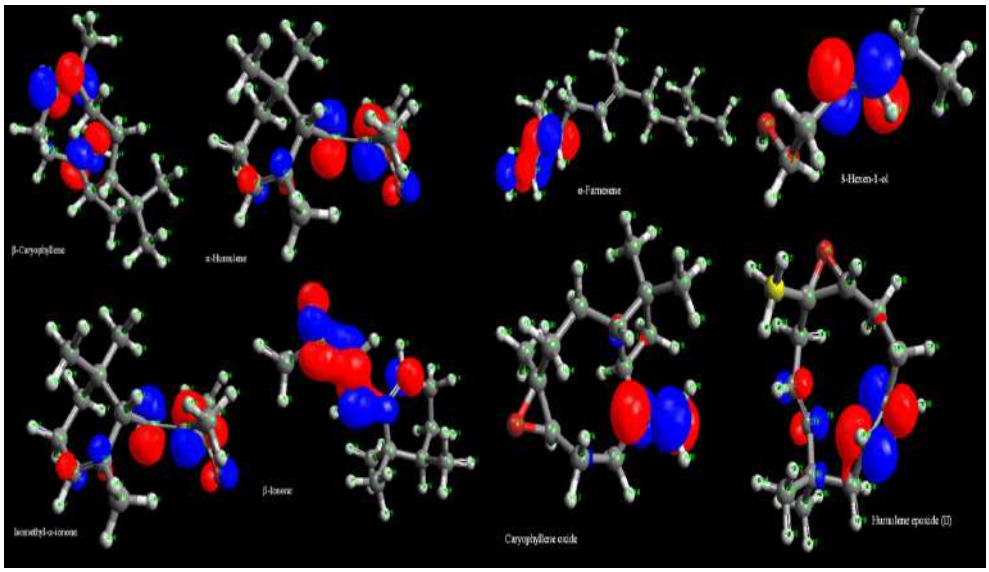

Fig.10. LUMO orbitals of β-Caryophyllene, α-Humulene, Isomethyl – α-ionone, β Ionone , α-Farnesene, 3-Hexen-1-ol, Caryophyllene oxide, Humulene epoxide

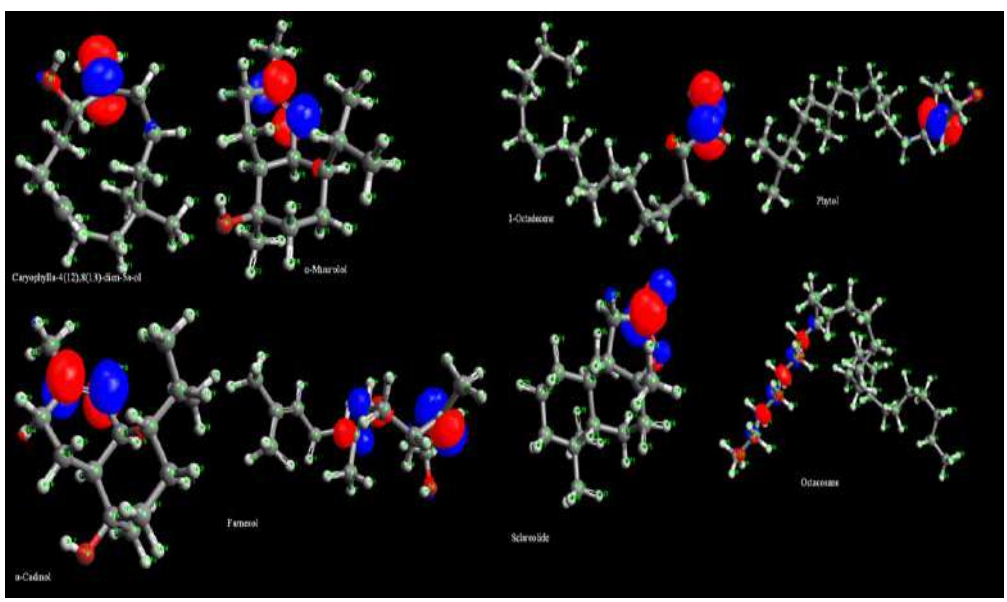

Fig.11. LUMO orbitals of Caryophylla-4(12), 8(13) – dien-5a-ol, α-Muurolo,α-Cadinol, Farnesol, 1-Octadecene, Phytol, Sclareolide, Octacosane

IV. CONCLUSION

- Results obtained from experimental data showed that BAL can act as an effective inhibitor for the corrosion of steel in 1N HCl.
- BAL extract showed presence saponins, terpenoid, reducing sugar, alkaloids and quinines by qualitative analysis.
- Maximum inhibitor efficiency was observed at an optimum concentration of 2.5 % v / v. The inhibition efficiency increased with the increasing concentration of inhibitor. Corrosion of mild steel in HCl acid medium was significantly reduced on additions of BAL extract. BAL showed maximum of efficiency 97.50 % in 1N HCl at 7 hours of immersion.

- SEM revealed that BAL acts as corrosion inhibitor for mild steel. The comparison of surface images revealed that BAL is absorbed on metal surface, thereby decreasing corrosion attack on metal surface.
- Quantum chemical parameters such as highest molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), energy levels, HOMO-LUMO energy gap and electronic density were virtually identified. Quantum analysis demonstrated reactive centers of electrophilic and nucleophilic attack and strong inhibition properties of bioactive molecules of BAL. 1-Octadecene is best inhibitor has highest value of EHOMO-5.509 (eV) and would be better adsorbed on metal surface. 1-octadecene has highest reactivity in comparison to other compounds.

From experimental and theoretical analysis, BAL in 1N HCl acid can be used as corrosion inhibitor for mild steel as corrosion preventive inhibitor.

REFERENCES

1. S. Saravanamoorthy, Velmathi, S. Prog. Org. Coat., 76, 2013, 1527–1535.
2. T. Ramde, S. Rossi, C. Zanella, Appl. Surf. Sci., 307, 2014, 209–216.
3. J. B. Harborne, "Phytochemical Methods: A Guide to Modern Techniques of Plant Analysis", Chapman and Hall, London, 2rd Ed., 1984.
4. A. Kokate, "Phytochemical Methods", Phytotherapy Res., Vol.78, 126 – 129, 1999.
5. V. Kavitha and Dr. N. Gunavathy, "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(7), 2014, 146-154.
6. R. Karthikaiselvi, D. S. Subhashini, R. Rajalakshmi, "Biodegradable green inhibitor (Myristica Frangans) as a corrosion inhibitor of mild steel in 1M HCl", The Journal of corrosion science and engineering, Vol.12, 2009.
7. J. I. Bhat, V. Alva, "Corrosion inhibition of aluminium by 2- chloronicotinic acid in HCl medium", Indian Journal of Chemical Technology, Vol. 16(3), 2009, 228–233.
8. M. Abdallah, H. E. Megahed, M. A. Radwan, E. Abdfattah, "Polyethylene glycol compounds as corrosion inhibitors for aluminium in 0.5M hydrochloric acid solution", Journal of American Science, Vol. 8(11), 2012, 49–55.
9. M. Bouklah, A. Attayibat, S. Kertit, A. Ramdani, B. Hammouti, "Corrosion in Mild Steel", Applied Surface Science Journal, Vol 242, 2005, 399 - 406.
10. T. Koopmans, Uber die Zuordnung von Wellenfunktionen und Eigenwerten zu den einzelnen Elektronen eines Atoms,Physica, Vol. 1, 1933,104–113.
11. Wan Nik, W. B. Ahmad, R. Rosliza, Prawoto, F. Zuklifi. "The Study of Temperature Effect on Mild Steel", International Journal of Engineering Science and Technology, Vol 36, 2011, 6462 – 6471.
12. S. Hadisaputra, S. Hamdiani, A. A. Purwoko, "Corrosion Inhibition of Steel in Acidic Medium by Eugenol Derivatives: Insight from Density Functional Calculation", J Applied Chem. Sci., Vol 4, 2017, 312-317
13. H. Zarrok, M. Assouag, A. Zarrouk, H. Oudda, A. Hallaoui, R. Touzani, M. Allali, B. Hammouti, M. El Hezza , M, Bouachrine, "Quantum Chemical Study on the Corrosion Inhibition of Some Bipyrazoles", Research Journal of Pharmaceutical, Biological and Chemical Sciences, Vol 6(4), 2015, 1853-1860.
14. L. Herrag, M. Bouklah, N. S. Patel, B. M. Mistry, B. Hammouti, S. Elkadiri, M. Bouachrine. "Research on Chemical Intermediates", Journal of Chemical Science, Vol 38, 2012, 1669 – 1690.