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Leaves Extract of *Grevillea Robusta* as Eco-Friendly Corrosion Inhibitor for Mild Steel in 1N Hydrochloric Acid Medium

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Abstract— ***An attempt was made to characterize leaf extracts of Grevillea robusta (GRL) by phytochemical screening, weight loss method, FTIR, surface examination analysis and quantum chemical studies. Influence of bioactive compounds in Grevillea robusta leaf extract contributes for adsorption properties towards Mild Steel (MS). The maximum inhibition efficiency of GRL extract was 97.05 % in 1N HCl for immersion period of 5 h at 2.5 % v / v. SEM analysis confirmed formation of protective layer on mild steel surface. Inhibition efficiency was found to increase with increasing concentration of GRL extract at room temperature. Results from various studies show that GRL can serve as an effective inhibitor for mild steel corrosion in 1N HCl medium.***

Keywords— Grevillea robusta, weight loss method, quantum chemical studies, bioactive compounds, corrosion inhibitor

I. INTRODUCTION

Mild steel is extensively used in many industries due to its exceptional mechanical properties, ready availability and low cost. Hydrochloric acid solutions are widely used in several industrial processes, like acid pickling of steel, chemical cleaning and processing, ore production and oil well acidification, due to general aggression of acid solutions, inhibitors are commonly used to decrease corrosive effect on metallic materials [1]. Selection of inhibitor is influenced by its economic availability, efficiency to inhibit material and environmental side effects. Plants are natural sources for variety of compounds, and that contain different chemical, biological and physical properties. So, study of plant extracts as corrosion inhibitors has received more attention due to environmental benefits. Natural compounds are used, as they are environmentally acceptable, cost effective and have abundant availability. Most of acid inhibitors for corrosion of steel in acidic medium are organic compound containing nitrogen, oxygen and/or sulphur atoms [2]. Quantum chemical analysis is particularly significant in study of electrochemistry and also to understand structure and behaviour of corrosion inhibitors.Present work investigated the inhibition efficiency of *Grevillea robusta* leaf extract **(**GRL**)** in controlling corrosion of mild steel immersed in HCl in absence and presence of inhibitor.

II. MATERIALS AND METHODS

A. Collection of Grevillea robusta and extract preparation

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

Fig.1. Grevillea robusta Leaf Powder

Fig. 2. Photograph of Experimental Setup for Obtaining Grevillea robusta Leaf Extract Using Reflux Condenser

B. Phytochemical Screening of GRL

HCl extract of GRL was subjected to preliminary phytochemical screening to identify chemical bioactive constitution using standard qualitative method as described by Harborne (1984) [3] and Kotate (1999) [4].

C. Materials preparation

Rectangular mild steel coupons of size 5 × 1 × 0.2 cm were cut from a large sheet of mild steel, with a small hole of about 1.0 mm diameter near 1.5 cm side end for suspending. Specimens were polished in sequence using silicon carbide emery papers of grade 200, 400, 600 starting with coarse one and proceeding in steps to finest grade, then washed with distilled water, dried with clean tissue paper, degreased with acetone and dried using hot air drier. Specimens were kept in desiccators to avoid adsorption of moisture.

D. Weight loss measurements

Mild steel specimens were immersed in beaker containing 100ml acid solution without and with different concentrations of GRL using glass hooks for a predetermined time period at room temperature. Trial was carried out in triplicate for excellent reproducibility. Weight loss measurements were carried out using a SHIMADZU model AY 220. Test specimens were removed and washed with deionised 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, 2.50%v/v)
- Different time intervals (1h, 3h, 5h, 7h, and 24h)

From initial and final mass of specimens, weight loss was calculated, and corrosion rate (in mpy) [5] was computed with following equation:

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

Where D is the density of the coupon (7.8 g/cm^3), W is weight loss (mg) of the coupons, A is surface area of coupon (cm^3), and T is immersion time (h). Inhibition efficiency of mild steel was then calculated [6].

F. Surface morphology

Mild steel coupons was prepared by immersing coupons in 1N HCl for determined time period with and without GRL extract, after polishing successively with 400, 600 grades of emery paper, and immersed in test solution. After specified time, MS coupons were removed and washed gently with distilled water, dried carefully. Scanning electron microscopy and Fourier Transforms Infrared (FTIR) spectroscopic studies were utilized for surface examination of uninhibited and inhibited mild steel samples.

G. Quantum chemical studies

Quantum chemical studies have been successfully implemented to correlate corrosion protection efficiency of organic inhibitors with their calculated molecular orbital energy levels [7]. Quantum chemical descriptors are related to electronic structure of organic materials and to chemical mechanisms that are involved in covalent bond formation between phytocompounds and metal surfaces. MOPAC is a popular computer program used in computational chemistry. It is designed to implement semi - empirical quantum chemistry algorithms. Argus Lab is molecular modeling graphics, and drug design program for Windows operating systems. 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 [8] which relates to energy of HOMO and LUMO (Table 1). 3D structure of phytoconstituents (Fig. 3) of GRL was taken as input for analysis.

TABLE 1. QUANTUM CHEMICAL PARAMETERS FOR THEORETICAL ANALYSIS

S. No	Quantum parameters	Formulation
1.	Chemical potential (μ)	$\mu = -\chi$
2.	Ionization potential (I)	$I = -E_{HOMO}$
3.	Electron affinity (A)	$A = -E_{LUMO}$
4.	Electronegativity (χ)	$\chi = \frac{I + A}{2}$
5.	Global hardness (η)	$\eta = \frac{I - A}{2}$
6.	Chemical softness (σ)	$\sigma = \frac{1}{\eta}$
7.	Electrophilicity index (ω)	$\omega = \frac{\mu^2}{2\eta}$

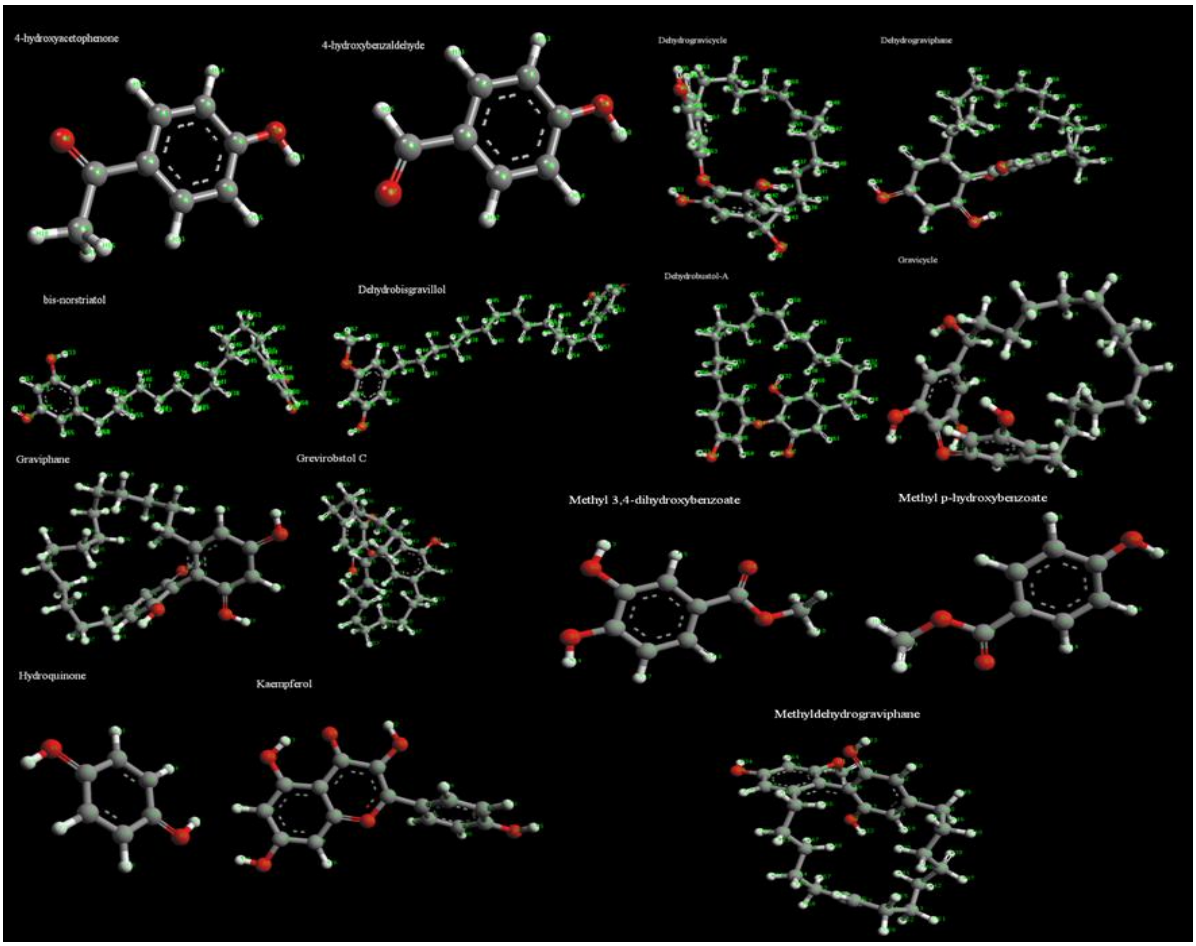

Fig.3 Structure of 4-hydroxyacetophenone, 4- hydroxybenzaldehyde, Bisnorstriatol, Dehydrobisgravillol, Dehydrogravicycle, Dehydrograviphane, Dehydrobustol - A, Gravicycle, Graviphane, Grevirobstol C, Hydroquinone, Kaempferol, Methyl 3, 4 - dihydroxybenzoate, Methyl p - hydroxybenzoate, Methyl dehydrograviphane

III. RESULTS AND DISCUSSIONS

A. Phytochemical analysis

Plant analysis is devoted to isolation and identification of secondary constituents in a particular species or group of species or species with expectation that some of the constituents may be novel or of an unusual structure. The phytochemicals present in leaf extract of GRL in HCl medium are summarized in Table 2. Carbohydrates, tannins, saponins, reducing sugar and coumarins were present in GRL extract.

TABLE.2. PHYTOCHEMICAL CONSTITUENTS PRESENT IN GRL EXTRACT

PHYTO COMPOUND	GRL
Carbohydrates	+
Reducing sugar	+
Alkaloids	–
Saponins	+
Tannins	+
Flavonoids	–
Terpenoids	–
Phlobatannins	–
Coumarins	+
Cycloglycoside	–
Quinones	–

B. Weight loss Measurements

The weight loss method of monitoring corrosion rate and inhibition efficiency is useful because of its versatility, reliability and simplicity. Inhibition efficiency was calculated using formula [9],

$$IE\% = \frac{W_1 - W_2}{W_1} \times 100 \quad (2)$$

Where, W_1 and W_2 are weight loss of mild steel after immersion in solutions without and with inhibitor respectively. Table 3 gives values of inhibition efficiency obtained from weight loss measurements of mild steel for various concentrations of GRL in 1N HCl at 303K after different hours of immersion. As concentration of inhibitor increases, rate of corrosion decreases because inhibitor molecules prevent dissolution of mild steel by effective adsorption of phytonutrients of plant extract on metal surface area.

TABLE 3. INHIBITION EFFICIENCY (IE) AND CORROSION RATE (CR) OF GRL/1N HCL AGAINST MILD STEEL AT VARIOUS CONCENTRATIONS AND DIFFERENT IMMERSION PERIOD

Conc. of GRL (% 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	0.82	-	0.82	-	0.82	-	0.72	-	0.52	-
0.10	0.16	80.36	0.14	82.61	0.12	84.38	0.12	83.07	0.09	77.79
0.50	0.14	82.15	0.12	84.51	0.11	85.75	0.15	84.12	0.11	78.04
1.00	0.11	86.33	0.09	88.11	0.08	89.26	0.09	87.18	0.10	79.08
1.50	0.07	90.93	0.05	93.06	0.04	94.12	0.07	90.21	0.07	86.02
2.00	0.71	91.33	0.06	94.06	0.04	94.41	0.06	90.94	0.05	88.8
2.50	0.06	92.66	0..03	96.31	0.02	97.05	0.05	92.88	0.05	90.32

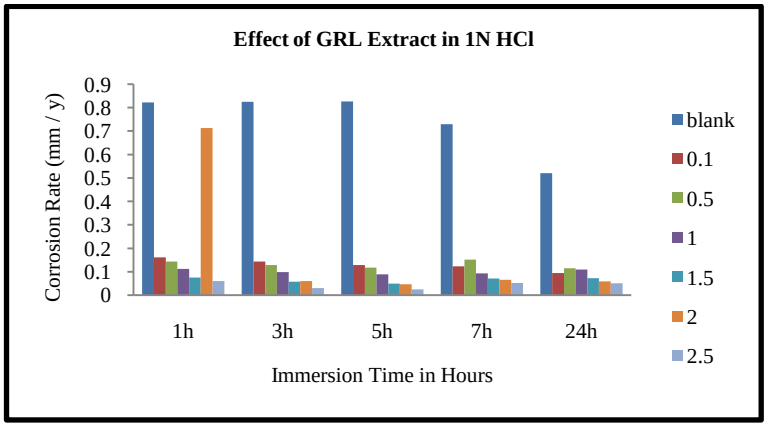

Fig.4. Effect of immersion time on CR of mild steel in 1N HCl without and with GRL Extract

Effect of concentration of GRL on Corrosion rate and Inhibition Efficiency

The effect of concentration of inhibitor on inhibition efficiency of plant extract and corrosion rate of mild steel in acid medium (Fig.4) shows that corrosion inhibition by plant extracts was taking place by adsorption mechanism. With increase in concentration, more phytoconstituents are being adsorbed on to surface of metal, enhancing of increasing inhibition efficiency with increasing inhibitor concentration has been reported in literature [10]. This accounts for no further increase in inhibition efficiency with increase in concentration greater than 2.5% [5].

C. Fourier Transform Infrared Spectroscopy (FTIR) Studies

FTIR spectroscopy is a powerful tool that can be used to determine type of functional group and bonding for organic inhibitors adsorbed on metal surface. The results of FTIR and possible functional groups [11] are represented in Table 4. FTIR spectrum of mild steel exposed to 1N HCl has spectral bands at different wave numbers OH group (3573.23 cm^{-1}), C – H aromatic bend (3034.44 cm^{-1}) corresponding to COOH or C≡ C (2981.16 cm^{-1}), Aromatic C – N (2245.7 cm^{-1}) (Fig. 8). The adsorption product on the mild steel exposed to 1N HCl/GRL extract has FTIR spectral bands at different wave numbers OH group (3496.31 cm^{-1}), C – H aromatic bend (3336.25 cm^{-1}) corresponding to COOH or C ≡ C groups (2787.6 cm^{-1}), C = C Aromatic C – N (2241.84 cm^{-1}), Aromatic bend (1540.00 cm^{-1}) (Fig.8 and 9). The adsorption of compounds may be through bond formation with functional groups, physical adsorption and chemical reactions with surface sites.

TABLE 4. FTIR PEAK VALUES OF MILD STEEL EXPOSED TO 1N HCL WITHOUT AND WITH GRL EXTRACT

MS in Blank	MS in 1N HCl/ GRL	Possible groups
	3496.31	Saturated O-H Stretch
3573.23		OH Strong Sharp Band
3468.35		OH Strong Broad Band
	3336.25	C-H Aromatic group
3034.44	3094.23	C-H Aromatic group
	3162.89	N-H Aromatic Stretch
2981.16	2787.60	COOH or C ≡ C groups
2841.60	2709.50	COOH or C ≡ C groups
2768.31		COOH or C = C groups
2628.50		COOH or C = C groups
2245.70	2241.84	Aromatic C N
1755.07	1763.58	Aromatic C = O bend
1470.46	1540.00	C = C Aromatic,Stretch

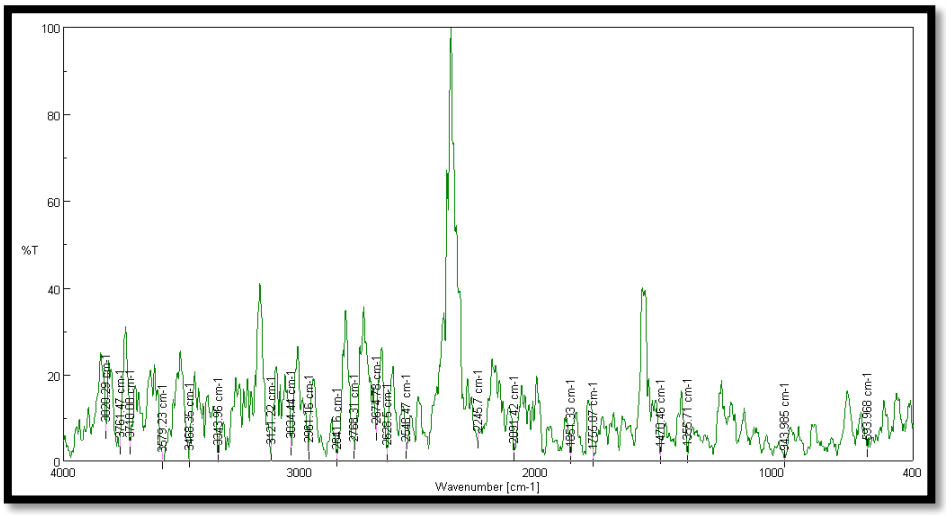

Fig.5. FTIR Spectra of Mild Steel surface Immersion in 1N HCl Acid without GRL Extracts

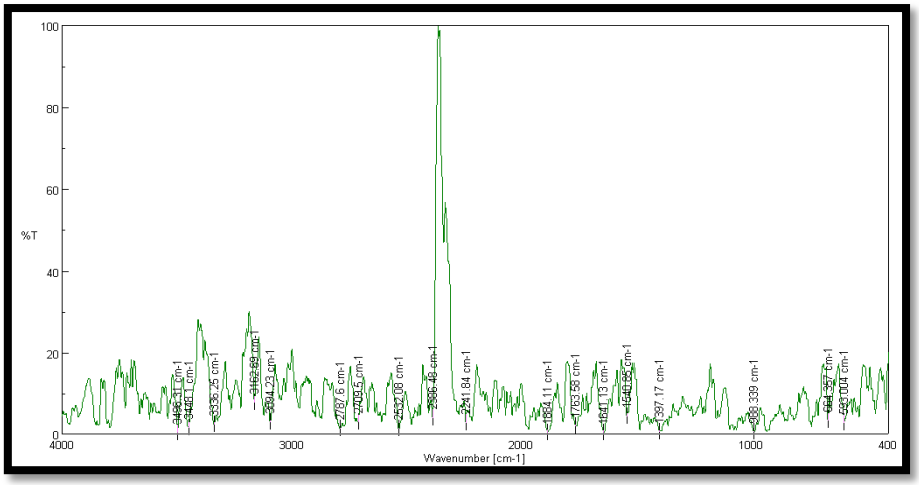

Fig.6. FTIR Spectra of Mild Steel surface after Immersion in 1N HCl with GRL Extract

D. Scanning Electron Microscopy (SEM)

The surface morphological characteristics of uninhibited mild steel in 1N HCl and inhibited mild steel using GRL in 1N HCl analyzed at an accelerating voltage using SEM photographs of 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. SEM photographs (Fig.5 & 6) of mild steel exposed to acids containing inhibitors showed that there was less damage on surface which clearly confirms inhibition action due to formation of protective film by phytochemical components present in plant extract on mild steel surface.

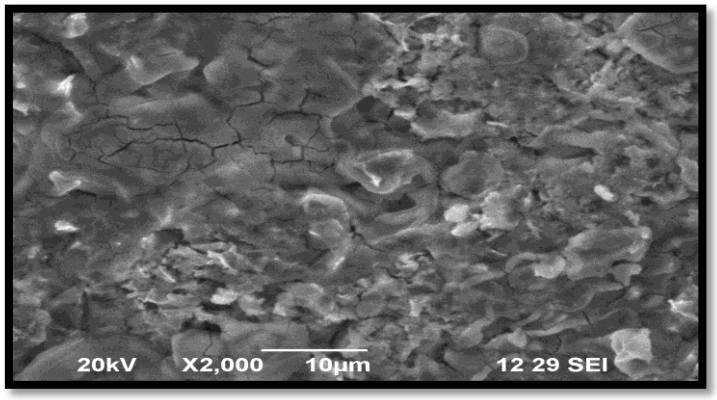

Fig. 7. Photograph of Mild Steel exposed to IN HCl (Blank)

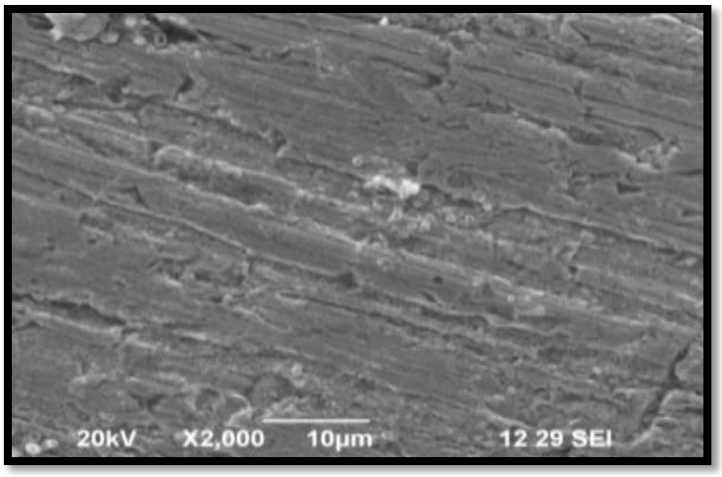

Fig.8. Photograph of Mild Steel exposed to IN HCl + 2.5% GRL extract

E. Quantum Chemical Calculations

The structures of phytoconstituents of *Grevillea robusta* 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). This method is suitable for analyzing closely resembling molecules that are subject of correlation studies. Table 5 represents quantum chemical parameters for organic molecules present in GRL extract.

TABLE 5. QUANTUM CHEMICAL PARAMETERS FOR ORGANIC MOLECULES OF GRL EXTRACT

COMPOUNDS	HOMO eV	LUMO eV	ENERGY GAP eV
4 – Hydroxyacetophenone	-8.532	-0.696	7.836
4 – Hydroxybenzaldehyde	-8.697	-1.018	7.679
Bis – norstriatol	-9.089	0.144	9.233
Dehydrobisgravillol	-9.125	0.155	9.280
Dehydrogravicycle	-8.952	-0.351	8.601
Dehydrograviphane	-8.661	-0.022	8.639
Dehydrobustol – A	-8.876	0.158	9.034
Gravicycle	-8.861	-0.182	8.679
Graviphane	-8.865	-0.026	8.839
Gravirobustol C	-8.990	0.259	9.249
Hydroquinone	-9.824	0.236	10.06
Kaempferol	-9.349	-1.436	7.913
Methyl 3, 4 – dihydroxybenzoate	-9.089	-0.586	8.503
Methyl P-hydroxybenzoate	-10.08	-0.576	9.506
Methyldehydrograviphane	-8.605	0.140	8.745

The molecule with highest E_{HOMO} value has highest tendency to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy [12]. E_{HOMO} is associated with electron donating ability of molecules. High values of E_{HOMO} are likely to indicate a tendency of molecule to donate electrons to appropriate acceptor molecules to unoccupied d orbital of a metal. Energy of lowest unoccupied molecular orbitals indicates ability of molecule to accept electrons. Lower value of E_{LUMO} more probability of molecule to accept electrons [13]. Higher energy gap (ΔE) may enhance corrosion inhibition efficiency. The molecular orbitals of the chemical compounds are generated using Arguslab (Fig.9 & 10).

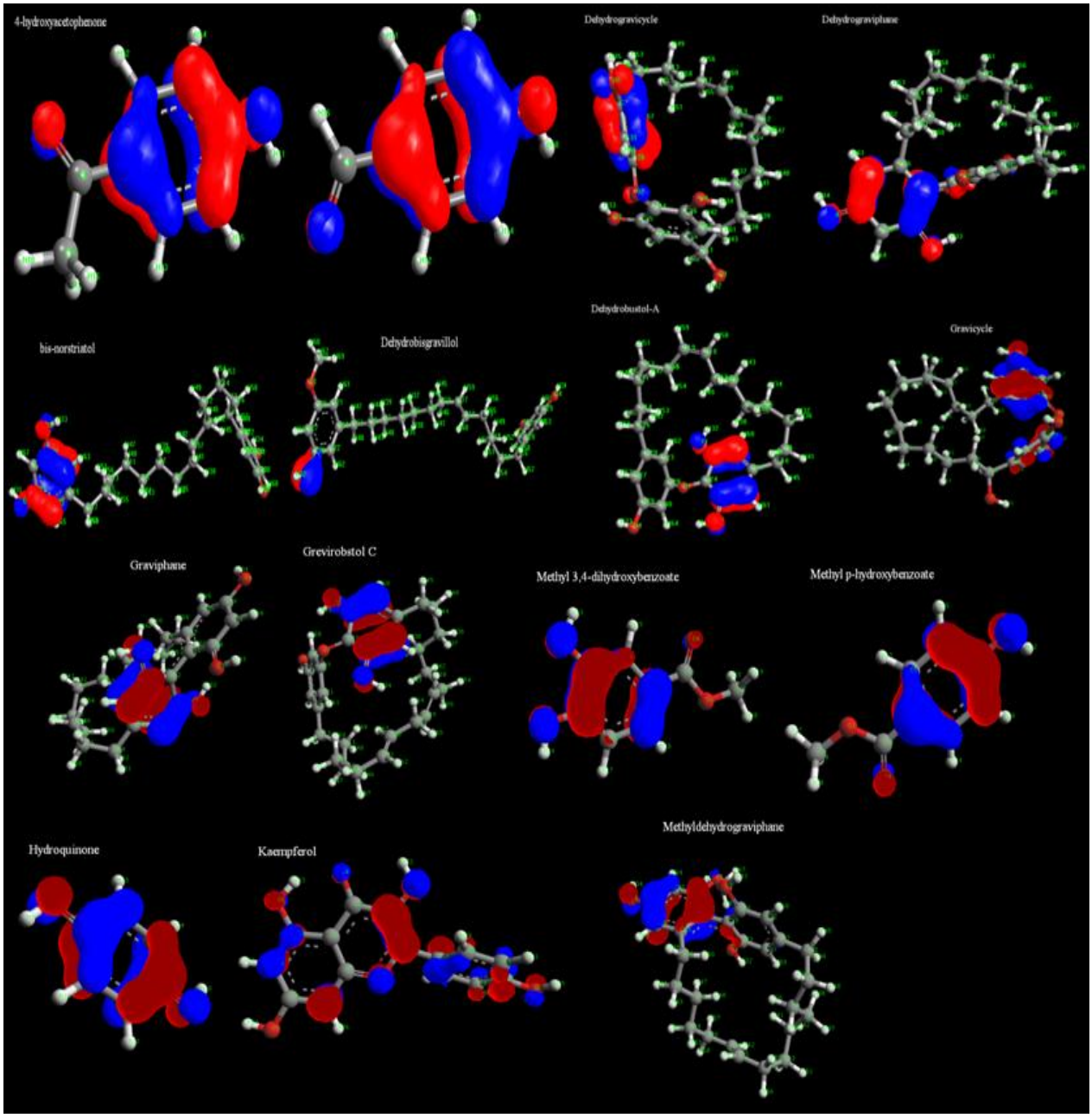

Fig. 9. HOMO Orbital of 4-hydroxyacetophenone, 4 - hydroxybenzaldehyde, Bis-norstriatol, Dehydrobisgravillol, Dehydrogravicycle, Dehydrograviphane, Dehydrobustol - A, Gravicycle, Graviphane, Grevirobstol C, Hydroquinone, Kaempferol, Methyl 3,4-dihydroxybenzoate, Methylp-hydroxybenzoate, Methyl dehydrograviphane

From results of quantum chemical calculations, it was evident that 4 - hydroxyacetophenone which is best inhibitor has highest value of E_{HOMO} - 8.532 (eV) and would be better adsorbed on metal surface. Energy gap (ΔE) provides information about overall reactivity of a molecule. As ΔE decreases, reactivity of molecule contributes to increase in inhibition efficiency of molecule [14]. Low values of ΔE gap will render good inhibition efficiencies since energy to remove an electron from last occupied orbital will be minimized. In quantum chemical study, tendency for (ΔE) values follows order : 4-hydroxyacetophenone < methyldehydrograviphane < dehydrograviphane < 4–hydroxybenzaldehyde < gravicycle < graviphane < dehydrobustol - A < dehydrogravicycle < gravirobustol C < bis – norstriatol < methyl 3, 4 - dihydroxybenzoate < dehydrobisgravillol < kaempferol < hydroquinone < methyl p - hydroxybenzoate which suggests that inhibitor 4 - hydroxyacetophenone has highest reactivity in comparison to other compounds and would therefore likely interact strongly with metal surface.

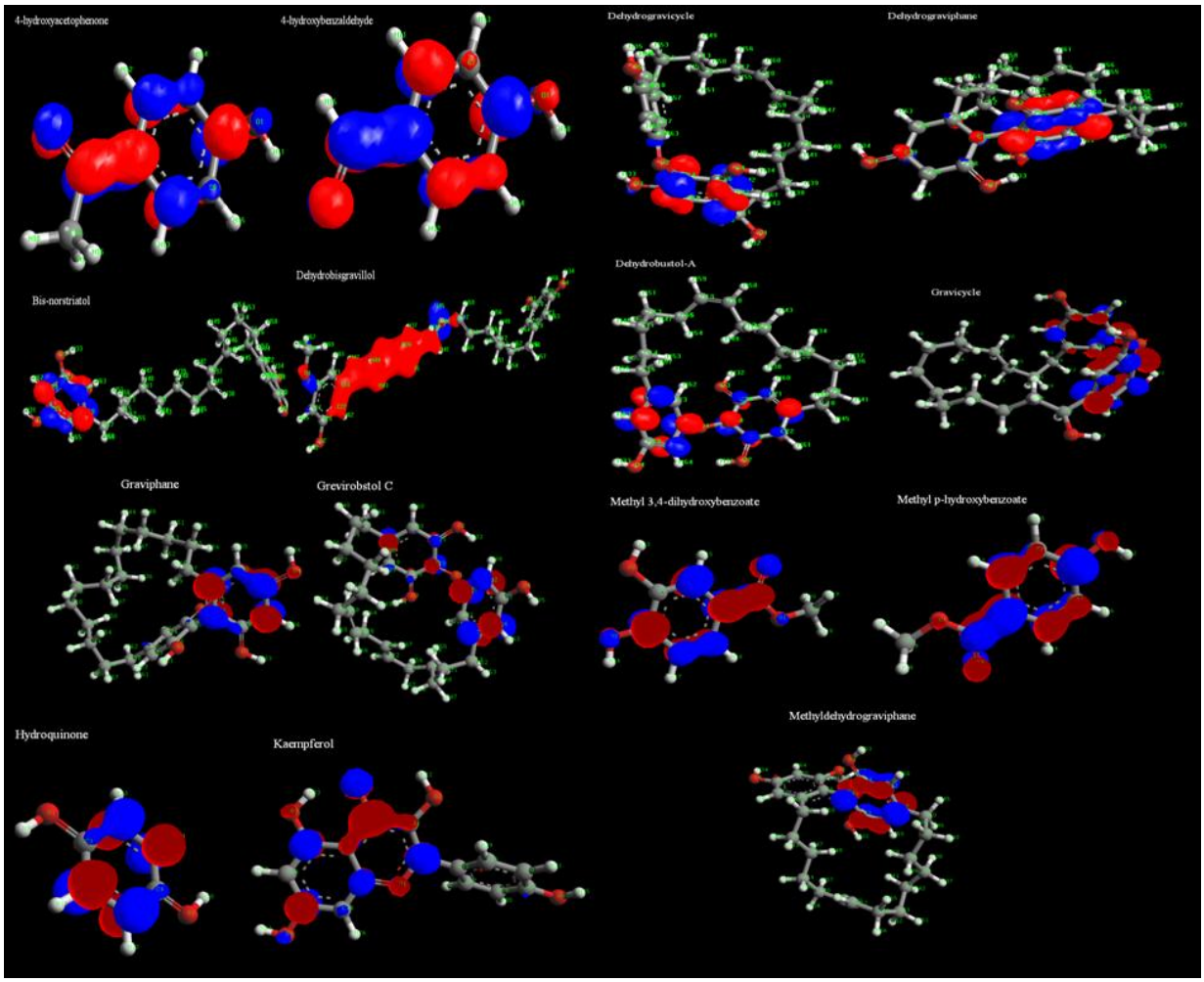

Fig.10.LUMO orbitals of 4 - hydroxyacetophenone, 4 - hydroxybenzaldehyde, Bis - norstriatol, Dehydrobisgravillol, Dehydrogravicycle, Dehydrograviphane,Dehydrobustol - A, Gravicycle, Graviphane, Grevirobstol C, Hydroquinone, Kaempferol, Methyl 3, 4 - dihydroxybenzoate, Methyl p - hydroxybenzoate, Methyl dehydrograviphane

IV. CONCLUSION

Based on the above results, following conclusion can be drawn,

- Qualitative analysis of GRL extract showed presence of alkaloids, saponins, tannins, carbohydrates and coumarins.
- Corrosion of mild steel in HCl acid medium was significantly reduced on additions of GRL extract. The inhibition efficiency increased with the increasing concentration of inhibitor. The maximum inhibitor efficiency was observed at an optimum concentration of 2.5 % v / v.
- GRL showed maximum of efficiency 97.05 % in 1N HCl at 7 hours of immersion.
- FTIR spectra of film product of mild steel in GRL/1N HCl, showed strong evidence for the interaction between metal and functional group in OH, C - X, NH leading to formation of film of large surface coverage which serve as a barrier between corrosive medium and metal.
- SEM confirmed efficiency of GRL as corrosion inhibitor for mild steel. The comparison of images from scanning electron microscopy revealed that molecules of the GRL are absorbed on the metal surface, thereby decreasing corrosion attack on metal surface.
- Quantum studies revealed that inhibition was due to adsorption of active molecules that form a protective layer on mild steel 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 GRL.

Results of present study indicate that GRL in 1N HCl acid can be used as corrosion inhibitor for mild steel as green friendly inhibitor.

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