

Lawsonia inermis Leaves Extract to Impede Acid Corrosion of Copper

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Abstract: The inhibitive propensity of ethanolic extracts of *Lawsonia inermis* leaves on corrosion of copper in 0.5M HCl was studied at room temperature using chemical method. Inhibition efficiency was observed to increase with increase in the concentration of *Lawsonia inermis* extract and was found maximum (90.01%) at its 1.09g/L concentration. Various corrosion, kinetic and thermodynamic parameters were calculated using experimental data. The adsorptive propensity of the inhibitor was endorsed by carrying out Quantum chemical analysis (QCA) and other surface morphological analyses (FT-IR spectroscopy, UV-Vis spectroscopy, SEM etc.). Gibb's free energy for adsorption was also evaluated and it was found that the inhibitor's active components were spontaneously adsorbed onto the copper surface through a physical adsorption mechanism. The adsorption of inhibitor onto copper surface obeyed Langmuir adsorption isotherm.

Keywords: Copper, acid corrosion, kinetic and adsorptive parameters, SEM

1. Introduction

Copper, due to its high technological value, high thermal and electrical conductivities, is a widely used common constructing material for industrial and domestic tools for house hold appliances [1]. Under normal conditions, copper shows high resistance and noble behavior to corrosion, but a considerable metal dissolution occurs when exposed to harsh environment, therefore, corrosion prevention studies becomes utmost significant and needs to explore extensively. Use of inhibitors to mitigate corrosion of metals in corrosive media is a widespread phenomenon [2-3]. Corrosion inhibitors impede the metal-surface dissolution either by forming a protective film on the surface or by reducing the aggressiveness of the media toward the metal surface. Selection of corrosion inhibitors depends on the nature of corrosive media and the metal. For prevention of copper getting corrode in acidic media, many organic compounds are well established as corrosion inhibitors, but toxicity of these organic inhibitors and economic factors associated with their production restricts their use and hence, as per environmental legislations, search for alternatives moiety becomes inevitable. *Green inhibitors* are rich source of compounds with good inhibitive and adsorptive property, moreover, they inexpensive, biodegradable, readily available and renewable [4-5].

An attempt was made to mitigate the acid corrosion of copper (in 0.5 M HCl) employing extract of *Lawsonia inermis* leaves. *Lawsonia inermis* leaves are richly constituted with carbohydrates, proteins, flavonoids, tannins and phenolic compounds, alkaloids, terpenoids, quinones, coumarins, xanthenes and fatty acids, in addition to high percentage of lawsone, gallic acid, ascorbic acid, p-caumaric acid, apigenin, β -sitosterol, luteolin and 2-methoxy,3-methy,1,4-naphthoquinone compounds (figure 1) [6-10].

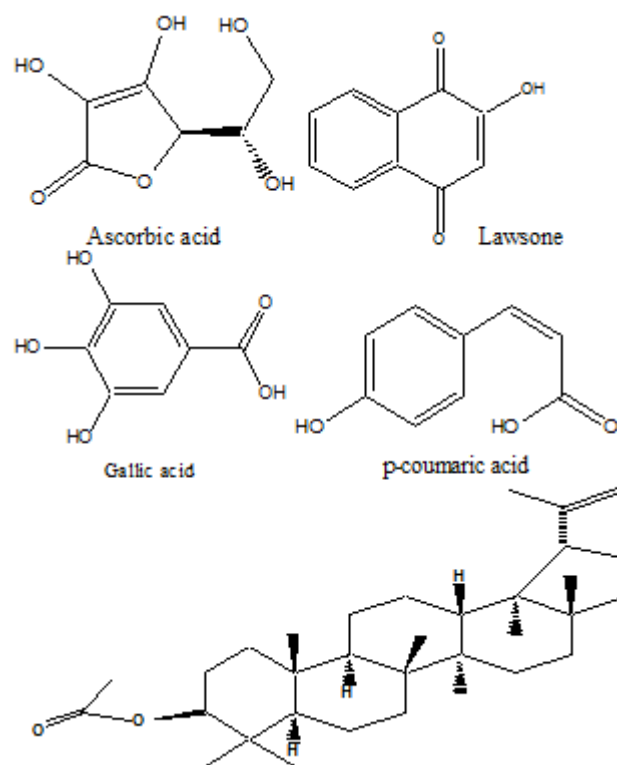


Figure 1: Some of the major constituents of *Lawsonia inermis* leaves

2. Experimental

2.1 Chemical method

Chemical measurements were performed by the similar procedure as reported earlier [4-5, 11-14]. The pre-surface treated specimens or coupons were suspended in the test solutions without and with inhibitor. Difference in loss in weight of the specimen before and after immersion in different concentration of inhibitor and was determined using an analytical balance (Adair Dutt 205 ACS).

2.2 Preparation test coupons

Rectangular coupons of copper were mechanically press-cut with dimensions (3 cm x 2.4 cm x 0.16 cm) and a hole about 0.12 mm diameter drilled for free suspension. Each coupon was surface treated and dried in desiccators prior to experimentation as per standard procedures [4-5, 11-14].

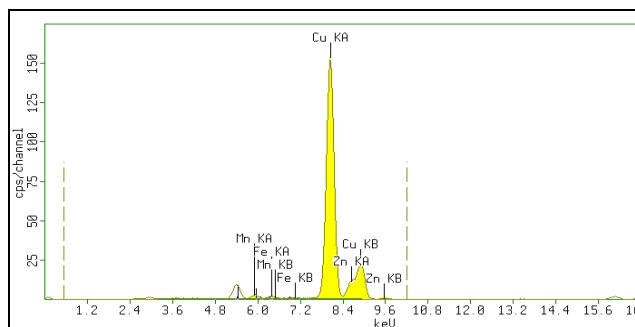


Figure 2: XRF analysis of Cu metal coupon

These coupons were investigated for exact composition using XRF and were found to have: (Mn) 0.51%, (Fe) 0.19%, (Cu) 93.6%, (Zn) 5.7% (figure 2)

2.3 Preparation of *Lawsonia inermis* leaves extract

Weighed amount of leaves of *Lawsonia inermis* were shade dried and finely powdered which was soaked in distilled ethanol in a properly corked container. On completion of soaking period, the ethanolic solution was refluxed by the soxhlet extractor to concentrate the inhibiting chemicals and finally filtered to remove any suspended impurities [11-14]. The stock solution of the extract is stored in a clean corked bottle for further use.

2.4 Preparation of test solutions

All reagents used for the study were of AnalR grade. The test solutions of 0.5 M HCl was prepared using doubly distilled water. Seven separate (100 ml) beakers were labeled as C0, C1, C2, C3, C4, C5, C6 and EELiL was added in the order of increasing concentration so as to have following concentrations of extract viz. 0, 0.0312, 0.158, 0.312, 0.463, 0.78, and 1.092 g/L respectively [11-14].

2.5 Quantum Chemical Analysis (QCA)

Quantum chemical analysis were carried out by using the PM3 method of the quantum chemical Package MOPAC 6.0 of Hyperchem 7.5. The energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the Lowest unoccupied molecular orbital (E_{LUMO}), energy band gap, $\Delta E = E_{HOMO} - E_{LUMO}$, binding energy, heat of formation and the dipole moment (μ) were calculated by Quantum Chemical Analysis (QCA).

2.6 Surface Morphological Analysis

2.6.1 UV-visible Spectroscopy

The adsorption behavior of organic compounds present in the extract was also investigated by the help of UV-Visible spectrum. UV-Visible absorption spectra achieved on (8400

Shimadzu, Japan) with help of quartz glass cell in 400-800 nm visible range.

2.6.2 SEM

Surface morphology of metal surface was studied by taking SEM images of the coupon surface before and after immersion in corrosive medium and without and with inhibitor (EELiL) at its different concentrations.

2.6.3 FT-IR Spectroscopy

FT-IR spectroscopic inspections were carried out on 8400 Shimadzu, Japan, FT-IR spectrometer in the IR range from 4000 to 400 cm^{-1} to justify the formation of the adsorbed protective film over the surface of copper metal coupon. The FT-IR spectrum of the protective film was recorded.

3. Results and Discussion

3.1 Chemical Method

The inhibitive efficacy of EELiL for Copper coupons in 0.5 M HCl was studied at various immersion time periods and at room temperature using the chemical measurements. Corrosion, kinetic and adsorptive parameters like corrosion rate (ρ_{corr} , in mmy^{-1}), percentage inhibition efficiency (IE%), fractional surface coverage (Θ), adsorption equilibrium constant (K_{ad}) etc. were evaluated and tabulated in table 1.

3.1.1 Effect of inhibitor concentration

Effect on inhibition efficiency (IE%) on copper coupons immersed for different time intervals was investigated using different concentrations of inhibitor and the results were tabulated (table 1). On adding EELiL to the test solution, a remarkable decrease in corrosion rate was observed (table 1 and fig. 3) and minimum corrosion rate found in presence of inhibitor (1.09 g/L) at 72h immersions. This may be attributed to the adsorption of active constituents onto the coupon surface as a barrier for mass and charge transfers and protecting it from further attack by the aggressive medium.

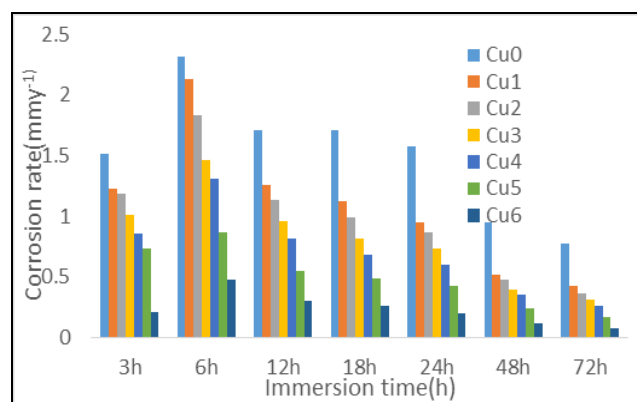


Figure 3: Corrosion rate vs. Immersion period (h) without and with various concentration of EELiL at room temperature $303 \pm 1\text{K}$

The inhibition efficiency (IE %) increases with increase in inhibitor concentration and a significant efficiency (90.01%) was obtained with 1.092g/L concentration of EELiL at 72 hours immersion periods (figure 4-5). Since the area of coupon surface covered by the adsorbed molecules of

Lawsonia inermis increased with increase in concentration of inhibitor, resulting significantly high % IE.

Table 1: Corrosion Parameters of Acid Corrosion of Copper without and with different concentrations of EELi at various Immersion Period (h) at Room Temperature.

Time period (h)	EELiL Conc. (g/L)	Corrosion parameters				
		Corros. rate (ρ_{corr}) (mmpy)	IE %	Fractional Surface coverage $\times 10^{-2}$ (θ)	Adsorption Equilibrium Constant (K_{ad})	Gibbs Free energy (ΔG)
3	C0	1.52	-	-	-	-
	C1 0.0312	1.23	19.23	19.23	7.63	-15.23
	C2 0.158	1.19	21.79	21.79	1.78	-11.57
	C3 0.312	1.01	33.33	33.33	1.60	-11.30
	C4 0.463	0.86	43.58	43.58	1.65	-11.38
	C5 0.780	0.74	51.28	51.28	1.34	-10.87
	C6 1.091	0.22	85.89	85.89	5.57	-14.44
6	C0	2.31	-	-	-	-
	C1 0.0312	2.13	7.98	7.98	2.78	-12.69
	C2 0.158	1.84	20.58	20.58	1.66	-11.39
	C3 0.312	1.47	36.55	36.55	1.84	-11.66
	C4 0.463	1.31	43.27	43.27	1.63	-11.34
	C5 0.780	0.87	62.60	62.60	2.14	-12.04
	C6 1.091	0.48	79.41	79.41	3.53	-13.29
12	C0	1.71	-	-	-	-
	C1 0.0312	1.26	26.25	26.25	11.40	-16.25
	C2 0.158	1.14	33.3	33.3	3.21	-13.0
	C3 0.312	0.96	43.62	43.62	2.47	-12.40
	C4 0.463	0.82	52.16	52.16	2.33	-12.24
	C5 0.780	0.54	68.10	68.10	2.73	-12.65
	C6 1.091	0.31	82.06	82.06	4.18	-13.72
18	C0	1.70	-	-	-	-
	C1 0.0312	1.1	34.22	34.22	16.67	-17.20
	C2 0.158	0.99	41.82	41.82	4.60	-13.96
	C3 0.312	0.81	52.28	52.28	3.51	-13.28
	C4 0.463	0.69	59.69	59.69	3.16	-13.02
	C5 0.780	0.49	71.10	71.10	3.15	-13.01
	C6 1.091	0.26	84.60	84.60	5.03	-14.18
24	C0	1.58	-	-	-	-
	C1 0.0312	0.95	40.16	40.16	21.51	-17.84
	C2 0.158	0.87	45.23	45.23	5.29	-14.31
	C3 0.312	0.73	53.85	53.85	3.74	-13.44
	C4 0.463	0.60	62.00	62.00	3.48	-13.26
	C5 0.780	0.42	73.23	73.23	3.50	-13.28
	C6 1.091	0.20	87.07	87.07	6.17	-14.70
48	C0	0.95	-	-	-	-
	C1 0.0312	0.52	45.47	45.47	26.73	-18.39
	C2 0.158	0.48	49.98	49.98	6.40	-14.79
	C3 0.312	0.39	59.10	59.10	4.63	-13.9
	C4 0.463	0.35	63.18	63.18	3.66	-13.39
	C5 0.780	0.24	74.90	74.90	3.8	-13.49
	C6 1.091	0.12	87.38	87.38	6.34	-14.77
72	C0	0.78	-	-	-	-
	C1 0.0312	0.43	44.40	44.40	25.84	-18.31
	C2 0.158	0.7	52.84	52.84	7.18	-15.08
	C3 0.312	0.31	60.24	60.24	4.85	-14.10
	C4 0.463	0.26	66.70	66.70	4.28	-13.78
	C5 0.780	0.17	78.15	78.15	4.5	-13.95
	C6 1.091	0.07	90.01	90.01	8.25	-15.43

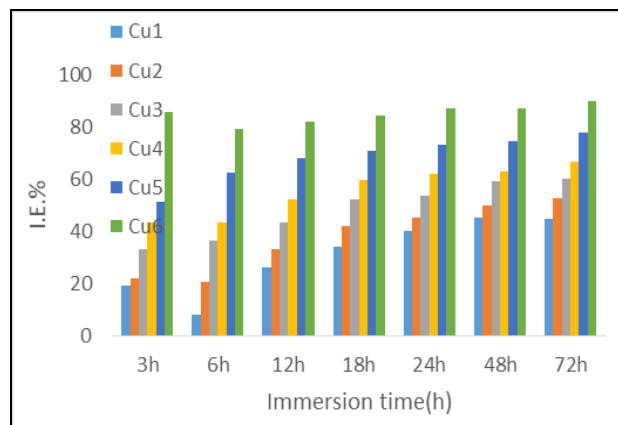


Figure 4: IE % vs. Immersion period (h) with various concentration of EELi

3.1.2 Effect of immersion period

The inhibition effectiveness improved with the increase in concentration as well as increasing immersion time period. At all concentrations, IE increased with immersion time and maximum efficiency (90.01%) was achieved at longest immersion (72h) (figures 4-5). This trend indicates the stability of adsorbed layer on the copper coupon surface which is also clear from figures 3 and 4. Minimum corrosion rate (0.078 mmpy^{-1}) was observed at 72h of exposure. Increase in dielectric constant or decrease in the thickness of the electrical double layer treated major factors affecting corrosion rate [15-16].

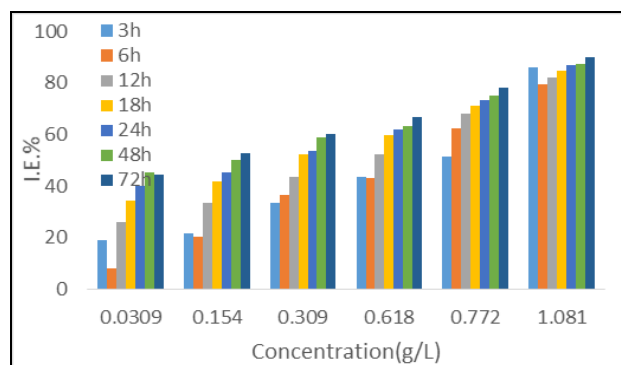


Figure 5: IE % vs. various concentration of EELi

3.1.3 Thermodynamic and Kinetic treatment

The thermodynamic property, free energy of adsorption $\Delta G^{\circ}_{\text{ads}}$ was evaluated using equation 1.

$$\Delta G = -RT \ln (K_{\text{ad}} \times 55.5) \quad (1) \text{ where, } K_{\text{ad}} = \text{adsorption equilibrium constant; } T = \text{absolute temperature (K); } R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$$

The negative values of $\Delta G^{\circ}_{\text{ads}}$ (table 1) clearly indicate the spontaneous adsorption of the inhibitor molecules of EELiL. Generally, values of $\Delta G^{\circ}_{\text{ads}}$ up to -20 kJ mol^{-1} are consistent with electrostatic interaction between charged molecules and a charged metal which clearly specifies physical adsorption process, while those more negative than -40 kJ mol^{-1} involves charge transfer from the inhibitor to the metal surface to form a coordinate type of bond which indicates chemisorption [11-20]. The values obtained under present study clearly indicated physical adsorption.

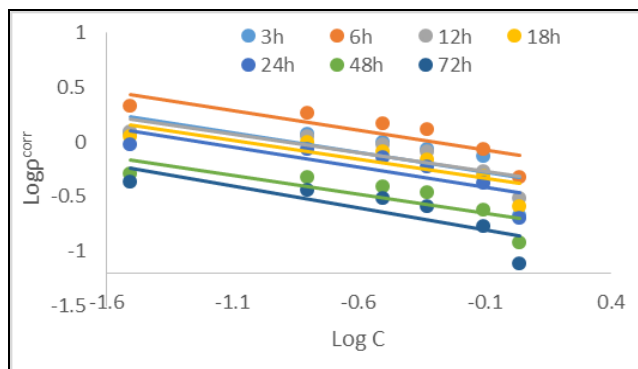


Figure 6: represent the curves of $\log p_{\text{corr}}$ versus $\log c_{\text{inh}}$ at various Immersion time.

The corrosion rate of against the concentration obeys the kinetic relationship [11-20] expressed as:

$$\log p_{\text{corr}} = \log k + B \log c_{\text{inh}} \quad (2)$$

here k is the rate constant and equal to p_{corr} at inhibitor concentration of unity, B is the reaction constant which is the measure for the inhibitor effectiveness, C is the concentration of the inhibitor. Plot between $\log p_{\text{corr}}$ vs. $\log c_{\text{inh}}$ gave straight lines (figure 6) and the kinetic parameters (k and B) (Table 2) were calculated using equation 2.

Table 2: Kinetic parameters for Copper with EELiL

Immersion Period (h)	B	K
3	-0.34	0.49
6	-0.36	0.77
12	-0.34	0.50
18	-0.35	0.43
24	-0.36	0.36
48	-0.34	0.21
72	-0.40	0.14

The negative sign for reaction constant B indicates that the rate of corrosion process is inversely proportional to the concentration of inhibitor and the inhibitor becomes more effective with increase in its concentration. So when the change of p_{corr} with inhibitor concentration become steep (high negative value for constant B) it reflects potential inhibitive propensity of the inhibitor (EELiL).

3.1.4 Adsorption isotherm

Different adsorption models were considered for the experimental data and the best fitted was obtained for the plot of C_{inh}/θ vs. C_{inh} with slopes around unity (figure 7).

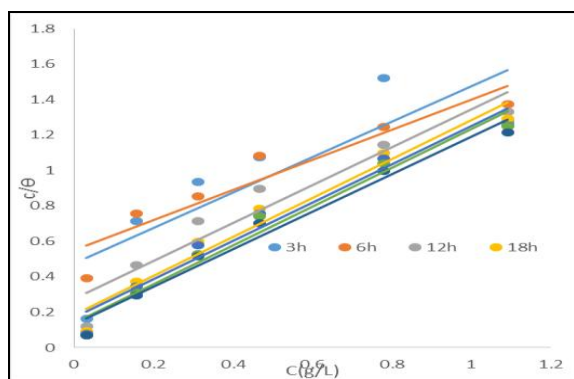


Figure 7: Plot of C_{inh}/θ vs. C_{inh} (Langmuir Adsorption isotherm)

The adsorption of active molecules of EELiL onto the metal surface obeyed Langmuir adsorption isotherm, which is mathematically expressed as:

$$(C/\theta) = C + 1/K_{\text{ad}} \quad (3)$$

where, C is the concentration of the inhibitor, θ is the fractional surface coverage, and K_{ad} is the adsorption equilibrium constant. From the intercepts of the straight line C_{inh}/θ -axis, K value was calculated which was in good agreement with theoretical value [15-16].

Table 3: Correlation coefficient, slopes from Langmuir adsorption isotherm at different Immersion time.

Immersion period (h)	R ²	Slope	K _{ad}
3	0.71	1.00	2.11
6	0.89	0.85	1.82
12	0.92	1.07	3.66
18	0.96	1.10	5.36
24	0.96	1.08	5.92
48	0.97	1.09	7.20
72	0.97	1.06	7.57

3.1.5 Quantum Chemical Analysis (QCA)

The adsorptive propensity of inhibitor and the experimental results can be justified by carrying out QCA of the major active constituent of *Lawsonia inermis*. Data were tabulated (table 4) and the chemical structure, optimized structure, E_{HOMO} and E_{LUMO} of lawsone, gallic acid and ascorbic acid (figures 8-10). To estimate the reactivity of the Chemical species (lawsone, gallic acid and ascorbic acid), Frontier Molecular Orbital Energies (E_{HOMO} and E_{LUMO}) are the significant parameters. Effective corrosion inhibitors are the organic compounds that not only provide electrons to unoccupied orbitals of the metal but also receive free electrons from the metal [20-23]. E_{HOMO} is usually linked with the electron donating ability of a molecule. A high value of E_{HOMO} suggests that the molecule has a trend to donate electrons to the suitable acceptor molecules with a low-energy empty molecular orbital while the lower value of E_{LUMO} , indicates that the electrons are without difficulty accepted by the molecule from the donor.

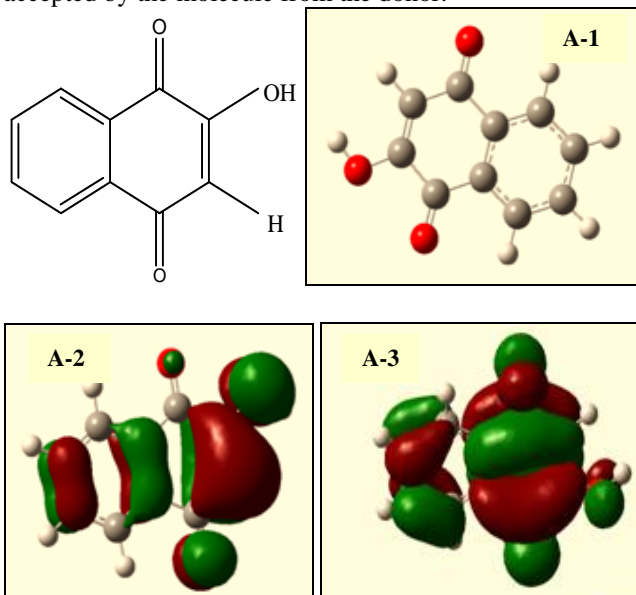


Figure 8: Optimized structure (A-1), HOMO (A-2) and LUMO (A-3) of Lawsone (as one of the major constituents of LiL)

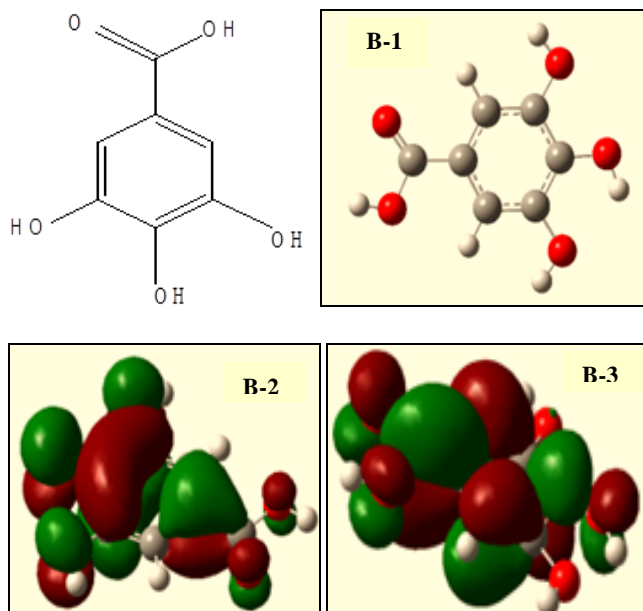


Figure 9: Optimized structure (B-1), HOMO (B-2) and LUMO (B-3) of Gallic acid (as one of the major constituents of *LiL*)

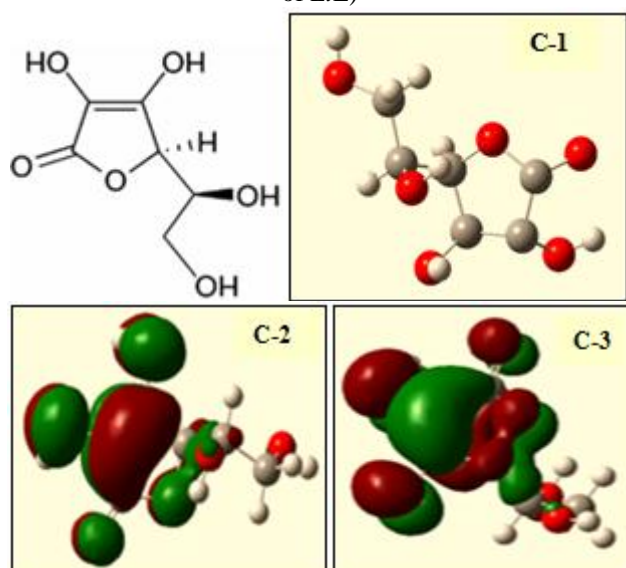


Figure 10: QCA of Ascorbic acid (one of the major constituents of *LiL*): Optimized structures (C-1), HOMO (C-2) and LUMO (C-3).

Table 4: Calculated (energies and gradient) QCA parameters of lawsone, gallic acid and ascorbic acid

Compound	Total E (kcal/mol)	μ (Debye)	E_{HOMO} (eV)	E_{LUMO} (eV)	$\Delta E_{HOMO-LUMO}$ (eV)
Lawsone	-383015.36	0.67	-7.46	-3.37	4.080
Gallic acid	-405703.53	2.87	-6.34	-1.60	4.730
Ascorbic acid	-429729.91	2.20	-8.71	-4.65	4.056

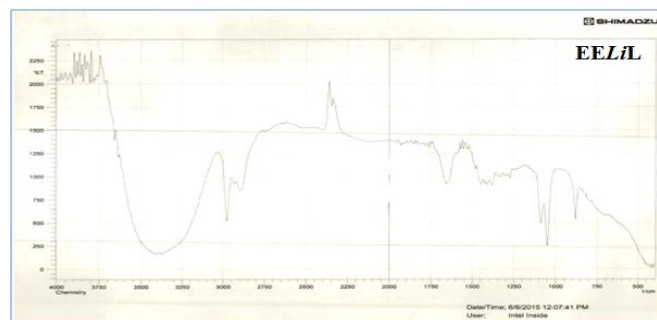
Above QCA data clearly explained the adsorptive and inhibitive action of the active major organic compounds present in *LiL* towards metal coupon surface. Therefore, with increase in the values of E_{HOMO} the inhibition efficiency also increased. It is described that smaller values of ΔE and greater values of μ enhances the inhibition efficiency of the inhibitor molecules. The energy difference, ΔE , as well as the dipole moment, μ , illustrated the effectiveness of *LiL* as corrosion inhibitor. The negative value of the heat of formation (total

energy) of the *LiL* clearly assures that the stability and spontaneous formation of inhibitor molecules (table 4).

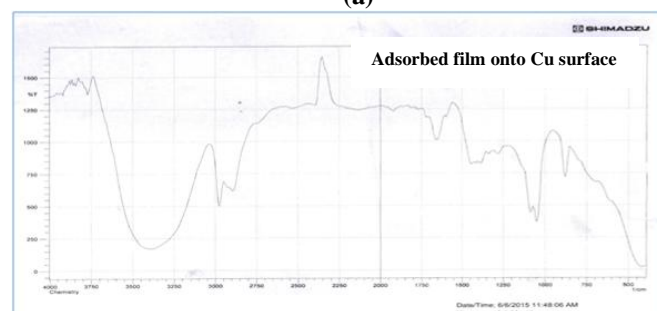
3.1.6 Surface Morphological Analyses

(a) FT-IR spectroscopy

The adsorption of *EELiL* onto Copper coupon surface was further validated by carrying out FT-IR spectral studies of using KBr pellet method. To understand the adsorption mechanism of *LiL*, the peaks in the spectra were identified for various functional groups present in it.



(a)



(b)

Figure 11: FT-IR spectrum of test solutions with coupon immersed for 72h without (a) and with 1.09 g/L *EELiL* (b).

FT-IR spectra (figure 11a) illustrated the functional groups of the active molecules of inhibitor, viz., lawsone, gallic acid, ascorbic acid etc. present in *LiL* (alcoholic -OHstr (3400-3500cm⁻¹), carbonyl of a ketone (1750-1800 cm⁻¹) and aromatic -C=Cstr (benzene moiety) at 1500-1600 cm⁻¹) [11-19]. The heteroatoms and the π -electrons present in the active constituents of the extract are generally regarded as adsorption centres responsible for its adsorptive effect. Figure 11b illustrate the FT-IR spectrum of the film formed onto the metal coupon surface immersed at 72h with 1.09 g/L of *EELiL* in 0.5 M HCl.

The shifts or disappearance of peaks illustrate the formation of copper-*EELiL* complex on the coupon surface, indicating the development of protective film through active functional groups present in *LiL*.

(b) UV-visible Spectroscopy

The UV-Visible spectra (figure 12) were recorded for *LiL* extract and for metal inhibited solution with maximum concentration (1.09 g/L) at 72h immersion period. The spectral studies indicate that pure *EELiL* show main absorption band around 650-700 nm and absorbance at 1.6 which can be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. *EELiL* contain active constituents with functional groups like carbonyl group (-C=O) in conjugation with an olefinic group (-C=C) as well as phenolic group (-O-H) in conjugation with

an olefinic group ($-C=C$) thus its absorption observed at longer wavelengths due to lower energy gap between n , π and π^* energy levels. A slight deviation in the position of transition for the metal inhibited solution was also observed (figure 12).

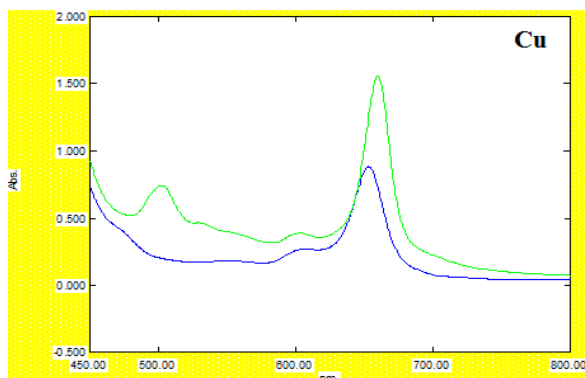


Figure 12: UV-visible spectra of test solutions without and with EELiL.

However, the absorbance decreases due to possibility of formation of EELiL-metal complex, because absorbance is affected by change in concentration as well as chemical structure, thus confirm the possibility of the formation of EELiL-copper metal complex [19-20].

(c) SEM analysis

On comparing the SEM images of surface treated metal, corroded coupon surface and inhibited coupon surface, figures 13-A, B and C respectively, it is clearly illustrated that the inhibited metal surface is found to be smoother with less ridges or grooves due to corrosion as compared to uninhibited metal surface or corroded surface. As the inhibitor gets adsorbed by physisorption onto the copper metal surface, scratch and grooves became less. Thereby the adsorbed film onto copper coupon effectively inhibits its dissolution [21-23].

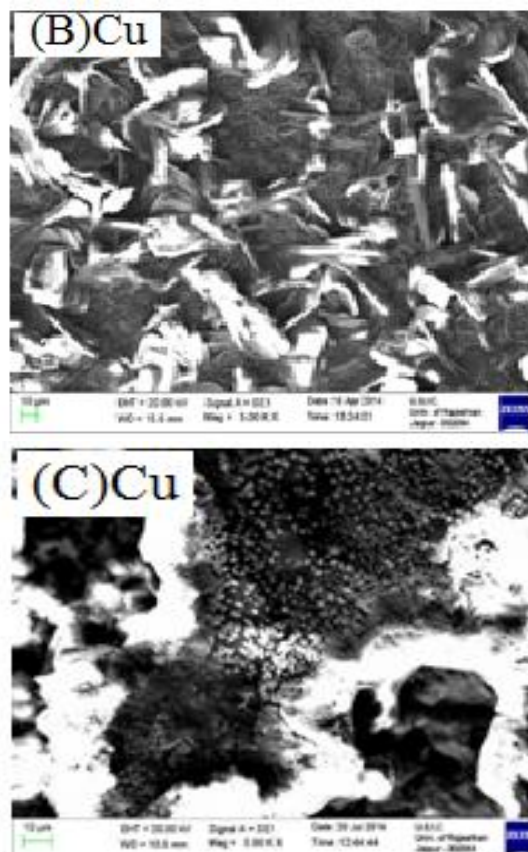
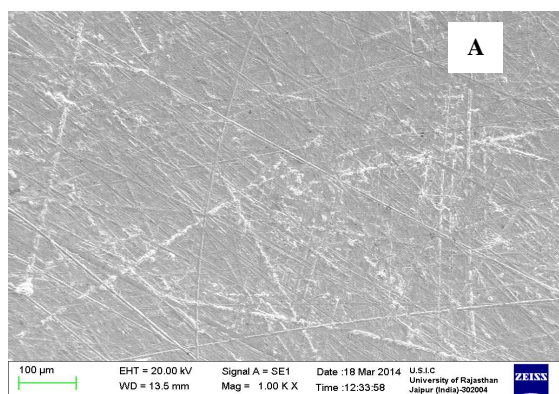


Figure 13: SEM micrographs of copper coupons: (A) surface treated, (B) corroded (without inhibitor) and (C) inhibited

4. Conclusions

- *Lawsonia inermis* was found to be an efficient corrosion inhibitor towards acid corrosion of copper at room temperature.
- Significant IE % (90.01%) at 1.092 g/L concentration of inhibitor. Inhibition increases with increase in concentration of inhibitor.
- Significant inhibition is due to the active phytochemical present in the *Lawsonia inermis* extract which block the active sites on metal surface by physical adsorption.
- The negative values of free energy of adsorption reveal strong and spontaneous adsorption of extract on the copper surface.
- Quantum Chemical Analysis justified strong adsorptive propensity of the active molecules of *Lawsonia inermis*, thus endorsing it to be a better corrosion impeder.
- Langmuir adsorption isotherms, FT-IR and UV-Vis spectroscopic studies strongly reveal the adsorption phenomenon onto the metal surface.
- SEM images depict the formation of protective film onto metal coupon surface.
- *Lawsonia inermis* is a promising *green inhibitor*, meeting environmental legislations, besides, it is biodegradable, low cost and readily available and an effective corrosion inhibitor for copper in HCl.

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