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EXPERIMENTAL AND COMPUTATIONAL ELUCIDATION OF CORROSION INHIBITION POTENTIAL OF L-HISTIDINE ON MILD STEEL IN AQUEOUS HYDROCHLORIC MEDIUM

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ABSTRACT

Deterioration of materials, usually metals, by chemical or electrochemical reactions in relation to their environment has been greatly described by corrosion and inhibitors have been effective in curbing its adverse potential on metals. Experimental and computational elucidation of corrosion inhibition potential of L-histidine in interaction with mild steel in HCl medium has been conducted using weight loss method and quantum chemical calculations. Results obtained revealed that raising the concentration of L-histidine from 0.003 to 0.01 mol dm-3 in aqueous HCl medium, for 2 – 6 hours, inhibits the corrosion progression rate of the coupons. The corrosion rate (CR) was observed to slightly decrease with increase in reaction temperature from 323k to 363k. Decrease in CR (i.e increase in inhibition efficiency) was very significant with the time of contact of the mild steel when the inhibitor was increased from 2hrs to 6 hrs. As the inhibitor's concentration increases, the inhibition efficiency (IE %), was found to increase. Langmuir adsorption isotherm was used to fit surface coverage values and the significantly high value of the correlation (R2) suggests that Langmuir isotherm perfectly describes the adsorption process. R2 values obtained at 343 k and 363 k temperature is 0.9932 and 0.9921 respectively. The computational elucidation were performed by carry out electronic parameters characterize through quantum chemical calculations which were associated with inhibition efficiency. The electrochemical results are corroborated by theoretical data where E-HOMO and E-LUMO were calculated.

Keywords: Corrosion, Computational, Inhibition, Isotherm, L-histidine, Theoretical, Quantum

INTRODUCTION

Inhibitors of corrosion, are compounds of chemicals applied in small concentrations to decrease metals corrosion rate, retard its process and keeps rate at minimum and thus hindering economic deprivation due to metallic corrosion (Jones, 1991; Ibrahim *et al.*, 2012; Oladunni *et. al.*, 2024).

Industrially, contact of metals and aggressive medium is inevitable, the role of corrosion inhibitors are most important in controlling the deterioration of the metals (Oguzie, 2006; Eddy, 2010). Inorganic compounds are mostly utilized as inhibitors to safeguard metals against corrosion but only few are environmental friendly due to their poisonousness, bioconcentration and nonbiodegradability (Al Mubarak *et al.,* 2010).

In generally, corrosion proceeds through adsorption mechanism producing a formation of a film over the active site of metallic materials. Heterocyclic compounds represent the most commonly applied inhibitors with atoms, such as nitrogen, sulphur or oxygen, and bonds, which bring about sorption on the metal surface (Ali *et al*., 2003; Silva *et al.*, 2006). The uptake on surface of the metal through inhibitors active surface site leading to reducing the rate of corrosion (Machnikova *et al*., 2008; Fu *et al*., 2010).

Additionally, quantum chemical calculations can now effectively study the association between molecular structure and inhibitory properties at the microcosmic level through theoretical prediction. By using the quantitative structure–activity relationship (QSAR) method, quantum chemical simulations have proven to be a very effective tool for researching corrosion inhibition mechanisms and have aided in the invention of novel, highly effective inhibitors (Huang *et al.*, 2021). The quantum chemistry (theoretical prediction) technique studies the interaction between inhibitors and the metal surface. This approach makes it easy to investigate the complex system, which consists of the metal surface, hundreds of solvent molecules, and one inhibitor molecule (Chen *et al.*, 2022; Li *et al.*, 2024). It also resolves the issue that tiny systems with 10–100 atoms are typically the focus of the quantum chemical technique.

This indicate a vital role, since protection degree on metal depend on adsorption process, hence, the research of new corrosion inhibitors which are eco-friendly, non-toxic and naturally required. Also, with the ongoing advancement of computer hardware and software technology, it can be concluded that these two approaches will become increasingly significant in the study of corrosion inhibitors due to its low cost and duration of experimental methods.

MATERIALS AND METHODS

Experimentally, ethanol, acetone, hydrochloric acid, digital analytical balance, distilled water, flasks (1000 cm^3), water bath, thermometer, conical flask volumetric, oven, different sets of beakers (pyrex), press knife, desiccator, measuring cylinder (50 cm^3, 100 cm^3), mild steel (3×3 cm^2 coupons) and L-histidine (Figure 1) while computationally QSAR were used.

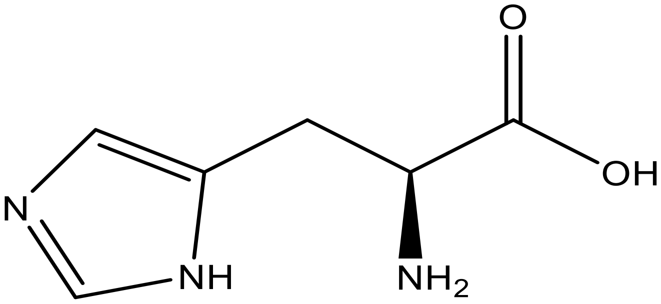


Figure 1: Structure of L-histidine

Preparation of Materials

The mild steel sheets was divided into a pieces of 3.0 cm × 3.0 cm area coupons with the aid of machine and polished with emery papers to smoothen their surfaces. Grease, oil and other contaminant were then removed from their surfaces by washing with detergent, dried and stored in desiccators before commencing the studies. The composition of the element in mild steel is presented in Table 1, with Fe having the largest percentage composition.

Table 1: Norminal Elements (w %) of the Mild Steel

Element Symbol	C	Mn	Si P	S	Cu	Pb	Mo	V	Fe	
% Composition	0.05	1.13	0.05	0.91	0.85	0.09	0.15	0.08	0.13	96.6

Preparation of Inhibitor Concentrations

0.1 moldm^{-3} of L-histidine with molecular weight 155.15g/mol, was prepared by transferring 7.76g of the compound into a 500 cm^3 measuring cylinder and made up to mark using 0.1 mol dm^{-3} HCl. This solution was then used as stock solution to attain 0.003, 0.005, 0.007 and 0.01 moldm^{-3} inhibitor solution using dilution formula and blank of 0.1 moldm^{-3} HCl to make it up to mark.

Measurement of Weight Loss

This was carried out with 100 cm^3 beaker filled with 50 cm^3 solution soaked in aerated condition at 323 K, 343K and 363 K maintained in a thermostatic bath. The weighed mild steel coupons were fully soaked in beakers. The withdrawn coupons after 2, 4, and 6 hours interval, were cleaned and reweighed (Bobina *et al*., 2009; Oladunni *et al*., 2021). The lost in weight was determine by talking the difference in the weight of the mild steel coupons before and after immersion in different test solutions.

Blank solution (0.1 moldm^{-3} HCl) and in L-histidine solution within the concentration range of 0.003 - 0.01 moldm^{-3} at temperatures of 323 K, 343K and 363 K were provided. The measurements were done in triplicate to ensure reproducibility.

Calculation of Corrosion Rate

Calculation of corrosion rate (CR) given in millimeter per year was carried out using equation 1

Corrosion rate (mpy)

$$C_R = \frac{87.63\ W \times 1000}{DAT} \qquad (1)$$

Where:

Weight loss (W) = initial weight (W_1) – final weight (W_2) in milligrams.

Total surface area of specimen in cm^2 (A)

Total time sample was immersed in hours (T)

Density of the specimen in g/cm^3 (D)

Corrosion rate (CR) in millimeters per year.

Surface Coverage and Percentage Inhibition Efficiency (%IE)

The Surface coverage (ϴ) was calculated in degree using equation 2 while inhibitor efficiency was determined in percentage by equation 3

$$\Theta = \frac{CR_o - CR_1}{CR_o} \qquad (2)$$

$$IE\ (\%) = \frac{CR_o - CR_1}{CR_o} \times 100 \qquad (3)$$

Where CR_o = corrosion rates in the absence of concentration of inhibitor,

CR_1 = corrosion rates in the presence of concentration of inhibitor,

The percentage inhibitor efficiency was calculated for all the inhibitors throughout the exposure period.

Adsorption Isotherms

Langmuir isotherm (equation 4) was used to study the relationship between inhibition efficiency and inhibitors concentration C.

Langmuir isotherm = log IE versus C (4)

Quantum Chemistry Calculations

B3LYP Density Functional Theory (DFT) of 6-311G (d,p) basis set with Gaussian 03W program was used to optimize histidine, knowing that it has capacity to give accurate geometry and electronic properties for a wide range of organic compounds. Quantum chemical parameters such as E_{HOMO}, E_{LUMO}, ΔE (energy gap), μ (chemical potential or dipole moment) and Fraction of electron transfer (ΔN) estimate which provide structural characteristics of this inhibitor, were considered. DFT has also been used severally in providing insights into the chemical reactivity and selectivity, in terms of global parameters such as electronegativity (v), hardness (g) and local ones such as the Fukui function. Summary of key equations are

$$E_{HOMO} = -I = -(E+ - E0) \qquad (5)$$

$$E_{LUMO} = -A = -(E0 - E-) \qquad (6)$$

$$\Delta E = E_{LUMO} - E_{HOMO} \qquad (7)$$

$$\chi = -(E_{LUMO} + E_{HOMO})/2 \qquad (8)$$

$$\mu = -\chi \qquad (9)$$

$$\Delta N = \frac{X F_e}{\eta F_e} - \frac{X_{inh}}{X_{inh}} \qquad (10)$$

Where

X is electronegativity

Ƞ is Chemical hardness

RESULTS AND DISCUSSION

Effect of Inhibitor Concentration, Contact Time and Temperature on Corrosion Behaviour of Mild Steel in 0.1 mol dm^{-3} HCl Acid

Histidine concentration at 0.003, 0.005, 0.007 and 0.01 mol dm^{-3}, contact time of 2 - 6 hrs and temperature of 323 K - 363 K on corrosion inhibition of mild steel in 0.1 moldm^{-3} HCl were studied and the outcome results are displayed in the Table 2- 4. It was evidenced that corrosion rate of mild steel in 0.1 mol dm^{-3} hydrochloric acid containing a known concentration of the histidine decreases when compared to the blank. The corrosion rate (CR) was observed to slightly decrease with increasing histidine concentration from 0.003 mol dm^{-3} to 0.01 mol dm^{-3} at increasing temperature from 323k to 363k (Table 2-4). The decrease in CR (i.e increase in inhibition efficiency) was very significant when the time of contact of the mild steel with histidine increases from 2hrs to 6 hrs (Figure 1-2). This implies that with longer time of exposure of the mild steel to the inhibitor's solution, adsorption of the L-histidine to the surface of the metal become more efficient, thereby reducing the corrosion rate. The inhibition efficiency (IE %) of the inhibitor was also found to increase with increase in inhibitor's concentration and reaction temperature (Table 2-4).

Table 2: Corrosion Rate (CR), Inhibitor Efficiency(IE) and Surface Coverage (SC) of Histidine at Temperature of 323k

	After 2 hours			After 4 hours			After 6 hours		
Histidine (mol/dm^3)	**CR (mpy)**	**IE (%)**	**SC**	**CR (mpy)**	**IE (%)**	**SC**	**CR (mpy)**	**IE (%)**	**SC**
-	0.4046			0.2265			0.3022		
0.003	0.2666	34.11	0.3410	0.1201	46.97	0.4697	0.1577	47.82	0.4781
0.005	0.2629	35.02	0.3502	0.1126	50.28	0.5028	0.1370	54.67	0.5466
0.007	0.2516	37.82	0.3781	0.1038	54.17	0.5417	0.1333	55.89	0.5589
0.01	0.1952	51.76	0.5175	0.1013	55.27	0.5527	0.1182	60.89	0.6088

This is similar to the finding of Oladunni *et al.*, (2020) on *sida acuta* leaves extracts kinetics studies as corrosion inhibitor on tannery machine's parts in environmental acidic medium. Eddy *et al.*, (2012) also made similar observation in his research to determine the inhibition potential of *ficus platyphylla* gum on mild steel.

It was discovered that 90.19% highest inhibition efficiency was obtained at reaction temperature of 363 k when the mild steel was exposed to the highest inhibition concentration of 0.01moldm^{-3} for 6 hrs.

Table 3: Corrosion Rate (CR), Inhibitor Efficiency(IE) and Surface Coverage (SC) of Histidine at Temperature of 343k

	After 2 hours			After 4 hours			After 6 hours		
Histidine (mol/dm^3)	**CR (mpy)**	**IE (%)**	**SC**	**CR (mpy)**	**IE (%)**	**SC**	**CR (mpy)**	**IE (%)**	**SC**
-	2.4228			4.4228			4.1888		
0.003	1.2467	48.54	0.4854	1.3467	69.55	0.6955	1.2007	71.34	0.7133
0.005	1.1938	50.73	0.5072	1.2838	68.55	0.7097	1.05	74.93	0.7493
0.007	1.1707	51.68	0.5167	1.2707	71.27	0.7126	0.9567	77.16	0.7716
0.01	1.1223	53.68	0.5367	1.1223	74.62	0.7462	0.77	81.62	0.8161

Table 4: Corrosion Rate (CR), Inhibitor Efficiency (IE) and Surface Coverage (SC) of Histidine at Temperature of 363k

	After 2 hours			After 4 hours			After 6 hours		
Histidine (mol/dm^3)	**CR (mpy)**	**IE (%)**	**SC**	**CR (mpy)**	**IE (%)**	**SC**	**CR (mpy)**	**IE (%)**	**SC**
-	3.7228			5.5210			5.4123		
0.003	1.5467	58.45	0.5845	1.6567	69.99	0.6999	1.0567	89.48	0.8047
0.005	1.4467	61.14	0.6113	1.4567	73.62	0.7361	0.9110	83.17	0.8316
0.007	1.2467	66.51	0.6651	1.2667	77.06	0.7705	0.7240	86.62	0.8662
0.01	0.9467	74.57	0.7457	0.9567	82.67	0.8267	0.5310	90.19	0.9018

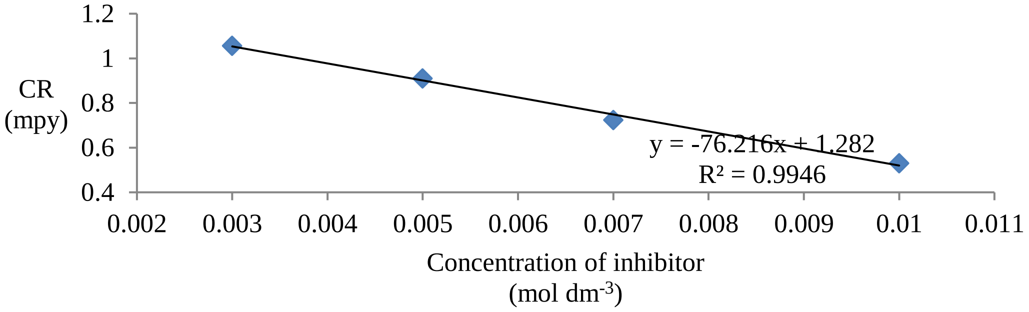


Figure 2: Graph of CR Versus Histidine Concentration at 363 k after 6hrs of Contact of the Inhibitor with the Coupon

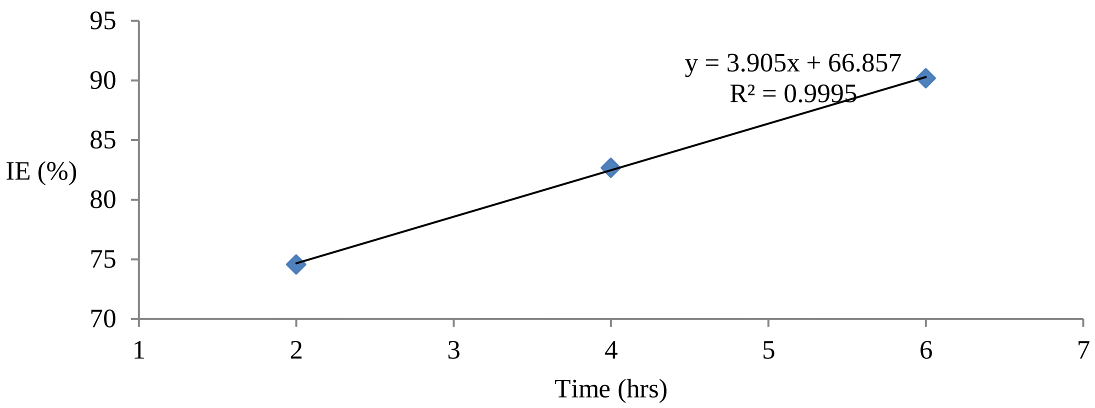


Figure 3: Graph of IE Versus Histidine Concentration at 363 k after 6hrs of Contact of the Inhibitor with the Coupon

Adsorption Mechanism and Isotherm for the Inhibitor
The inhibition of corrosion of metals by organic compounds may be of formation complex of insoluble compounds on metal surface which acts as a barrier between the metal surface and the corrosive medium (Okafor *et al*., 2008).

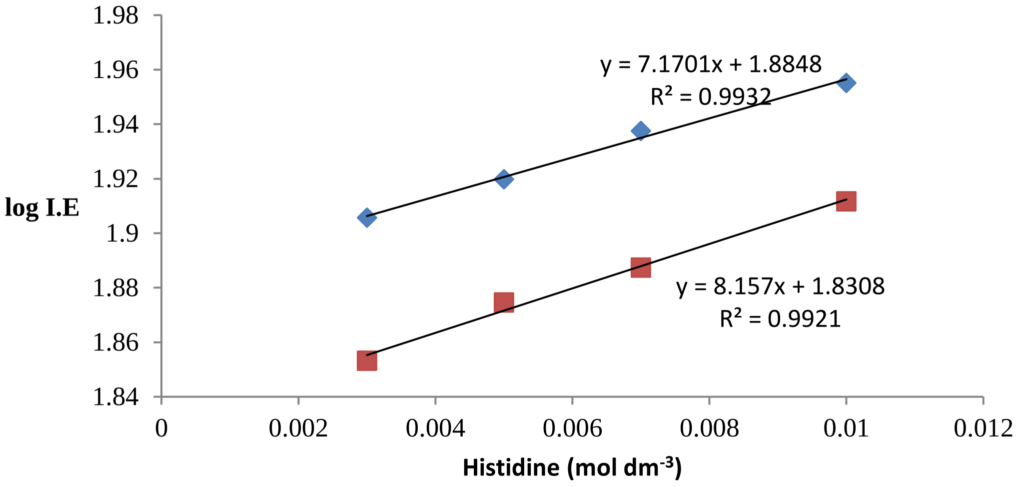


Figure 4: Langmuir Adsorption Isotherm: Log IE Against Concentration of Histidine (mol dm^{-3}) at 363k for 2hrs and 6hrs

Careful observation in this case showed that there is lack of insoluble material found on the metal surface, hence the inhibitive action of L-histidine was due to its adsorption on the metal surface. The net adsorption of L-histidine on the corroding mild steel surface creates a barrier that isolates the metal from the corrodent. The relationship between inhibition efficiency and the bulk concentration of the inhibitor as seen in Figure 3 which is known as isotherm (Tsuru *et al*., 1978), gives a clue into the adsorption process. Langmuir adsorption isotherm was used to fit inhibition efficiency and the significantly high value of the correlation (R^2) suggests that Langmuir isotherm (Table 5) perfectly describes the adsorption process as R^2 (Figure 3) values obtained at 363 k temperature for 2hrs and 6hrs are 0.9932 and 0.9921 respectively.

Quantum Chemistry Calculation
Investigation of relationship of the molecular electronic structure of histidine and its inhibition efficiency, quantum chemical calculations were performed. The optimized structure of L-histidine compound was shown in Figure 4. Quantum chemical parameters such as E_{HOMO}, E_{LUMO}, ΔE and μ were given in Table 6. Additionally, the orbital density distributions of E_{HOMO} and E_{LUMO} for amino acid compound (L-histidine) was shown in Figure 5.

Table 5: Various Concentrations of Histidine and Log IE at 323 k, 343 k and 363 k for 2-6 hrs

	At 323 k			**At 343 k**			**At 363 k**		
Histidine (mol/dm^3)	**2hrs**	**4hrs LogIE**	**6hrs**	**2hrs**	**4hrs LogIE**	**6hrs**	**2hrs**	**4hrs LogIE**	**6hrs**
0.003	1.53	1.67	1.68	1.67	1.83	1.85	1.77	1.85	1.91
0.005	1.54	1.73	1.74	1.70	1.84	1.87	1.79	1.87	1.92
0.007	1.58	1.70	1.75	1.71	1.85	1.89	1.83	1.89	1.94
0.01	1.71	1.74	1.78	1.73	1.87	1.91	1.88	1.92	1.96

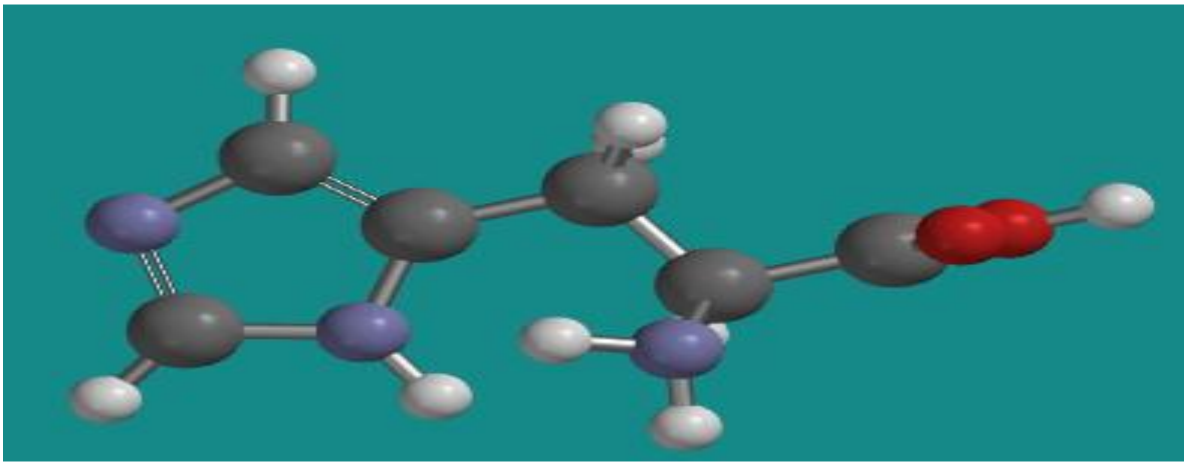


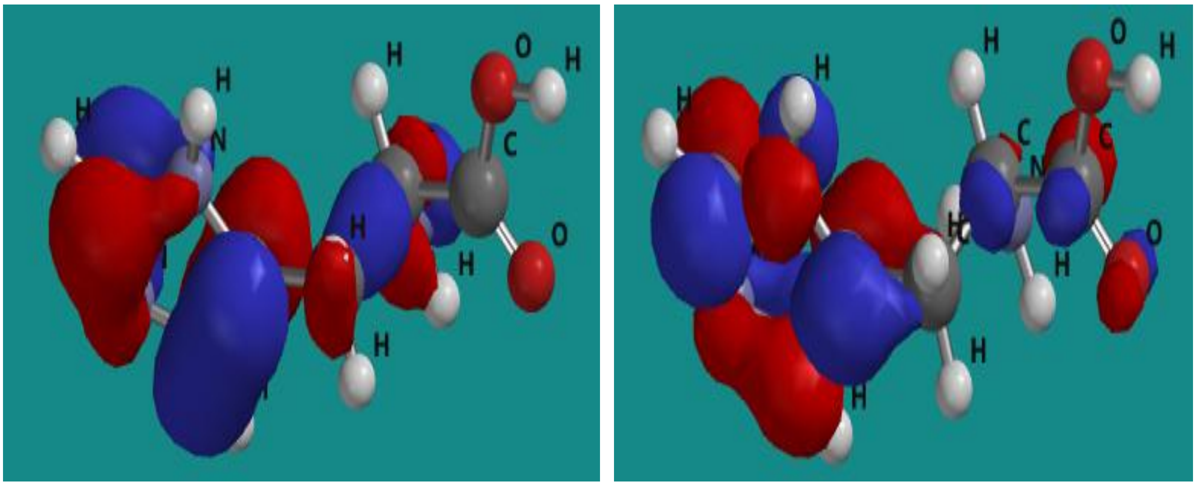
Figure 5: Optimized Structure of L-Histidine Compounds

In Table 6, the values of E_{HOMO} of L-histidine compound indicates that L-histidine can act as an electron donor, but it is not extremely high in HOMO energy compared with many strong organic donors. The HOMO is sufficiently low in energy to allow donation to empty d-orbitals of Fe, consistent with coordination through N and O atoms (as your HOMO and LUMO images show). E_{HOMO} (positive) and a negative electron affinity ($A \approx -0.23$ eV) imply that direct, favorable electron acceptance by the inhibitor is limited — i.e., back-donation from metal to inhibitor is possible but not strongly favored by global energetics (Shimizu *et al.* 2020). Still, local orbitals (π-system of imidazole, lone pairs) can accept some back-donation when chemisorption geometry is favorable. ΔE is a relatively large HOMO–LUMO gap, which suggests relatively low global chemical reactivity (i.e., the molecule is overall fairly stable). That tends to reduce the tendency for spontaneous chemical reactions with the metal, but it does not predict adsorption-driven inhibition. Localized donor sites (N, O on imidazole and carboxyl) can still form coordinate bonds even when the global gap is large. This indicates net electron donation from inhibitor → metal, supporting formation of a donor–acceptor interaction (chemisorption) and consistent with a protective coordination film (Fe–N, Fe–O bonds). A ΔN of ~0.5 is moderate and consistent with effective but not extremely strong electron donation. A moderate dipole moment (μ) supports favorable orientation/adsorption at the metal–solution interface and can enhance physisorption (electrostatic interactions), especially under acidic conditions where parts of the molecule may be protonated (Hassa *et al.* 2022).

Table 6: Calculated Quantum Chemical Parameters

Molecule	Total energy (kj/mol)	E-HOMO (eV)	E –LUMO (eV)	ΔE (eV)	μ	ΔN
L-His	-274	-9.6	0.23	9.83	3.81	0.47

Figure 5 represents how L-histidine's electron-rich sites (HOMO) align with Fe atoms' vacant orbitals, enabling chemisorption that blocks corrosive species. The small HOMO–LUMO gap and high electron density at donor atoms confirm its strong corrosion inhibition potential for mild steel in acidic (HCl) environments. The Red and blue lobes represent electron density (positive and negative phases of the orbital). HOMO region (usually red) → sites that can donate electrons to the metal surface. LUMO region (usually blue) → sites that can accept electrons from the metal (back-donation). From the image, electron density is concentrated around the imidazole ring nitrogen atoms and the carboxyl oxygen atoms (Award *et al*. 2025). This indicates potential adsorption centers for coordination with Fe^{2+} ions on the mild steel surface.



HOMO of L-His LUMO of L-His

Figure 6: Molecular Orbital Density Distribution of L-Histidine Compound

CONCLUSION

L-histidine which is ecofriendly and biodegradable has showed success as an efficient organic compound inhibitor for corrosion of mild steel in 0.1 mol dm^{-3} HCl. The inhibition efficiency increased with both increase in inhibitor's concentration and in temperature. The inhibitive action was realized through adsorption of the amino acid onto mild steel surface as demonstrated by fitting to Langmuir adsorption isotherm. The highest inhibition efficiency was 90.19%, obtained at reaction temperature of 363 k when the mild steel was exposed to the highest inhibition concentration of 0.01moldm^{-3} for 6 hrs. These conditions will efficiently curtail metallic deterioration and essentially prolong the life span of mild steel

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