Phytochemical Screening, Weight Loss Measurement, Surface Examination and Quantum Chemical Analysis of *Phaseolus Vulgaris* Seed Extract as Green Corrosion Inhibitor for Mild Steel in 1N HCl Medium

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Abstract: Extract of *Phaseolus vulgaris* (Dragon Tongue Beans) seeds (DBS) was investigated as corrosion inhibitor of mild steel in 1N HCl medium using phytochemical screening, weight loss method, surface examination analysis and quantum chemical studies. Stability of inhibition efficiency of DBS extracts was examined by weight loss method and maximum inhibition efficiency of DBS extract was 97.85 % in 1N HCl for immersion period of 7h at 2.5 % v / v. SEM analysis established formation of protective layer on mild steel surface. Quantum studies showed molecular orbitals, nucleophilic and electrophilic regions present in phytoconstituents of DBS extract. Scanning Electron Microscopic studies revealed evidence of improved surface condition, due to adsorption of phytoconstituents, for the corrosion protection

Keywords — Phaseolus vulgaris, weight loss method, surface examination, corrosion inhibitor, Quantum studies

I. INTRODUCTION

Plant extracts have become significant as an environmental safe, easily available, and renewable source for a wide range of corrosion inhibitors. Extracts from plants are rich source of naturally synthesized chemical compounds and these potential compounds can be extracted by simple procedures at low cost. Several investigations have been reported for corrosion control using economic plant extracts. Avwiri and Igho studied inhibitive effect of *V. amygdalina* on corrosion of aluminium alloys in HCl and HNO_3 medium at concentrations of 0.2 and 0.4 g/L at 29°C. El-Etre et al. [2], [3] examined some naturally occurring substances as corrosion inhibitors for different metals in various environments. In the current work, *Phaseolus lunatus* seeds (DBS) were evaluated experimentally and computationally to find its use as green corrosion inhibitor.

II. MATERIALS AND METHODS

A. Preparation of DBS extract

Phaseolus vulgaris DBS (Fig 1a and 1b) seeds were collected from Ukkadam Market, Coimbatore, Tamilnadu, India. Seeds were cleaned and shade dried to prevent loss of phytoconstituents. The dried seeds were powdered and stored in dessicator to prevent moisture contents. 25 gm of dried seed powder were boiled in 500 ml of 1N HCl in reflux condenser for 3 hours and was kept overnight. Following day, extract was filtered and filtrate volume was made up to 500 ml using 1N HCl medium.

Fig 1a & 1b. Dragon Tongue Beans (*Phaseolus vulgaris*) Pods and Seeds

B. Preparation of Mild Steel Coupons

Mild steel samples were cut into size with dimensions 5 × 1 × 0. 2 cm and were abraded with different grades of

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emery papers, washed with distilled water, degreased with acetone and dried. These coupons are stored in dessicator and used for further studies. Percentage composition of elements (Table 1) present in material was determined using ARL QUANTRIS optical emission spectrometer at SiTARC, Coimbatore.

Table 1. Chemical Composition of Mild Steel Coupons

S. No.	Elements	Values %
1	Carbon (C)	0.045
2	Silicon (Si)	0.063
3	Manganese (Mn)	0.380
4	Phosphorous (P)	0.031
5	Sulphur (S)	0.017
6	Nickel (Ni)	0.035
7	Chromium (Cr)	0.013
8	Molybdenum (Mo)	0.001
9	Copper (Cu)	0.013
10	Titanium (Ti)	0.001
11	Cobalt (Co)	0.001
12	Aluminium (Al)	0.023

C. Phytochemical Analysis

Plant sources rich in chemical compounds can be used as a organic agent for application in various field with greater commercial value**.** Preliminary qualitative phytochemical analysis was carried out to identify secondary metabolites and standard methods were used for assessment of phytochemicals such as, terpenoids, phenols, flavonoids, steroids, tannins, saponins, and alkaloids in seed powder of *Phaseolus vulgaris*[4], [5].

D. Weight Loss Measurement

Polished and pre-weighed Mild steel specimens were suspended in 100 ml test solutions, without and with inhibitor of different concentrations (Fig 2). After specified time of exposure, specimens were removed and then reweighed. Experiments [6] 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 was calculated using formula:

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

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.

Fig 2. Various Concentrations of DBS extract in 1N HCl

E. Surface Examination Studies

Scanning Electron Surface morphology analysis of mild steel coupons were examined to evaluate change in surface formation due to contact with inhibitor solutions, and to monitor effect of addition of the inhibitor to medium using JEOL-JSM-6390 at Karunya University, Coimbatore.

F. Quantum Chemical Studies

Quantum chemical calculations were carried out using Semi empirical (PM3 and PM7) method. MOPAC is commonly used in computational chemistry and is based on semi-empirical quantum chemistry algorithms. MOPAC2016 is able to perform calculations on small molecules and enzymes using PM7, PM6, PM3, AM1, MNDO and RM1 [7]. Molecular structure of phytoconstituents (Fig 3 and 4) were geometrically optimized by ArgusLab 4.0.1 and taken as input for quantum studies. Molecular parameters like ionization potential (I), electron affinity (A), electronegativity (χ), global hardness (η) and softness (σ), were determined to study molecular orbitals of phytoconstituents present in DBS extract [8].

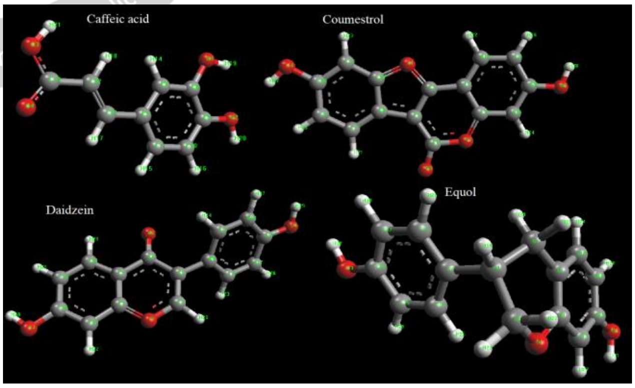

Fig 3. Molecular Structures of Caffeic acid, Coumestrol, Daidzein and Equol.

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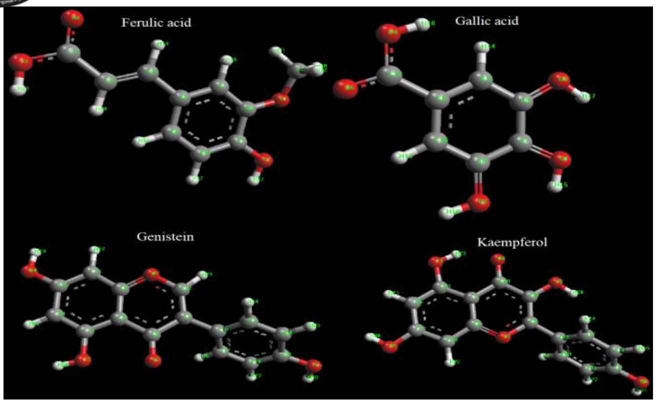

Fig 4. Molecular Structures of Ferulic acid, Gallic acid, Genistein and Kaempferol.

III. RESULTS AND DISCUSSION

A. Phytochemical Screening

Knowledge of the chemical constituents of plants is attractive because these data are valuable for synthesis of complex chemical substances. DBS extract was analyzed to determine presence of functional groups using standard qualitative procedures. DBS extract showed presence of alkaloids, flavonoids, glycosides, steroids, saponins, amino acids, reducing sugar, terpenoids and carbohydrates (Table 2). Presence of active constituents in seed extract reveals good inhibition efficiency towards protection of material surface.

Table 2. Phytochemical Analysis of DBS Extracts

Phytocompounds	DBS
Alkaloids	+++
Phenols	-
Flavonoids	++
Tannins	-
Saponins	++
Steroids	++
Glycosides	++
Reducing Sugars	++
Amino Acids	+++
Terpenoids	++
Carbohydrates	++

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

B. Weight Loss Method

Mild steel coupons exposed to various concentrations of extract ranging from 0.10 % v/v to 2.50 % v/v in 1N HCl medium was investigated using weight loss technique. Table 3a and 3b shows that effect of DBS / 1N HCl on corrosion rate and inhibition efficiency (Fig 5) increases with increase in concentration of seed extracts DBS / 1N HCl.

Table 3a. CR of Mild Steel of DBS Extract in 1N HCl acid at Various Concentration and Immersion Period

Conc. of extract in v/v %	Corrosion Rate (CR) Immersion time in hours				
	1	3	5	7	24
BLANK	17.275	20.28	36.00	40.73	48.03
0.10	2.898	3.01	3.28	2.53	4.92
0.50	2.452	2.53	2.54	2.34	3.88
1.00	2.118	1.97	2.35	1.67	3.55
1.50	1.783	1.75	1.85	1.32	2.86
2.00	1.672	1.49	1.49	1.02	2.80
2.50	1.449	1.00	1.11	0.88	2.06

Table 3b. IE of DBS Extract in 1N HCl acid at Various Concentration and Immersion Period

Conc. of extract in v/v %	Percentage Inhibition Efficiency (IE %) Immersion time in hours				
	1	**3**	**5**	**7**	**24**
0.10	83.23	85.16	90.90	93.78	89.75
0.50	85.81	87.55	92.94	94.25	91.93
1.00	87.74	90.29	93.46	95.90	92.61
1.50	89.68	91.39	94.86	96.76	94.04
2.00	90.32	92.67	95.85	97.50	94.18
2.50	91.61	95.05	96.90	97.85	95.72

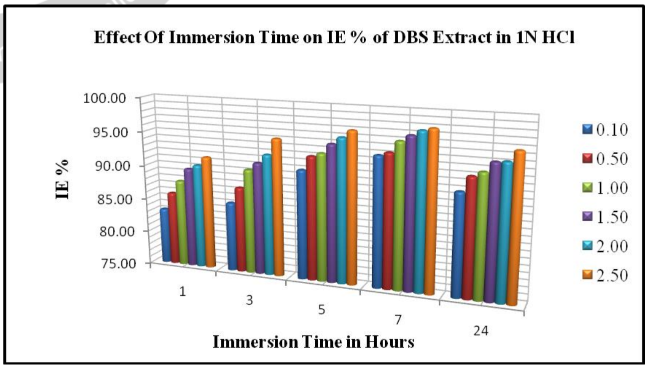

Fig 5. Effect of Concentration on IE % of DBS / 1N HCl on Mild Steel

C. Surface Morphological Studies

SEM photographs (Fig 6 & 7) of mild steel specimens with and without DBS / 1N HCl show inhibitive layer sediment on surface that has ability to produce a good protection on metal surface. Protective film formed on mild steel surface contributed by phytochemical compounds in DBS extract / 1N HCl extract render good inhibition efficiency.

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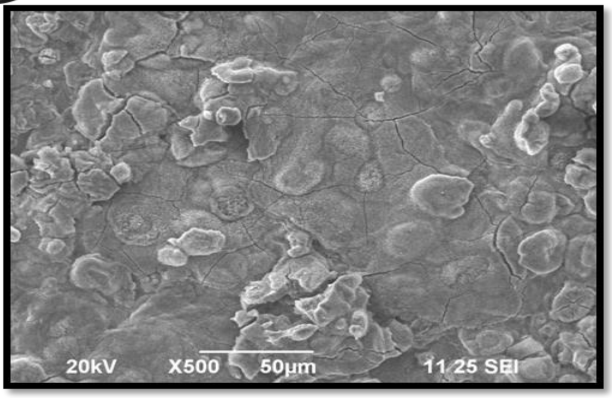

Fig 6. Mild Steel Exposed to 1N HCl Medium.

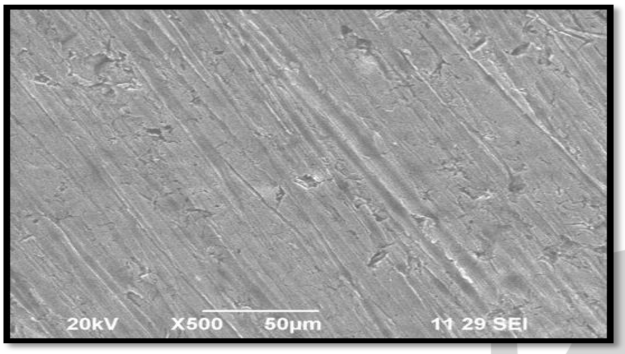

Fig 7. Mild Steel Exposed to IN HCl + 2.5 % DBS extract

D. Quantum Chemical Analysis

Quantum chemical calculations of molecular compounds in DBS extract was performed by MOPAC 2016 with Parameterized Model 3 (PM3). MOPAC program determined HOMO, LUMO, energy gap, ionization potential, Eigen values, dipole moment etc. Table 4 represents quantum chemical parameters for phytoconstituents present in DBS extract.

Tendency of molecules to donate electrons are predicted by highest occupied molecular orbital (E_{HOMO}) energy. E_{HOMO} in higher value indicate excellent tendency to donate electron [9]. E_{LUMO} indicates ability of molecule to accept electrons [10]. Frontier molecular orbital diagrams of phytoconstituents of DBS extract are represented in Figures 8 - 13. From results of quantum chemical analysis, it was evident that Coumestrol was best inhibitor with highest value of E_{HOMO} - 8. 487 (eV) and would be better adsorbed on metal surface [10].

The energy gap (ΔE) provides information about overall reactivity of a molecule and decrease in ΔE gap will provide good inhibition efficiencies [11]. In quantum chemical study, tendency for (ΔE) values follows order; Coumestrol < Daidzein < Genistein < Kaempferol < Ferulic acid < Caffeic acid < Gallic acid < Equol. Coumestrol has highest reactivity in contrast to other molecules and molecule could interact strongly with surface of metal [11]. Assessments of molecular orbitals of phytoconstituents of DBS extract play a crucial role in determination of quality and effectiveness of extract.

Table 4. Quantum Chemical Parameters for Phytoconstituents of DBS extract

S. No.	Compounds	E_{HOMO} eV	E_{LUMO} eV	Energy Gap eV
1	Caffeic acid	-9.920	-1.042	8.878
2	Coumestrol	-8.487	-1.798	6.689
3	Daidzein	-8.665	-1.503	7.162
4	Equol	-9.003	0.085	9.088
5	Ferulic acid	-9.776	-0.928	8.848
6	Gallic acid	-9.824	-0.933	8.891
7	Genistein	-8.852	-1.420	7.432
8	Kaempferol	-9.351	-1.436	7.915

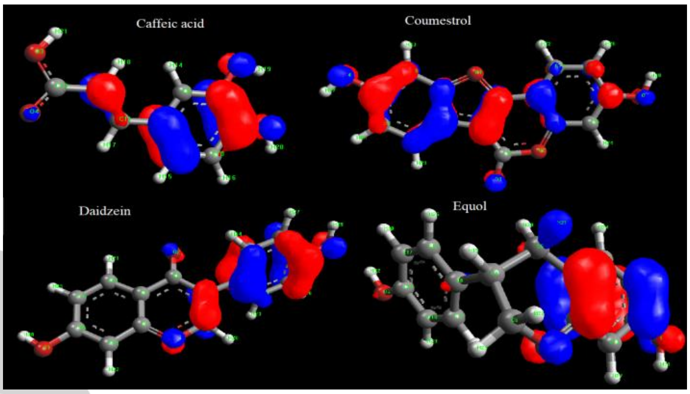

Fig 8. HOMO Orbitals of Caffeic acid, Coumestrol, Daidzein and Equol

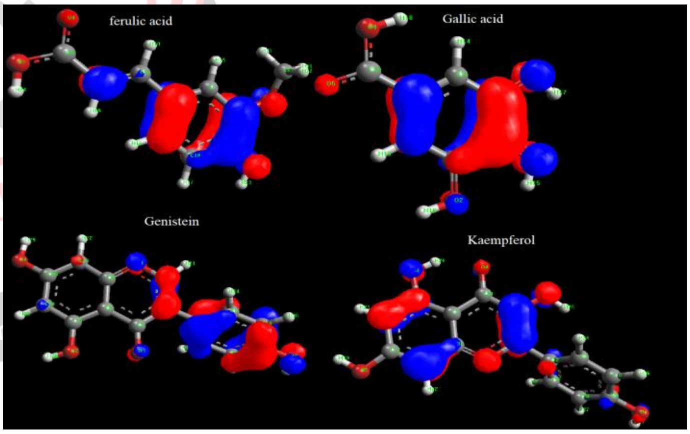

Fig 9. HOMO Orbitals of Ferulic acid, Gallic acid, Genistein and Kaempferol

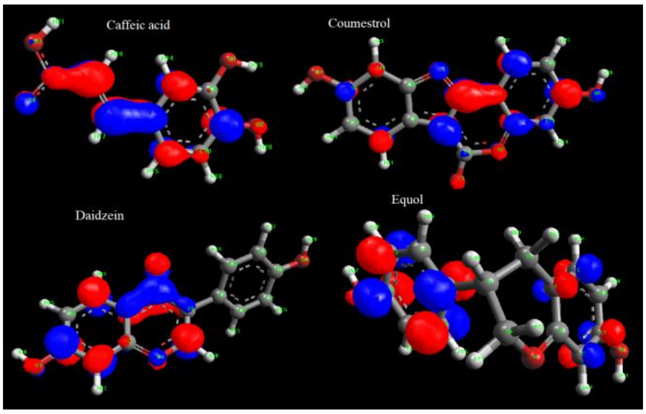

Fig 10. LUMO Orbitals of Caffeic acid, Coumestrol, Daidzein and Equol

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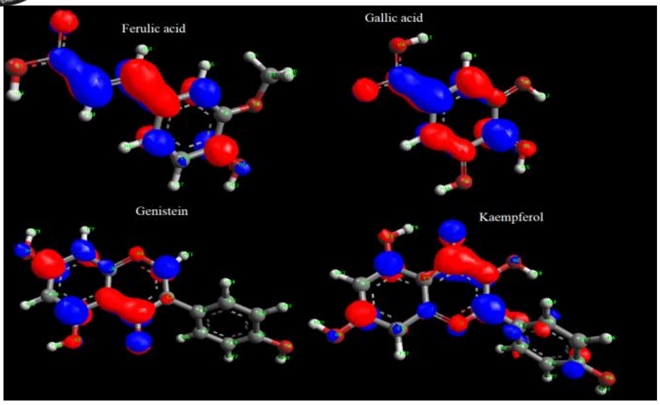

Fig 11. LUMO Orbitals of Ferulic acid, Gallic acid, Genistein and Kaempferol

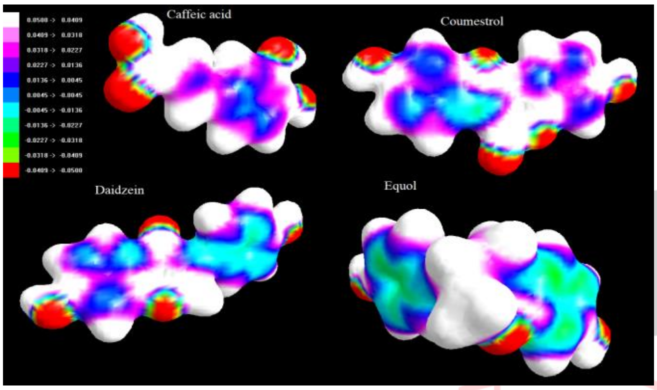

Fig 12. ESP of Caffeic acid, Coumestrol, Daidzein and Equol

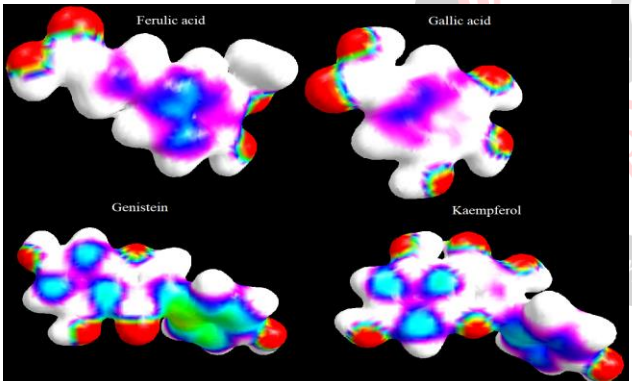

Fig 13. ESP of Ferulic acid, Gallic acid, Genistein and, Kaempferol

Three-dimensional surfaces of electrostatic maps (MEPs) of molecules generated revealed a positive potential in blueness and negative potential of molecule, shown in red color [12]. Electrostatic potential surfaces are valuable because they assist in understanding electrostatic interactions in molecular structures. Red-coloured region indicate negative values of electrostatic potential regions rich in electrons and blue colored region show electron deficient areas in the molecules. Chemical descriptors quantum play an important role in chemical reactions and formation of several charge transfer complex.

IV. CONCLUSION

Present studies conclude that DBS extract can act as a corrosion inhibitor because of presence of various phytochemical constituents such as alkaloids, terpenoids, saponin, flavonoids, reducing sugar and carbohydrates. Weight loss method revealed maximum inhibition efficiency of 97.85 % at 7h in 2.50 v/v %. Surface examination studies show protection by DBS extract on mild steel surface. Quantum chemical parameters indicate that phytoconstituents of seed extract was efficient to protect metal from corrosion environment. Phytoconstituents act as anti-corrosive reagents and responsible to enhance the effectiveness of DBS extract as corrosion inhibitor by formation of hydrophobic thin film through absorption process.

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