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# Evaluation of *Fennel* Seed Extract as a Green Corrosion Inhibitor for Pure Aluminum in Hydrochloric Acid: An Experimental and Computational Approach

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**Abstract-** Fennel seeds extract was investigated as a potential green corrosion inhibitor for pure Aluminum in 1M hydrochloric acid using gravimetric, galvanostatic polarization and electrochemical impedance techniques. The results from gravimetric measurements illustrate increase in inhibition efficiency with increment in extract concentration. Galvanostatic polarization curve revealed that the mode of inhibition was mixed type with predominance of cathodic inhibition. The results from impedance measurements revealed that with increase in concentration of inhibitor, charge transfer resistance increases while double layer capacitance value was deduced indicating adsorption of phytochemical constituents present in extract at metal/solution interface. The quantum chemical calculation facilitates the judgment that E-anethole pursues highest activity as a corrosion inhibitor in comparison with other molecules present in the extract.

**Keywords-** Corrosion inhibitor, *Fennel*, Gravimetric method, Electrochemical technique, Hydrochloric acid, DFT

## 1. INTRODUCTION

Corrosion is a naturally occurring phenomenon commonly defined as the deterioration of a metal that results from a chemical or electrochemical reaction with its environment. Generally, metal gets corroded in presence of acids, alkali, sulphides and salts. However, acids such as hydrochloric acid, phosphoric acid, nitric acid and hydrofluoric acid are used in pickling, etching and descaling of metals [1-4]. To combat corrosion of metal in acidic environment, use of inhibitors is the most practical approach.

The metal is protected from corrosion when inhibitor gets adsorbed at the metal/corrosive environment interface. The factors affecting the adsorption of inhibitor molecule depends on the functional groups, steric effect, molecular size and electron density at the donor atoms [5-8]. The previous research highlights that the organic compounds containing nitrogen, sulfur, and oxygen atoms in their structure were used as a corrosion inhibitor [9-12]. In spite of the fact that the synthetic organic compounds shows good inhibitive properties, their usage is still undesired due to their adverse effects on human beings, environment, as well as high costs. In the recent years, there has been an increasing awareness of environment and green chemistry [13-17]. It can be seen from the literature survey that exploration of plant extract was higher for corrosion inhibition of Aluminum (Al) in hydrochloric acid [HCl] as compare to the spice extract. To observe the inhibitive effect of spice on Al, present work is performed.

Spices are the dried seed, fruit, root, bark, or vegetable substance primarily used for flavoring or preserving food. Spices are the rich source of naturally synthesized organic compounds. There are wide varieties of spices grown in India such as black pepper, cumin, turmeric, coriander etc. The classification of compounds can be done according to the functional group present in them such as alcohol, aldehyde, amines, esters, ketones, ethers, terpenes and other miscellaneous compounds [18]. Due to the presence of phytochemical constituents, spices had pharmacological applications [19,20]. Further, their applications were expanded for corrosion inhibition of metal to explore the effects of the compound for inhibitive properties. The previous researches display that turmeric [21], black pepper [22], coriander [23], punica gratanum [24] and *fennel* [25,26] act as good corrosion inhibitor for steel. However, vanillin [27,28] and pipali [29] proved to be good protector of aluminum from corrosion.

The present work was focused to study the inhibitive effect of *fennel* extract molecules for pure Aluminum (Al) in 1M HCl medium. According to the literature survey, *fennel* seed possesses anethole and fenchone as its major constituents [18]. The chemical constituents present in spice consist of heteroatom (O) which can be easily protonated in the presence of HCl solution. The protonated compounds can then adsorb over surface of metal through the chloride ions present on its surface leading to protection of metal from corrosion.

## 2. EXPERIMANTAL

### 2.1. Specimen preparation

The pure Al specimen of dimension 3.0×6.0×0.05 cm was used for the gravimetric measurements. The composition of Al specimen was: Al (99.2%), Fe (0.498%), Si (0.144%), Mn (0.031%), Cu (0.007%), Mg (0.005%) and Zn (0.001%).

The Al specimen (working electrode) and platinum electrode (counter electrode) used for galvanostatic polarization and electrochemical impedance measurements were of circular design along with a handle. The exposed surface area of counter electrode should always be greater than working one, therefore, exposed surface area for working and counter electrode employed were 6.156 $cm^2$ and 13.886 $cm^2$ respectively.

### 2.2. Preparation and Characterization of inhibitor

The stock solution of extract was prepared by refluxing weighed amount of the grounded *fennel* seeds in methanol for 90 minutes, kept for 24 hours and then filtered.

Further, to know the chemical constituents present in the *fennel* extract, GC-MS analysis of the extract was performed by using GC-MS QP-2010 plus of Shimadzu. The GC column used for analysis was Rtx-5 of 30 m × 0.25 mm × 0.25 μm dimensions. The ion source of mass spectrometer (MS) detector was held at 230°C for the fragmentation of the eluted compounds which finally goes into the mass analyzer and was detected. The detection was performed in full scan mode with ratio of mass over charge varying from m/z 40 to 650.

### 2.3. Gravimetric method

Gravimetric measurements were carried out to study the inhibitive effect of test solution containing *fennel* extract on Al in 1 M HCl solution using Megatron thermostat for maintaining the temperature of water bath at 35ºC. The concentration of test solution concentration was varied from 0.03 g/l-0.80 g/l by diluting the stock solution of extract in 1 M HCl solution.

### 2.4. Electrochemical Methods

In galvanostatic polarization, the potential of working electrode (Al) was measured against a saturated calomel electrode. When current density varying from $2\times10^{-4}$ to $3.25\times10^{-2}$ A/$cm^2$ was applied across the cell, potential was generated which were further used to determine the corrosion parameters; corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$) and Tafel slope ($b_a, b_c$).

Electrochemical impedance study (EIS) was performed using AUTOLAB instrument. The potential was applied in the form of sine wave across the cell with a frequency ranging from 10 kHz to 1 Hz and amplitude of 10 mV at an open circuit potential of -831 V. EIS data so obtained from the measurement were analyzed using frequency response analyzer (FRA) electrochemical setup.

### 2.5. Quantum chemical study

Quantum chemical calculation was carried out for elucidating electronic structures and reactivity of molecules present in the extract. The structure optimization of extract molecules were performed using Gaussian 09 program. The minimum energy structure of molecules was achieved using B3LYP, a hybrid functional in Density Functional Theory (DFT) and 6-31G (d) basis set. B3LYP consists of Becke's three parameters exact exchange functional B3 combined with the nonlocal gradient corrected correlation functional of Lee-Yang-Par (LYP).

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of *fennel* extract

The characterization of *fennel* extract was performed with the help of GC-MS technique. From GC-MS analysis, six major compounds were identified in the methanol extract of *fennel* as shown in Table 1.

**Table 1.** GC-MS analysis of methanol extract of *fennel*

| Peak | R.Time (minutes) | Area (%) | Name |
|---|---|---|---|
| 1 | 13.579 | 2.78 | 1,5-Anhydro-6-deoxyhexo-2,3-diulose |
| 2 | 16.407 | 2.10 | Hydroxy methyl furfural |
| 3 | 17.740 | 6.59 | (E)-1-(4-Methoxyphenyl)propene |
| 4 | 33.442 | 7.98 | n- Hexadecanoic acid |
| 5 | 36.938 | 69.1 | (Z)-6-Octadecenoic acid |
| 6 | 45.985 | 3.09 | (Z)-9-Octadecenoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester |

### 3.2. Gravimetric measurements

When Al is introduced in HCl medium, the oxide film of $Al_2O_3$ over Al surface was broken and reacted with acid due to its amphoteric nature. The dissolution reaction of Al in HCl medium may be:

$$Al_2O_3 + 6HCl \leftrightarrow 2AlCl_3 + 3H_2O \ldots$$

The effect of inhibitor concentration was observed using gravimetric technique to protect Al metal from corrosion in 1 M HCl solution. To control the formation of aluminum chloride, *fennel* extract was used as an inhibitor and the molecules present in the extract gets adsorbed

over the surface of Al. The inhibition efficiency of *fennel* extract with its concentration varying from 0.03 g/l–0.80 g/l with an immersion period of 60 minutes at 308 K is shown in Table 2. It was observed from results that the inhibition efficiency enhances with rise in concentration of the inhibitor reaching inhibition efficiency of 92.90% at 0.80 g/l g/l of inhibitor concentration. The results so obtained were due to increase in surface coverage area of Al by inhibitor molecules with increase in its concentration.
The inhibition efficiency and surface coverage was obtained as:

$$I\,\% = \frac{W_u - W_i}{W_u}\ X\ 100 \qquad (1)$$

$$\text{Surface coverage } (\theta) = \frac{W_u - W_i}{W_u} \qquad (2)$$

where $'W_u'$is the weight loss of Aluminum without inhibitor and $'W_i'$isthe weight loss with inhibitor [30].

**Table 2.** Corrosion parameters for pure Al in presence and absence of *fennel* extract at 308 K for exposure period of 60 minutes

| Inhibitor | Inhibitor concentration (C) (g/l ) | Weight lossmgcm$^{-2}$ | Surface coverage (θ ) | I % |
|---|---|---|---|---|
| Blank | - | 23.68 | - | - |
| *Fennel* | 0.03 | 17.86 | 0.24 | 24.58 |
| *extract* | 0.11 | 5.49 | 0.76 | 76.82 |
| | 0.46 | 2.44 | 0.89 | 89.69 |
| | 0.80 | 1.68 | 0.92 | 92.90 |

### 3.3. Galvanostatic polarization

The behavior of inhibitor was evaluated as anodic, cathodic or mixed type with support of galvanostatic polarization measurements. The polarization measurements were performed for the corrosion process of Al in presence and absence of inhibitor in 1 M HCl environment at 308 K. The corresponding electrochemical parameters such as corrosion potential ($E_{corr}$), cathodicTafel slope ($b_c$), anodic Tafel slope ($b_a$) and corrosion current density ($I_{corr}$) determinedfrom Figure 1 are shown in Table 3. The value of $I_{corr}$ in absence and presence of inhibitor was used to obtain the inhibition efficiency(I %)of extract by using the following equation:

$$I\,\% = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}}\ X\ 100 \qquad (3)$$

where $I^0_{corr}$ and $I_{corr}$ are corrosion current density in absence and presence of inhibitor.

It was observed that the addition of *fennel* extract to the corrosive solution reduces anodic dissolution of Al and also retards cathodic hydrogen evolution reactions. The corrosion potential displays a very small change from -813 mV to -830 mV *vs* SCE with no definite trend suggesting the inhibition to be mixed type. It can be observed from Table 3 that corrosion current density decreases with increase in inhibitor concentration without change in the hydrogen evolution reaction. This suggests that *fennel* extract gets adsorbed on the Al surface and therefore protect it from the action of corrosion medium [31].

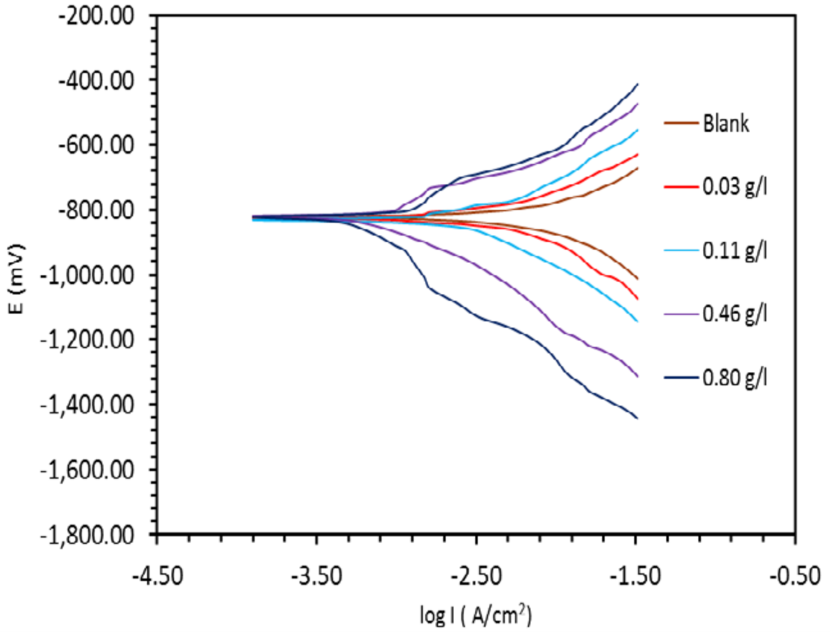



**Fig. 1.** Anodic and cathodic polarization curves obtained for pure Al at 308 K in 1.0 M HCl in various concentration of *fennel extract*

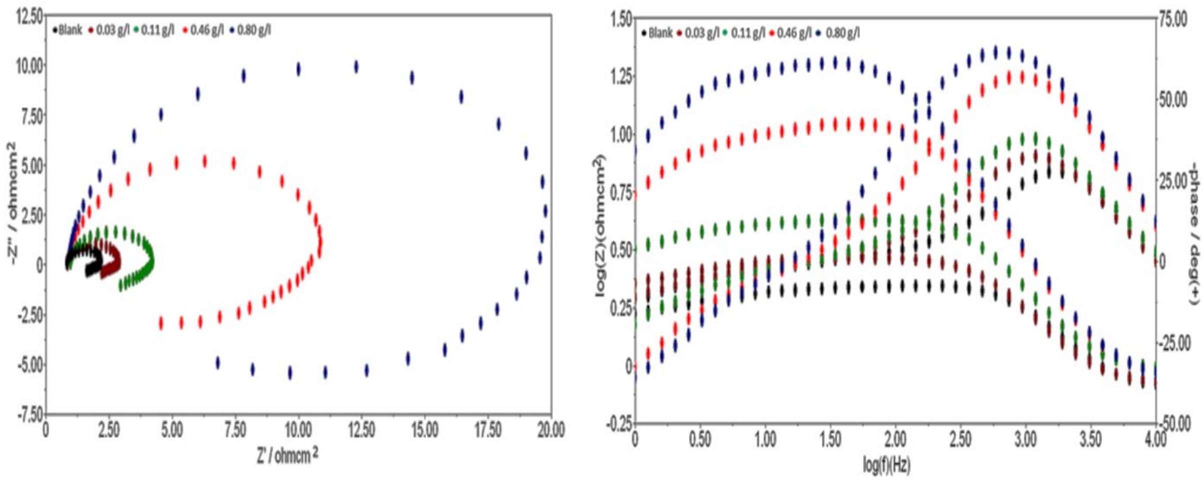
**Table 3.** Polarization parameters of corrosion of pure Al in presence of different concentration of *fennel extract* at 308 K and corresponding inhibition efficiencies

| Concentration (C) (g/l) | $E_{corr}$ (mV) | $\beta_a$ (mV/dec) | $\beta_c$ (mV/dec) | $I_{corr}$ (A/cm²) | I % |
|---|---|---|---|---|---|
| Blank | -820 | 153.84 | 200.00 | $7.76\times10^{-3}$ | - |
| 0.03 | -824 | 224.00 | 293.33 | $5.89\times10^{-3}$ | 24.14 |
| 0.11 | -830 | 190.08 | 226.66 | $2.24\times10^{-3}$ | 71.16 |
| 0.46 | -818 | 242.22 | 303.33 | $1.00\times10^{-3}$ | 87.12 |
| 0.80 | -821 | 168.72 | 358.00 | $6.30\times10^{-4}$ | 91.87 |

### 3.4. Electrochemical impedance spectroscopy (EIS) measurements

The evaluation of inhibition efficiency of *fennel* extract was further performed with the help of impedance measurements. Figure 2a depicts the Nyquist plot while Figure 2b illustrates Bode plot for the impedance measurements of Al specimens in 1 M HCl solution in presence and absence of different concentrations of *fennel* extract.

According to the basic principle of EIS for corrosion phenomenon, Nyquist plot always showed perfect semicircle. However, there was a formation of depression in the semicircle obtained from Nyquist plot suggesting presence of interfacial heterogeneity and roughness at electrode surface. The semicircle so obtained was a characteristic of parallel arrangement of constant phase element and charge-transfer resistance corresponding to the Al dissolution reaction. It was observed from the plots that diameter of depressed semicircle increases as the inhibitor concentration increases. The Bode plot consists of one time constant due to depression in the capacitive loop present in plot of phase angle versus logf. The impedance and phase angle at high frequency range demonstrate the adsorption of inhibitor molecules while at low frequency region, it provides information on charge transfer resistance. Their presence of inductive loop was also observed in Nyquist plot.




(a) (b)

**Fig. 2. (a)** Nyquist plot obtained at 308 K for corrosion inhibition of pure Al by *fennel* extract at various concentrations; **(b)** Bode plot obtained at 308 K for corrosion inhibition of pure Al by *fennel* extract at various concentrations

It is very common to have inductance part present in corrosion of Al in acid medium. The origin of the inductive loop on Al wasnot clearly understood till now. However, from previous works performed by various researchers attributed the presence of inductive loop to surface or bulk relaxation of species [32], existence of passive film on Al [33] or rearrangement of surface charge at metal/oxide interface [34]. It was also proposed that adsorbed intermediates in reduction of hydrogen ions could cause an inductive loop [35].

The appropriate circuit model which describes the impedance parameters after fitting experimental data obtained from the Nyquist plot was$R_s$ ($QR_t$ [$LR_L$]).The model includes solution resistance,$R_s$, charge transfer resistance, $R_t$,constant phase element (CPE), $Q$, and inductive elements, $L$ and $R_L$. CPE is used as a replacement for capacitance to obtain the best fit of experimental data in the equivalent circuit model. The CPE is defined by two values, Q and n and its impedance is represented by:

$$Z_{CPE} = Q^{-1}(j\omega)^{-n} \quad (4)$$

Where $j = (-1)^{\frac{1}{2}}$, $\omega$ is frequency in rad $s^{-1}$, $\omega = 2\pi f$and f is the frequencyin Hz. When n value is close to one, the impedance of CPE is identical to that of a capacitor, $Z_C = (iwc)^{-n}$. The impedance parameters derived from the Figure 2 are shown in Table 4.The increase of $R_t$ in the presence of studied extracts may be due to the gradual replacements of water molecules by adsorption of the molecule of fennel extract on the metal surface [36]. Since $R_t$ value is inversely proportional to corrosion rate and hence can be used to calculate the inhibition efficiency of inhibitor by using following equation:

$$I\,\% = \frac{R_t - R_t^0}{R_t}\ X\ 100 \quad (5)$$

Where, $R_t$ and $R_t^{\circ}$ are the value of charge transfer resistance in 1 M HCl in presence and absence of inhibitor, respectively.

**Table 4.** Impedance parameters and corresponding inhibition efficiency for the corrosion inhibition of pure Al by *fennel* extract at 308 K

| Inhibitor | Concentration (C) (g/l) | $R_s$ ($\Omega cm^2$) | $R_t$ ($\Omega cm^2$) | Q ($\mu F cm^{-2}$) | $R_L$ ($\Omega cm^2$) | L ($H cm^2$) | n | I % |
|---|---|---|---|---|---|---|---|---|
| Blank | - | 0.82 | 1.38 | 156.30 | 3.41 | 0.12 | 0.96 | - |
| | 0.03 | 0.85 | 1.98 | 155.40 | 3.24 | 0.41 | 0.97 | 30.34 |
| *Fennel* | 0.11 | 0.99 | 3.16 | 96.73 | 3.26 | 0.59 | 0.99 | 56.33 |
| extract | 0.46 | 0.91 | 10.01 | 69.98 | 12.81 | 1.14 | 0.98 | 86.21 |
| | 0.80 | 0.92 | 18.60 | 65.56 | 13.43 | 1.53 | 0.96 | 92.58 |

The decrease of CPE in comparison with that in HCl solution without *fennel* extract and also with increase in inhibitor concentrations was observed from impedance parameters. According to Helmholtz model, the capacitance of double layer is inversely proportional to the thickness of a protective layer suggesting that decrease in CPE illustrates increase in protective layer thickness with increase in inhibitor concentration indicating effective corrosion inhibition [37].

### 3.5 Adsorption isotherm

Adsorption isotherm can be utilized in elucidating the nature of interaction between extract molecules and Al surface. The data obtained from gravimetric measurements were used to determine the adsorption characteristics of extract over Al surface in 1 M HCl solution at 308 K for exposure period of 60 minutes. The best fit was obtained by evaluating regression coefficient value which was highest (0.998) in case of Langmuir adsorption isotherm as shown in Figure 3 which is best described by the below equation:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (6)$$

Where θ is the degree of surface coverage, $C$(g/l) is the inhibitor concentration in solution, $K_{ads}$is the equilibrium constant for adsorption process.

The adsorptive equilibrium constant for *fennel*obtained from isotherm at 308 K was found to be 66.809 $Lg^{-1}$. $K_{ads}$ value can be related to the standard free energy of adsorption ($\Delta G^0_{ads}$ ) by the following equation:

$$K_{ads} = \frac{1}{C_{H_2O}} \exp(-\frac{\Delta G^0_{ads}}{RT}) \quad (7)$$

Where $C_{H_2O}$ is the concentration of water in solution expressed in g $L^{-1}$, R (kJ $mol^{-1}$ $K^{-1}$) is the universal gas constant and T (K) is temperature. It must be noted that the concentration unit of water molecules has to be similar to that of the inhibitor (the unit of $C_{H_2O}$is g $L^{-1}$ with the value of approximate $1\times10^3$) [38]. The values of $\Delta G^0_{ads}$ up to -20 kJ $mol^{-1}$ are consistent with physisorption, while those around -40 kJ $mol^{-1}$ or higher are associated with chemisorptions and that in between -20 kJ $mol^{-1}$and -40 kJ $mol^{-1}$ is related to mixed adsorption [39].

$\Delta G^0_{ads}$ value obtained for *fennel* extract is -24.86 kJ $mol^{-1}$, indicating adsorption was not solely of physical type. There may be presence of some chemisorption but to a very less extent as the free energy of adsorption value was more close to physical adsorption mechanism.

### 3.7. Quantum chemical Study

The experimental finding shows that the corrosion inhibitory action of *fennel* extract was due to adsorption of extract molecules over metal surface. The complexity of molecules present in inhibitor makes difficult to interpret the major contributor towards inhibitory capability of fennel extract. Quantum study using DFT approach can provide individual inhibitory activity of molecule from which reasonable justification can be drawn to support the order in which molecules present in extract might be effective as a corrosion inhibitor.

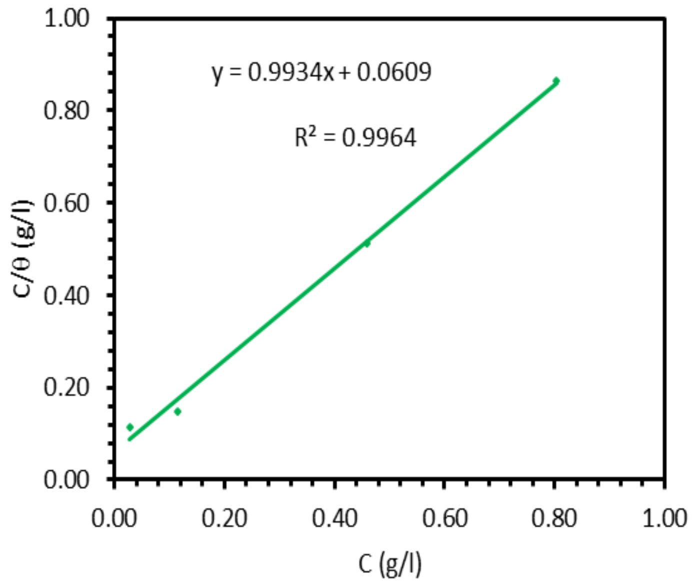



**Fig. 3** Langmuir adsorption isotherm plot for *fennel* extract at 308 K for 60 minutes

DFT approach was adopted to calculate the energy of highest occupied ($E_{HOMO}$) and lowest unoccupied ($E_{LUMO}$) molecular orbital of major compounds of *fennel* extract as shown in Figure 4. $E_{HOMO}$ is related to the tendency of molecular species to donate the electrons to empty orbital of metal while $E_{LUMO}$ describes the tendency of molecules to accept the electrons. Similarly, energy gap $\Delta E$ value is related to the energy required to remove an electron from the last occupied orbital. The inhibition efficiency increases with increase in the value of $E_{HOMO}$ but decreases with increase in $E_{LUMO}$ and $\Delta E$. The energy values of molecular orbital of main chemical constituents of *fennel* extract are presented in Table 5. It can be seen from the table that E-anethole has highest value of $E_{HOMO}$ indicating its maximum tendency to donate electrons.

HOMO and LUMO of E-anethole, MF, HA, OA, OAEE and ADD as depicted in Figure 5(a-l) respectively provide information about the distribution of electrons in the respective molecules. It was observed from the figures that E-anethole, MF, HA, OA and ADD has surplus of electrons either in the vicinity of oxygen atom (hetero atom) or near π-electron cloud of aromatic ring and unsaturated bonds. However, in case of OAEE excess of electron is observed near oxygen atoms and not at the unsaturated double bonded carbon atom. These observations indicate that oxygen present in different functional groups and π-electron clouds of different sorts of unsaturation have ability to donate electrons to the empty p-orbital of Al. The atoms present in these groups might also have a tendency to accept electrons from the filled s-orbital of Al.

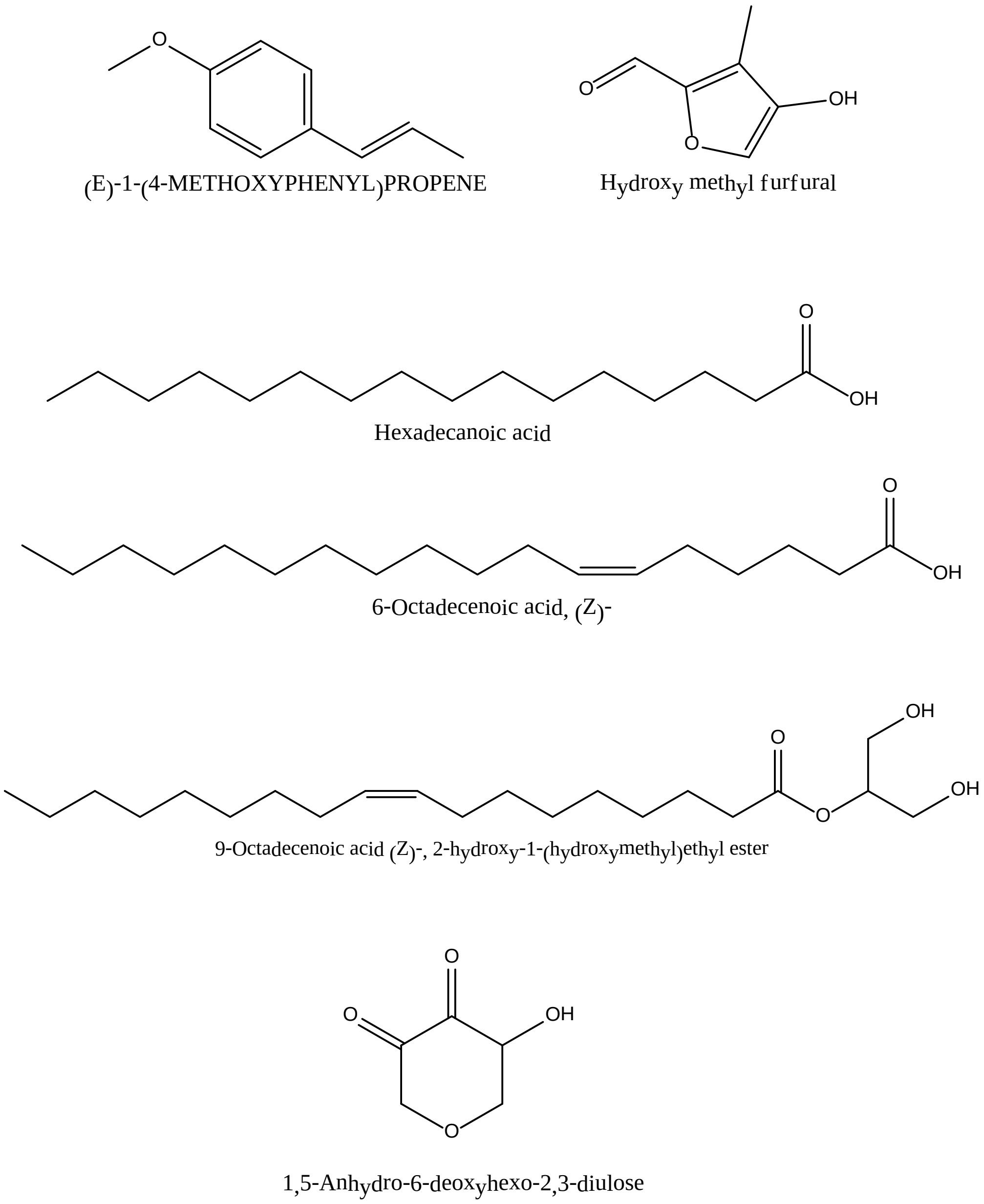



**Fig. 4.** Main chemical constituents of *fennel* extract

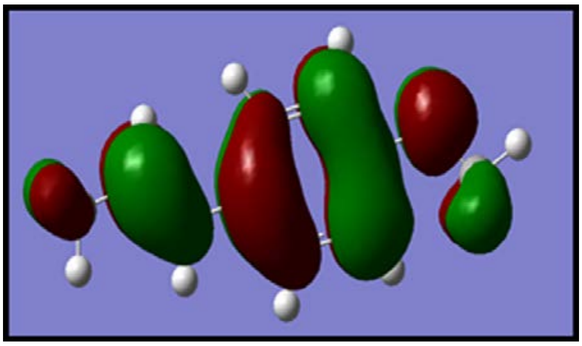
It was important to understand the tentative number of electrons which can be transferred individually by the inhibitor molecules to Al. The greater the ΔN value more will be the donating power of the molecule. According to previous study [40], if ΔN is less than 3.6, the inhibition efficiency increases with increase in electron donating ability at the metal surface. E-anethole has highest value for ΔN which is also less than 3.6 indicating its highest tendency to inhibit the Al specimen. Therefore, from DFT calculations the order of inhibitive activity of chemical compounds present in *fennel* extract can be:

$E - anethole > OAEE > MF > OA > HA > ADD.$

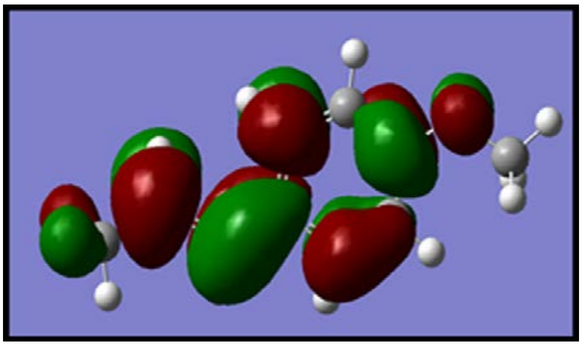
The molecular simulation can also be performed for better understanding of interaction between *fennel* extract molecules and Al which can leads more accurately in illustrating the major inhibitory activity contributor for Al in HCl medium among various molecules present in the extract.

**Table 5.** Quantum chemical parameters of *fennel* extract

| Compound | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | ΔE (eV) | η (eV) | σ (eV) | χ (eV) | ΔN (eV) |
|---|---|---|---|---|---|---|---|
| E-anethole | -5.41 | -0.27 | 5.14 | 2.57 | 0.39 | 2.84 | 0.56 |
| MF | -6.26 | -1.49 | 4.76 | 2.38 | 0.42 | 3.87 | 0.38 |
| OA | -6.39 | -0.29 | 6.69 | 3.07 | 0.32 | 3.34 | 0.35 |
| OAEE | -6.36 | 0.16 | 6.53 | 3.26 | 0.30 | 3.10 | 0.39 |
| ADD | -6.99 | -2.77 | 4.21 | 2.11 | 0.47 | 4.88 | 0.19 |
| HA | -7.43 | -0.29 | 7.13 | 3.56 | 0.28 | 3.86 | 0.26 |



(a)



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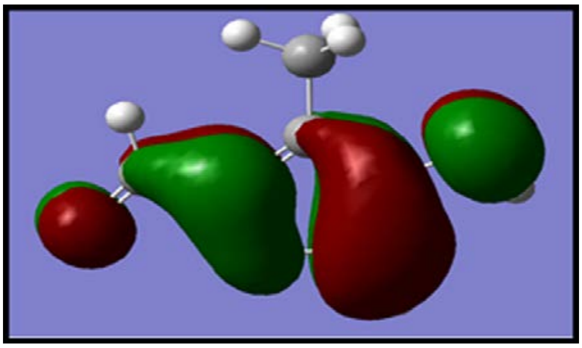

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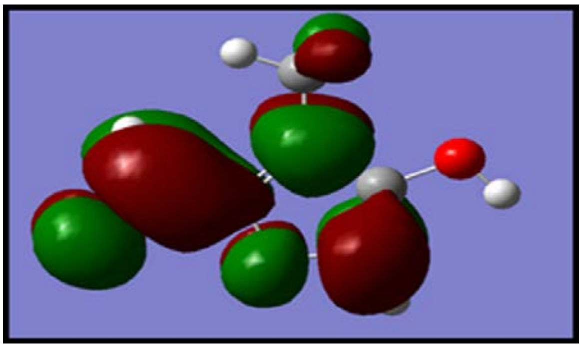

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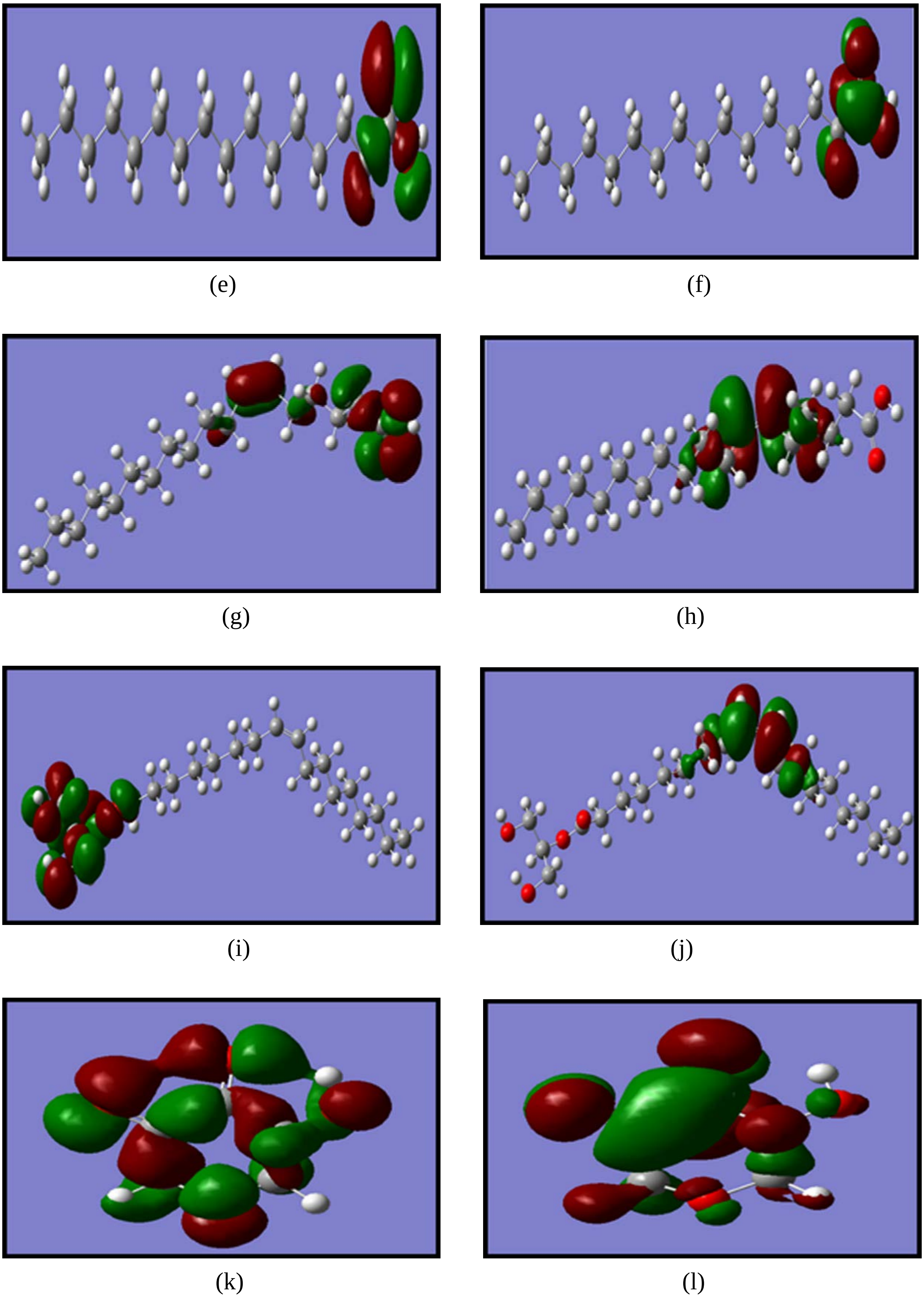


**Fig. 5.** HOMO and LUMO of (a,b) anethole, (c, d) MF, (e, f) HA, (g,h) OA, (i,j) OAEE, (k, l) ADD respectively

## 4. CONCLUSION

The inhibitive effects of various concentrations (0.03 g/l–0.80 g/l) of *fennel* extract were evaluated over pure Al in 1 M HCl medium by using gravimetric and electrochemical techniques. The result from gravimetric method shows that the molecules present in fennel extract was physisorbed over Al surface to inhibit the corrosion reactions occurring over Al specimen in presence of HCl solution. EIS measurement result display that the constant phase element value decreases and charge transfer resistance increases with increase in concentration of inhibition. On the basis of DFT calculation, E-anethole is the major active inhibitory compound among six other main compounds present in the extract.

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