Ixora coccinea extract as an efficient eco-friendly corrosion inhibitor in acidic media: Experimental and theoretical approach

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CHRONICLE	ABSTRACT
	The corrosion inhibition power of an eco-friendly green inhibitor *Ixora coccinea* extract (ICE) for mild steel in 1 M HCl and 0.5 M H_2SO_4 was analysed using physicochemical and electrochemical techniques. 1–5 v/v% ICE was prepared and added into the corrosive acidic media for different analyses. Weight loss measurements conducted for a period of 24hrs for mild steel immersion revealed 89.38% and 77.96% inhibition capacity of ICE in 1 M HCl and 0.5 M H_2SO_4 medium respectively. Electrochemical impedance parameters show that as concentration is increased, efficiency increases and double layer capacitance decreases. Potentiodynamic polarization techniques are also in good agreement with impedance studies and exhibit the mixed type inhibition character of ICE. Electrochemical noise spectrum also strongly supports the anti-corrosive property of ICE and the magnitude of noise signal decreases concerning the increase in ICE concentration. Ixorene, which is one of the major constituents of *Ixora coccinea* leaves was also studied for its corrosion inhibition nature by quantum mechanical calculations and was found to match with all other results. Adsorption studies of ICE are in accordance with Langmuir isotherm. Surface morphological studies confirm the formation of a protective barrier on mild steel surface in both media, i.e., 1 M HCl and 0.5 M H_2SO_4.

1. Introduction

In recent years, green chemistry has been gaining traction in the research world, owing to a demand for chemical technologies and commercial products that are less toxic and generate less waste. One of the promising domains, for the application of green chemistry principles, is the protection of metals from corrosion. Most of the industries work in an acidic environment which causes metal corrosion, leading to loss of metal. The best and favourable method to reduce metal degradation is the usage of corrosion inhibitors[1-3]. Organic compounds with heteroatoms like N, O, S, etc. in a conjugated system have been commonly used as inhibitors and they can interact with metal either by chemisorption or physisorption[4-5]. The adsorptive layer formed on the metal surface protects from the acidic solution and thereby minimizing corrosion. Due to eco-friendliness, low cost, readily available and renewable source of material, natural products like plant extracts can be used as green corrosion inhibitors[6-8].

Several plant-based extracts successfully inhibited the corrosion of metals in an acidic environment. For example, *Musa paradisica* indicates 90% inhibition efficiency at 300 mg/L[9], *Kola nitida* demonstrates 78% hindrance effectiveness at 1200 mg/L[10], *Butea monosperma* demonstrates 98% restraint effectiveness at 500 mg/L[11]. Logan seed and peel extract has been utilized for corrosion inhibitor in acidic media[12]. β-sitosterol isolated from rice hulls has been reported as a good corrosion inhibitor for mild steel in acidic environments[13]. *Strychnos nuxvomica*, *Piper longum* and *Mucuna pruriens* seed extracts have been found as eco-friendly corrosion inhibitors for copper in nitric acid[14]. Lemongrass extract was evaluated for its anti-corrosion action in produced oilfield water[15].

In the present work, we have studied the corrosion inhibition efficiency of ethanolic extract of *Ixora coccinea* (Rubiaceae family) leaves for mild steel in 1 M HCl and 0.5 M H_2SO_4 media. The major component of *Ixora coccinea* leaves is ixorene which is a triterpenoid containing a hydroxyl group and unsaturated bonds, which causes anti-corrosion potential[16]. To evaluate the corrosion inhibition ability of the leaf extract in more detail, the major component ixorene was subjected to theoretical calculations.

2. Results and Discussion

2.1 FT-IR Spectroscopy

To identify the functional groups existing in ICE, FT-IR spectroscopy of dried powdered *Ixora coccinea* leaves has been examined and it is shown in **Fig. 1**. The peak at 3438 cm^{-1} indicates O-H stretching bond. The peaks at 2928 cm^{-1} and 2850 cm^{-1} are pointed alkyl C-H stretching bonds. The peaks at 1384 cm^{-1} and 1628 cm^{-1} represent C=C and aromatic C=C stretching bonds respectively. The other significant peaks indicate the presence of minor components present in ICE.

2.2 Weight Loss Measurements

2.2.1 Effect of concentration of inhibitor

The weight loss measurements of mild steel in 1 M HCl and 0.5 M H_2SO_4 solutions at room temperature with and without various concentrations (1-5 v/v %) of ICE for 24 hours are recorded in **Table 1**. It is evident from the data that as the concentration of inhibitor is increased; the percentage inhibition efficiency also increases in both the acidic media. The results show that ICE is an efficient inhibitor in 1 M HCl attaining maximum inhibition efficiency at 5% as 89.38%. This is due to the number of adsorbed organic molecules of inhibitor ICE on mild steel is more in HCl than H_2SO_4 medium.
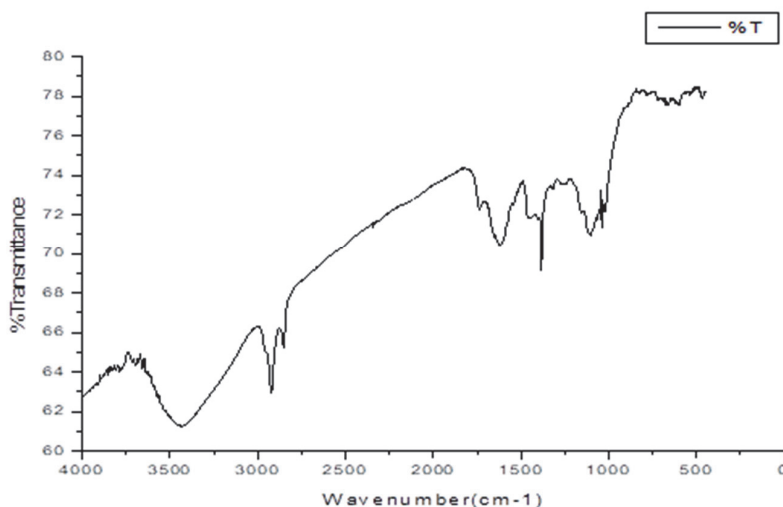

Fig. 1. FT-IR spectrum of dried powdered *Ixora coccinea* leaves

Table 1. Weight loss measurements of mild steel with and without various concentrations of ICE in 1 M HCl and 0.5 M H_2SO_4

ICE conc. (v/v %)	1 M HCl		0.5 M H_2SO_4	
	Corrosion rate (υ)	Inhibition efficiency (η %)	Corrosion rate (υ)	Inhibition efficiency (η %)
Blank	3.95	-	35.57	-
1	0.60	84.77	12.23	65.61
2	0.56	85.75	11.52	67.58
3	0.52	86.73	9.05	74.53
4	0.47	87.98	8.77	75.32
5	0.41	89.38	7.83	77.96

2.2.2 Effect of time on medium: UV-Visible Spectroscopy
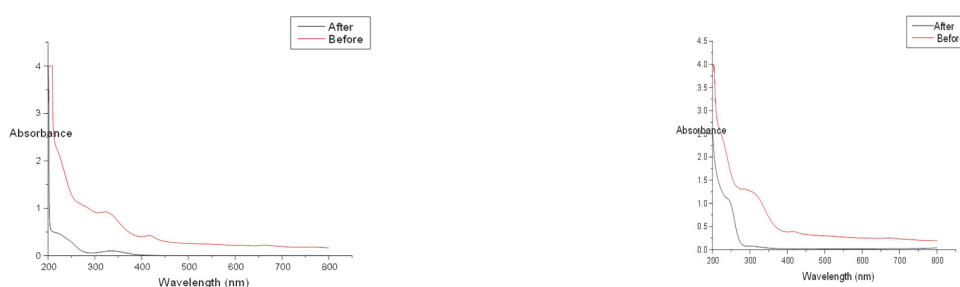
Fig. 2. UV-Visible spectroscopy of medium a) 1 M HCl and b) 0.5 M H_2SO_4 before and after 24 hrs of immersion period with 1% ICE solution

Any prominent shift in the position of the absorbance maximum of the medium measured before and after the immersion of mild steel with inhibitor points to an interaction between Iron and inhibitor molecules.[17-19]. From **Fig. 2**, it's clear that in both HCl and H_2SO_4 medium, there is a lowering of absorbance of absorption maxima after 24hrs of immersion of mild steel, even though both spectra have a similar shape. So, this lowering of absorbance after the immersion of mild steel can be attributed to the adsorption of some molecules of ICE from the solution on the mild steel surface.

2.3 Electrochemical studies

2.3.1 Electrochemical Impedance Spectroscopy

EIS studies are alternate current methods mainly used to analyse the corrosion behaviour at metal/solution interface[20]. The equivalent circuit employed in this study is Randle's circuit (**Fig. 3**). It includes solution resistance R_s, charge transfer resistance R_{ct} and double layer capacitance C_{dl}. The deformities on the metal surface cause deviations from the ideal dielectric property of the metal. So, a constant phase element (CPE) is preferred to C_{dl}[21].

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

where Q is the measure of CPE, n is the power of the magnitude of CPE, ω is the angular frequency and j is the imaginary unit. The Nyquist and Bode plots of mild steel without and with the inhibitor ICE using various concentrations (1-5v/v %) in 1 M HCl and 0.5 M H_2SO_4 at room temperature are shown in **Fig. 4** and **Fig. 5**. In Nyquist plots, it is seen that the low-frequency region is plotted to a straight line and the high-frequency region is plotted to a semi-circle. The slight fall in the semi-circular plot is ascribed to the heterogeneous and roughness of the mild steel. The straight-line portion represents the

diffusion from solution[22]. As the concentration of ICE is raised, the size of the loop also increases. This is can be ascribed to the increase in the impedance of inhibited mild steel. The efficiency also increases in the process. The impedance data obtained from the above equivalent circuit for both media are given in **Table 2**.
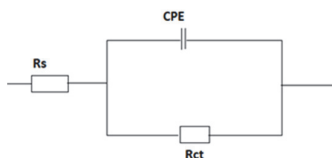

Fig. 3. Randles circuit used for electrochemical measurements

As the concentration of inhibitor increases, double-layer capacitance (C_{dl}) decreases which indicates that the thickness of the electrical double layer increases with respect to the concentration. This is due to the adsorption of inhibitor molecules on the mild steel surface. The maximum inhibition efficiency of 91.55% is seen at a 5% concentration of ICE in 1 M HCl.
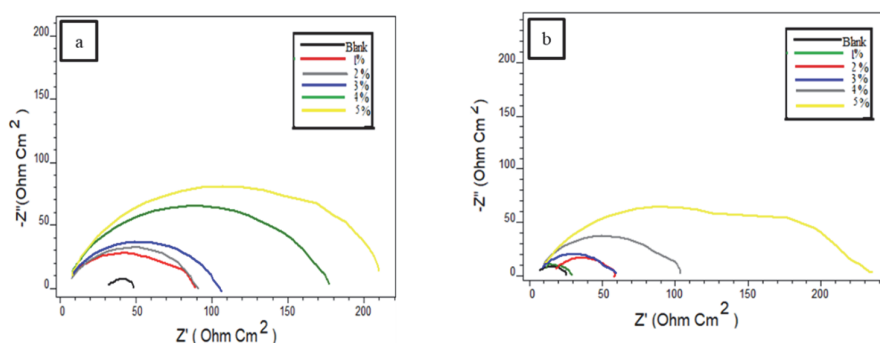

Fig. 4. Nyquist plots of mild steel with and without ICE in a) 1 M HCl and b) 0.5 M H₂SO₄
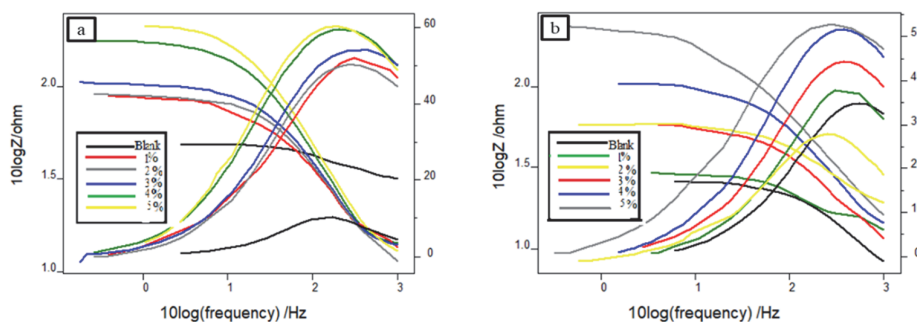

Fig. 5. Bode plots of mild steel with and without ICE in a) 1 M HCl and b) 0.5 M H₂SO₄

Table 2. Impedance parameters for mild steel in 1 M HCl and 0.5 M H₂SO₄ with and without various concentrations of ICE

ICE conc. (v/v %)	1 M HCl			0.5 M H₂SO₄		
	R_{ct} (Ωcm^2)	C_{dl} (μFcm^{-2})	η_{EIS}%	R_{ct} (Ωcm^2)	C_{dl} (μFcm^{-2})	η_{EIS}%
Blank	15.7	78.8	-	18.1	47.4	-
1	69.7	57.4	77.47	20.3	50.5	10.83
2	73.9	49.6	78.74	37.4	39.0	51.56
3	86.4	49.7	81.82	44.1	36.9	58.93
4	150	48.5	89.53	85.5	28.3	78.83
5	186	43.6	91.55	187	3.43	90.33

2.3.2 Potentiodynamic polarization studies

The potentiodynamic polarization data of mild steel in 1 M HCl and 0.5 M H_2SO_4 with and without ICE are given in **Table 3** and corresponding Tafel plots are depicted in **Fig. 6** and linear polarization curves are pictured in **Fig. 7**.
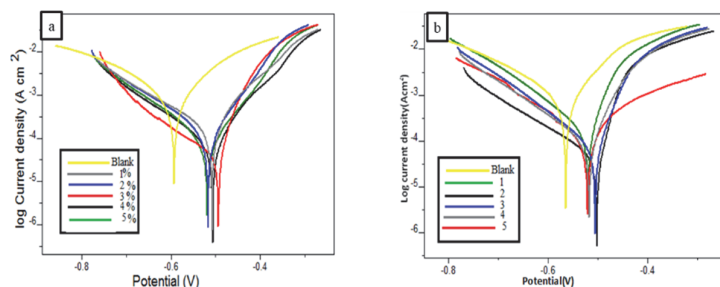

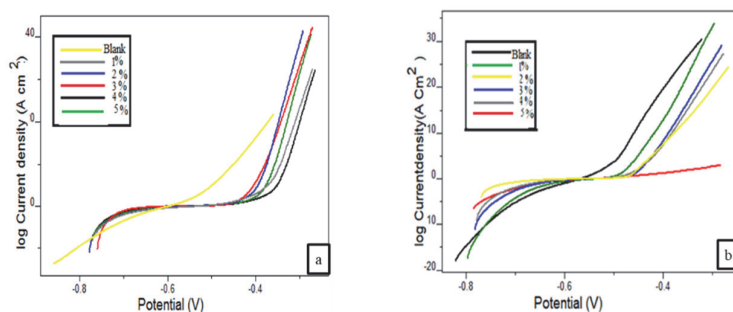**Fig. 6.** a) Tafel plots of mild steel with and without ICE in a) 1 M HCl and b) 0.5 M H_2SO_4

Fig. 7. Linear polarization curves of mild steel with and without ICE in a) 1 M HCl and b) 0.5 M H_2SO_4

Table 3. Potentiodynamic polarization parameters for mild steel corrosion in 1 M HCl and 0.5 M H_2SO_4 with various concentrations of ICE

Acid	Conc. (v/v%)	E_{corr} (mV)	I_{corr} (μAcm^2)	b_a (mv/dec)	$-b_c$ (mv/dec)	$\%\eta_{pol}$
	0	-597.9	1240	166	221	--
1 M	1	-522.8	193.6	106	170	84.41
HCl	2	-504.8	122.3	69	158	90.11
	3	-571.6	107.9	100	130	91.29
	4	-515.0	87.22	93	149	92.96
	5	-500.7	78.50	69	146	93.67
	0	-602.2	1616	184	193	--
0.5 M	1	-601.8	811.6	170	136	49.77
H_2SO_4	2	-649.6	415.5	199	156	74.28
	3	-588.9	368.4	142	128	77.20
	4	-587.4	306.9	138	137	81.00
	5	-555.7	209.6	221	142	87.02

The potentiodynamic polarization data reveals that the greater the concentration of ICE, the smaller is the corrosion current density. The inhibition efficiency is also seen to increase. The inhibition efficiency of ICE for mild steel reached an upper limit of 93.67% in 1 M HCl solution and 87.02% in 0.5 M H_2SO_4 solution at higher concentration. From the Tafel plots in **Fig. 6**, it is seen that both cathodic and anodic curves are influenced by the addition of various concentrations of ICE which shows the mixed type inhibition character of ICE.

2.3.3 Electrochemical Noise analysis

Fig. 8 represents the current noise for mild steel with and without various concentrations of ICE (1, 3, 5 v/v %) in 1 M HCl and 0.5 M H_2SO_4. It is seen that if the concentration of ICE is increased, the protecting power of ICE is also increased. For inhibitor molecules, current and potential noise is lower

than the uninhibited system. Higher magnitude of potential noise signal of uninhibited acid media indicates appreciable localised metallic corrosion on metal surface[23].
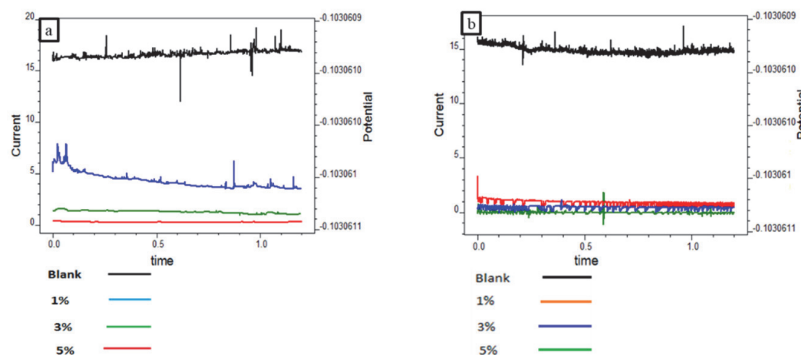

Fig. 8. Current noise for mild steel with and without ICE in a) 1 M HCl b) 0.5 M H_2SO_4

The frequency-domain analysis of noise parameters results from the Power Spectral Density (PSD) of the corresponding system. PSD doesn't affect time and signal statistics[24]. The time-dependent noise parameters were converted into PSD plots by Fast Fourier Transformation (FFT) method in the Ivium software. Maximum entropy method (MEM) was introduced by Burge for better spectral resolution.

PSD plots in **Fig. 9** reveal that the magnitude of the signals is higher for blank metal than metals with various concentrations of ICE (1, 3, 5 v/v %) in 1 M HCl and 0.5 M H_2SO_4. This indicates a considerable amount of localised corrosion on the mild steel surface in the absence of ICE. As the concentration of ICE becomes greater, the magnitude of the noise signal decreases showing its anti-corrosion property against mild steel in both acid solutions.
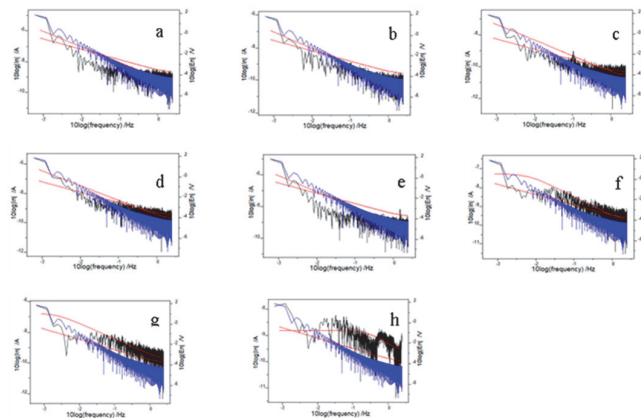

Fig. 9. Power spectral density of mild steel in 1 M HCl a) without ICE b) 1% ICE c) 3% ICE d) 5% ICE; Power spectral density of mild steel in 0.5 M H_2SO_4 e) without ICE f) 1% ICE g) 3% ICE h) 5% ICE

2.4 Adsorption studies

The mechanism of corrosion inhibition between inhibitor molecules and mild steel metal was illustrated using adsorption isotherms. Several adsorption isotherms like Langmuir, El-Awady, Frumkin, Temkin, Freundlich, and Flory-Huggins were considered for the study. The best suitable isotherm was detected using the value of correlation coefficient (R^2).

In this study, the metal-ICE interaction was observed to be obeying Langmuir adsorption isotherm. According to Langmuir adsorption isotherm, there are a large number of similar adsorption sites and little chance for lateral interaction. Equation (2) shown below explain Langmuir adsorption isotherm as[25]

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{2}$$

where C_{inh}, K_{ads} and θ represent the concentration of inhibitor, equilibrium constant and the surface coverage respectively.

Standard free energy of adsorption ΔG^0_{ads} can be derived from the given value of K_{ads} using Eq. (3)[26].

$$\Delta G^0_{ads} = -RT \ln (55.5\ K_{ads}) \tag{3}$$

where 55.5 is the molar concentration of water, R is the universal gas constant and T is the temperature in K. The value of ΔG^0_{ads} determines whether the interaction between the inhibitor molecules and the metal surface is physisorption or chemisorption. If it is up to -20 kJ/mol, the nature of the interaction is physisorption, whereas if it is more negative than -40 kJ/mol, interaction is chemisorption.
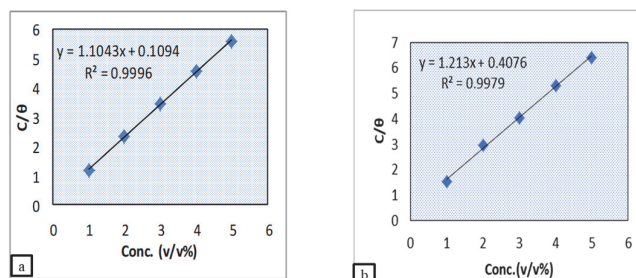

Fig. 10. Langmuir adsorption isotherm of ICE on mild steel in a) 1 M HCl b) 0.5 M H_2SO_4 at 28^0c.

From the values of R^2 in **Fig. 10**, it can be seen that Langmuir adsorption isotherm is the best suitable one for the adsorption of ICE on mild steel. The calculated ΔG^0_{ads} for ICE are -32.88 and -29.58 kJ/mol in 1 M HCl and 0.5 M H_2SO_4 respectively shows that an electrostatic and chemical interaction exists between the inhibitor and the charged metal surface. ICE is composed of various organic compounds in it. The major component of *Ixora coccinea* leaves is ixorene. The adsorption of all the components of ICE on the mild steel surface may be attributed to the inhibitive action of the extract. **Fig. 11** represents the predominant interaction of the major component ixorene with the mild steel surface. By transferring electrons from the Oxygen atom present in the -OH group and the interaction through the double bonds, ixorene molecules can be adsorbed onto the mild steel surface.
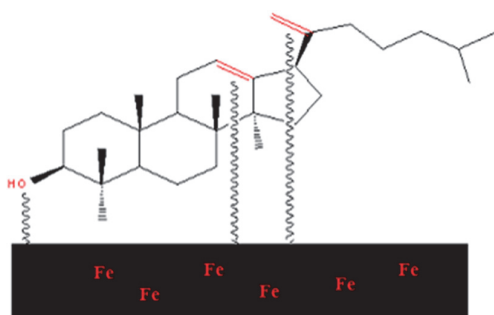
Fig. 11. Interaction diagram between Ixorene and mild steel surface

2.5 Suface Morphological Studies

To strengthen the understanding of the mechanism of ICE on the surface of mild steel, morphological studies were performed by taking the SEM images of metal coupons. **Fig. 12a** shows the SEM picture of smoothening mild steel metal. **Figs. 12b, c, d, e** shows the surface of mild steel metal after immersion in 1 M HCl and 0.5 M H_2SO_4 respectively without and with ICE. The SEM

images clearly exhibit that the surface is severely damaged in the absence of the inhibitor ICE. It could be seen that the surface corrosion is getting reduced in HCl solution with ICE and the surface is more smooth and perfect in it than H_2SO_4 solution. So it can be confirmed that ICE acts as an excellent green corrosion inhibitor in acidic media.

2.6 Quantum mechanical calculations

Quantum mechanical parameters like E_{HOMO}, E_{LUMO}, ΔE, Ionisation energy (I), Electron affinity (A), Chemical potential, electronegativity (χ), hardness (η) and the number of transferred electrons (ΔN) of ixorene are tabulated in **Table 4**. The HOMO and LUMO pictures of ixorene are depicted in **Fig. 13**. The ΔE value is low for ixorene, which indicates that ICE has remarkable inhibition efficiency. This low ΔE value 4.884 eV of ixorene attributes the low energy requirement for the transfer of electrons from HOMO of ixorene to the vacant orbitals of Fe. The ΔN values provide information regarding the interaction between donor-acceptor molecules[27]. This in turn proves agreement between quantum mechanical calculations and experimental results.
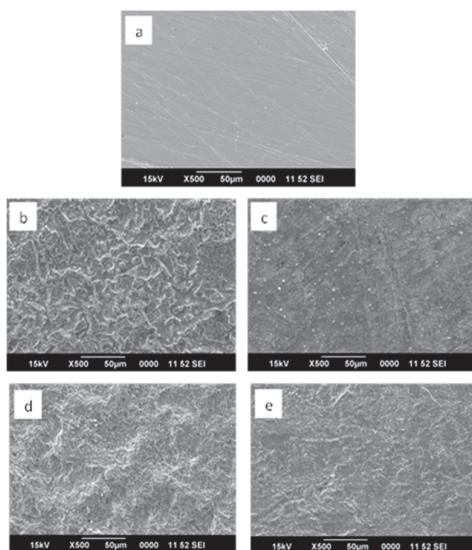
Fig. 12. SEM pictures of mild steel metal a) bare b) in 1 M HCl c) in 1 M HCl with ICE d) in 0.5 M H_2SO_4 e) in 0.5 M H_2SO_4 with ICE.

Fig. 13. A) HOMO and b) LUMO of Ixorene

Table 4. Quantum mechanical parameters of Ixorene

Molecule	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	I	A	Chemical Potential	Electronegativity (χ)	Hardness (η)	ΔN
Ixorene	-3.347	1.537	4.884	3.347	-1.537	-0.905	0.905	2.442	1.2479

3. Conclusions

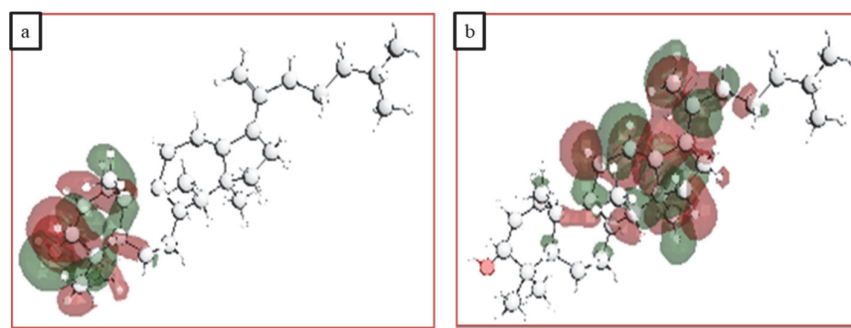- ➢ *Ixora coccinea* leaf extract (ICE) acts as an efficient green inhibitor for corrosion of mild steel in HCl and H_2SO_4 medium. As the concentration of the inhibitor increases, the protecting power also increases.
- ➢ On comparing, ICE in HCl medium shows higher efficiency than H_2SO_4 medium.
- ➢ UV-Visible spectrum of extract solutions suggests the possibility of adsorption of constituents present in ICE and also proves the inhibition capacity of ICE.
- ➢ Electrochemical impedance analysis exhibits that charge transfer resistance increases and double layer capacitance decreases according to the concentration of ICE.
- ➢ Potentiodynamic polarisation measurements exhibit a mixed type character of inhibition for ICE
- ➢ Quantum mechanical calculations of ixorene – a major component present in ICE supports the inhibition power of ICE.
- ➢ The adsorption studies of ICE shows that it obeys Langmiur adsorption isotherm.
- ➢ The protecting power of ICE is also confirmed by surface morphological studies.

4. Experimental

4.1 Inhibitor

The *Ixora coccinea* leaves were washed with distilled water; shade dried for two weeks and made fine-grain using a grinder. 5 g of the granulated leaves was refluxed with 100 ml ethanol for 4 hr. It is then filtered after keeping overnight and concentrated into 50 ml. The corrosion inhibition action of the *Ixora coccinea* extract (ICE) was analysed by preparing 1-5 v/v% solutions in 1 M HCl and 0.5 M H_2SO_4.

4.2 Mild steel coupon preparation

Mild steel composition %:- C-12.37% and Fe-87.63% were the specimens used. For weight loss measurements, the metal specimens were cut into 1 cm^2 coupon. For electrochemical analysis, the metal samples had a 1 cm^2 surface area exposed to 100 ml of the acidic medium. The metal coupons were physically abraded with 100, 220, 440, 800, 1000, 1500 and 2000 grade of sandpaper, washed with distilled water and acetone.

4.3 Acid media preparation

The electrolytic solution 1 M HCl and 0.5 M H_2SO_4 were made by dilution of analytical pure HCl and H_2SO_4 (Merck) using distilled water.

4.4 UV-Visible Spectroscopy

UV-Visible absorption spectrum of *Ixora coccinea* leaf extract (ICE) in 1 M HCl and 0.5 M H_2SO_4 separately was measured with UV- Visible spectrophotometer Shimadzu UV- 1800, before and after 24hrs of immersion of mild steel.

4.5 IR Spectroscopy

IR spectrum of dried powdered samples of *Ixora coccinea* leaves was recorded in Shimadzu IR Affinity -1 model FT-IR spectrophotometer using KBr pellet method.

4.6 Weight loss measurement

It is a gravimetric method to measure the corrosion rate. The dimensions of the polished metal coupons were measured, which were then pre-weighed and immersed in 50 ml acidic solutions of 1 M

HCl and 0.5 M H$_2$SO$_4$ separately, together with different inhibitor concentrations (1- 5 v/v%) for 24 hours at room temperature. After the immersion period, the metal coupons were washed with distilled water, dried and then weighed. The corrosion rate (υ) was calculated using equation (4)[28]:

$$\upsilon = \frac{KW}{DSt},$$ (4)

where K =87600, W- average weight loss of coupon (g), S- total area of the coupon (cm^2), D- density of metal (g cm^{-3}), t- period of immersion (h). The percentage of inhibition efficiency was deduced from the values of υ, using equation (5)[29].

$$\eta\% = \frac{\upsilon_0 - \upsilon}{\upsilon_0} \times 100,$$ (5)

where υ_0 and υ indicate the rate of corrosion of metal coupons immersed in acid solutions in the absence and presence of the inhibitor ICE, respectively.

4.7 Electrochemical Measurement

Electrochemical investigations were done in a three-electrode cell using Ivium CompactStat electrochemical work station and IviumSoft software. A platinum electrode was employed as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. Mild steel samples, 1cm^2 surface area exposed to 100ml acidic solutions, were made as a working electrode. The measurements were conducted at room temperature using 1 M HCl and 0.5 M H$_2$SO$_4$ with various concentrations (1- 5 v/v %) of ICE. The EIS measurements were conducted across a frequency range of 1 KHz to 100 mHz using a signal amplitude of 10 mV. Using R$_{ct}$ values from Nyquist plots, corrosion inhibition efficiency of ICE was determined using equation (6)[30].

$$\eta_{EIS}\% = \frac{R'_{ct} - R_{ct}}{R'_{ct}} \times 100$$ (6)

where R'$_{ct}$ and R$_{ct}$ are the charge transfer resistance of the working electrode in the presence and absence of inhibitor ICE, respectively. Potentiodynamic polarisation measurements were done under open circuit potential in the potential range of -250 to +250 mV at a scan rate of 1mV/sec. From the polarisation curves, polarisation resistance values were obtained. From which percentage of inhibition efficiency, $\eta\%$ was found by Eq. (7)[31].

$$\eta\% = \frac{R_p - R_p^0}{R_p} \times 100,$$ (7)

where R$_P^0$ and R$_p$ are the polarization resistance values in the absence and presence of inhibitor ICE respectively.

Electrochemical noise (ECN) analysis was performed in a three-electrode system, which includes two mild steel electrodes having an exposed surface area of 1 cm^2 and SCE as a reference electrode. Here one mild steel electrode acts as a working electrode and the other as a counter electrode. ECN analyses were performed for a period of 1200 s.

4.8 Scanning Electron Microscopy

The surface morphological analysis of the inhibited and uninhibited mild steel surfaces in 1 M HCl and 0.5 M H$_2$SO$_4$ was performed by scanning electron microscope (JEOL Model JSM- 6390LV). The polished metal coupons of surface area 1 cm^2 were dipped in acid solutions in the absence and presence of ICE. After keeping the systems for 24 hours at room temperature, they were removed and dried, which are then subjected to SEM analysis.

4.9 Quantum mechanical calculations

The corrosion inhibition power of inhibitors can be associated with the frontier molecular orbital energies[32]. There is a donor-acceptor interaction between Fe vacant orbitals and the inhibitor filled

molecular orbitals. This interaction can cause the prevention mechanism of metal corrosion[33]. As the ΔE ($E_{LUMO} − E_{HOMO}$) value of inhibitors lowers, greater is the tendency to bind on the metal surface strongly[34]. Quantum mechanical calculations for the major component ixorene were carried out using DFT method by GAMMES software.

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