



A Theoretical Approach to the Study of Some Plant Extracts as Green Corrosion Inhibitor for Mild Steel in HCl Solution

AMBRISH SINGH*, ASHISH KUMAR and TANAY PRAMANIK

Department of Chemistry, Faculty of Technology and Sciences,
SCVE, Lovely Professional University, Phagwara - 144 402, India.

*Corresponding author E-mail: ambrish.16752@lpu.co.in

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ABSTRACT

The plant extracts are environmental friendly, biodegradable, nontoxic, cheap and easily available source of material which can successively be used as corrosion inhibitor for mild steel in acid media. The effect of the plant extracts was investigated by theoretical approach. Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO), Dipole Moment, Mulliken charges on heteroatoms and Molecular Volume were calculated and interpreted. Quantum chemical calculations revealed the adsorption of molecules onto the surface.

Key words: Mild Steel, Corrosion inhibition, Plant extract, Quantum Chemical Calculations

INTRODUCTION

Inhibitors are added to many systems, namely, cooling systems, refinery units, chemicals, oil and gas production units, boiler, and so forth. Most of the effective inhibitors are used to contain heteroatom such as O, N, and S and multiple bonds in their molecules through which they are adsorbed on the metal surface. Plant extracts have become important because they are environmentally acceptable, inexpensive, readily available and renewable sources of materials, and ecologically acceptable. Plant products are organic in nature, and some of the constituents including tannins, organic and amino acids, alkaloids, and pigments

are known to exhibit inhibiting action¹. Moreover, they can be extracted by simple procedures with low cost. Many authors such as E. E. Ebenso, B. Hammouti, A. Y. El Etre, P. C. Okafor, E. Oguzie, and P. B. Raja, have contributed significantly to the green mitigation by investigating several plants and their different body parts as corrosion inhibitors²⁻²³. In present work, we have worked on the extracts of (Kalmegh) *Andrographis paniculata*, (Meethi Neem) *Murraya koenigii*, (Bael) *Aegle marmelos*, (Kuchla) *Strychnos nuxvomica*, (Shahjan) *Moringa oleifera*, (Orange) *Citrus aurantium*, and (Arjun) *Terminalia arjuna* as corrosion inhibitors [24-29]. The active constituents and inhibition efficiencies of the extracts used are shown in Fig. 1.

EXPERIMENTAL

Theoretical study

All the calculations were performed with Gaussian 03 for windows. The molecular structures of the species were fully and geometrically optimized using the functional hybrid B3LYP (Becke, three-parameter, Lee-Yang-Parr exchange-correlation function) Density function theory (DFT) formalism with electron basis set 6-31G (*, *) for all atoms. The quantum chemical parameters obtained were EHOMO, ELUMO, EHOMO-LUMO (ΔE), Dipole moment (μ), and Mulliken charges on heteroatoms (O,N,S).

RESULTS AND DISCUSSION

Quantum Chemical Calculations

Quantum chemical calculations were carried out in order to investigate adsorption and inhibition mechanism of various inhibitor molecules in the extract. Figure 2 show full geometry optimization of the inhibitor molecules with Mulliken charges. The Frontier molecular orbital (FMO) density distributions of the inhibitor molecules present in Plant extract are shown in Figure 3 (a-b). Frontier orbital theory is useful in predicting adsorption centers of the inhibitor molecules

Table 1: Calculated Quantum chemical parameters of studied inhibitor

Active Constituents	HOMO (hartree)	LUMO (hartree)	ΔE (LUMO-HOMO)	Dipole Moment (μ)
Mahabinine	-0.15192	-0.05321	-0.20513	11.3843
Pyrayafoline	-0.18073	-0.02971	-0.21044	3.9782
Skimmianine	-0.12264	-0.03787	-0.16051	1.3965
Andrographolide	-0.21563	-0.06824	-0.28387	5.1889
Threonine	-0.20226	0.00558	0.19668	1.9030
Arginine	-0.05594	0.02361	0.03233	1.0389
Brucine	-0.19868	0.07845	0.12023	3.1290
Sitosterol	-0.09471	0.02543	0.06928	3.0307

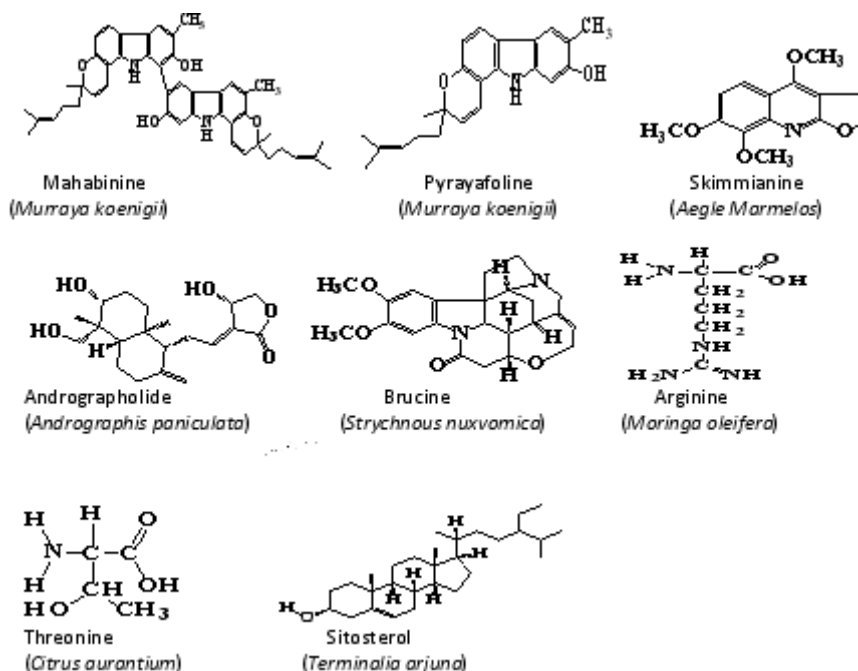
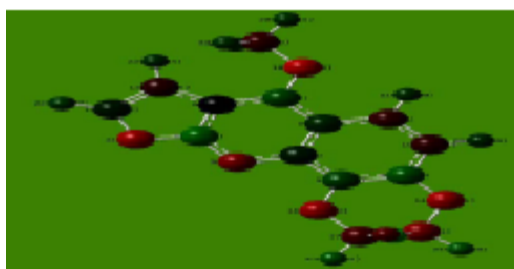
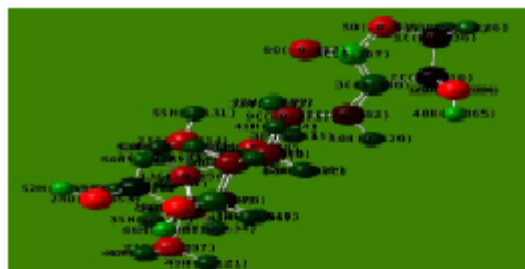


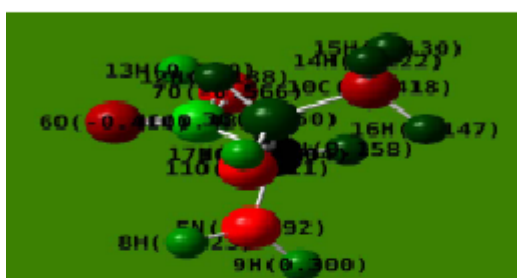
Fig. 1: Active Constituents of the studied plant extracts



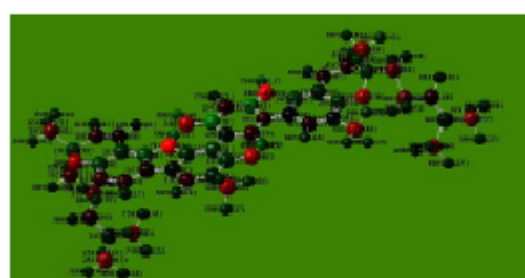
Skimmianine Optimised



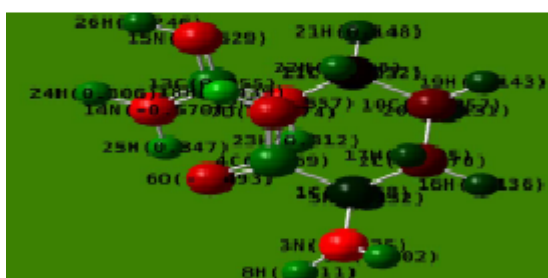
Andrographolide Optimised



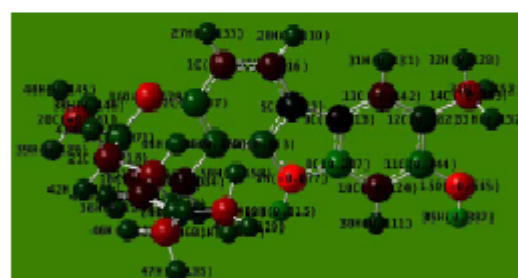
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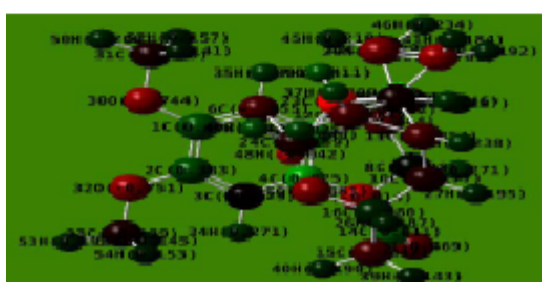
Mahabinine Optimised



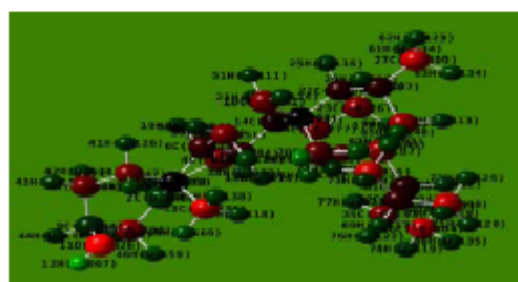
Arginine Optimised



Pyrayafoline Optimised

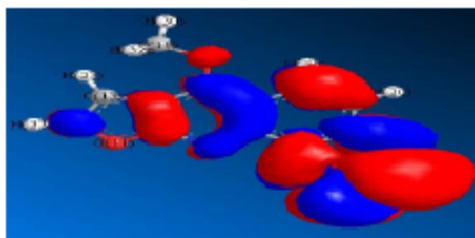


Brucine Optimised

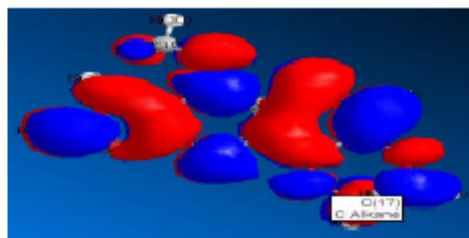


Sitosterol Optimised

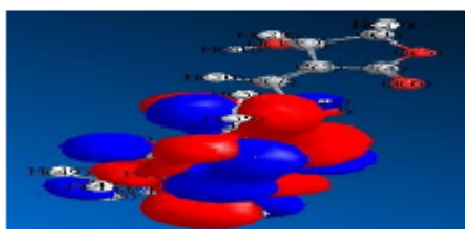
Fig. 2:



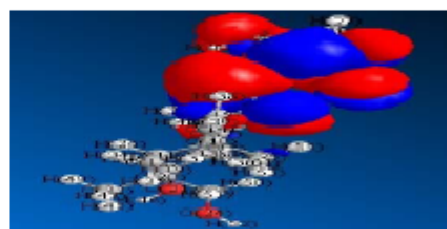
Skimmianine HOMO



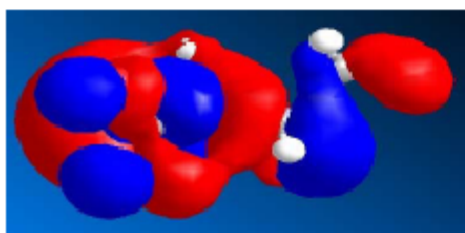
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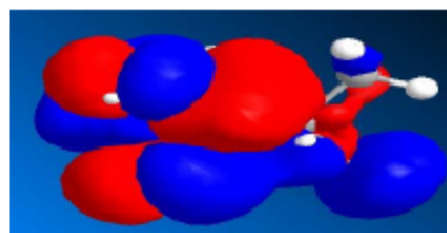
Andrographolide HOMO



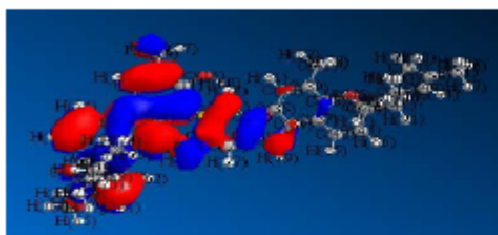
Andrographolide LUMO



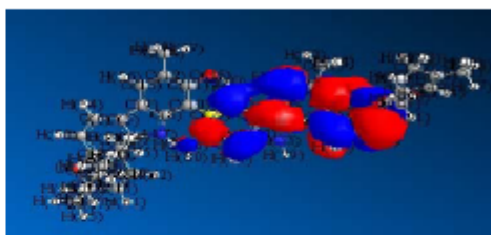
Threonine HOMO



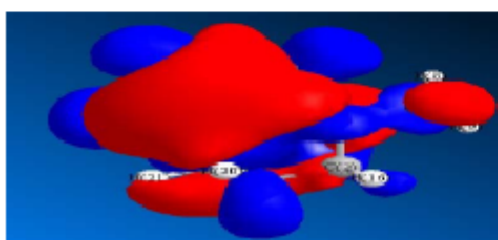
Threonine LUMO



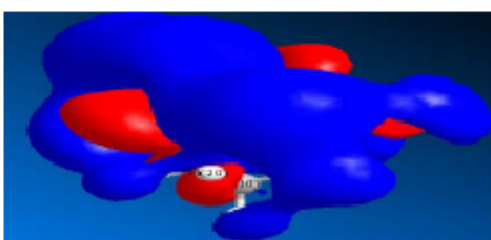
Mahabinine HOMO



Mahabinine LUMO



Arginine HOMO



Arginine LUMO

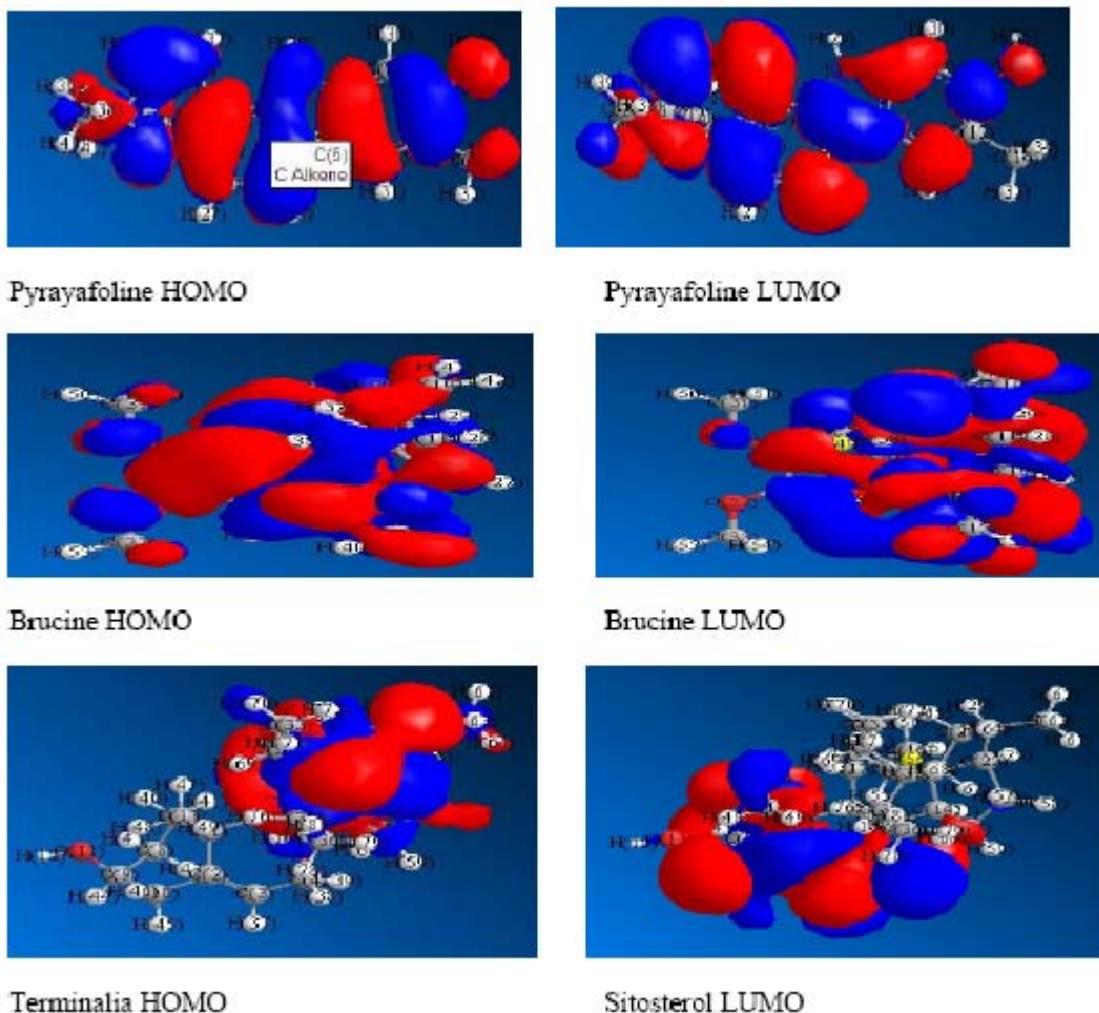


Fig. 3:

responsible for the interaction with surface atoms. Excellent corrosion inhibitors are usually those compounds who not only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal. It is important to focus on the parameters that directly influence the electronic interaction of the inhibitor molecules with the metal surface. These are mainly: E_{HOMO} , E_{LUMO} , ΔE ($E_{\text{LUMO}} - E_{\text{HOMO}}$), and dipole moment μ . The values of calculated quantum chemical parameters such as E_{HOMO} , E_{LUMO} , ΔE ($E_{\text{LUMO}} - E_{\text{HOMO}}$) and μ of Plant extracts are listed in Table 1. Higher values of the E_{HOMO} facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer. Therefore, the energy of the E_{LUMO}

indicates the ability of the molecule to accept electrons; hence these are the acceptor states.

The lower the value of E_{LUMO} , the more probable, it is that the molecule would accept electrons. As for the values of ΔE ($E_{\text{LUMO}} - E_{\text{HOMO}}$) concern; lower values of the energy difference "E" will cause higher inhibition efficiency because the energy to remove an electron from the last occupied orbital will be low. For the dipole moment (μ), higher values of μ will favor strong interaction of the inhibitor molecules with metal surface and lower values favor the accumulation of inhibitor molecules around electrode surface. Quantum chemical parameters presented in Table 1 confirmed strong

interaction of extracts molecules with the metal surface and thereby forming protective adsorption layer at mild steel/acid solution interface.

Mechanism of Inhibition

Inhibition performance of Plant extracts for mild steel in 1 M HCl interface depends on the extent of adsorption and adsorption depends on several factors such as the number of adsorption sites, molecular size, and mode of interaction with the metal surface and extent of formation of metallic complexes. The neutral molecules may be adsorbed on the mild steel surface through the chemisorption mechanism, involving the displacement of water molecules from the mild steel surface and the sharing electrons between the hetero atoms and iron. The inhibitor molecules can

also adsorb on the mild steel surface on the basis of donor–acceptor interactions between π -electrons of the aromatic ring and vacant d-orbitals of surface iron atoms.

CONCLUSIONS

1. The inhibitors studied had an excellent inhibition effect for the corrosion of mild steel in 1 M HCl. The high inhibition efficiencies of were attributed to the adherent adsorption of the inhibitor molecules on the mild steel surface.
2. Quantum chemical approach is adequately sufficient to predict the structure and molecule suitability to be an inhibitor.

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