Study of the Efficiency of the Amino Acid L-Histidine as a Corrosion Inhibitor of 1018 Carbon Steel in Saline Solution Without and with CO, Saturation

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L-histidine was analyzed in this work as a corrosion inhibitor for AISI 1018 carbon steel in chloride solution, without (pH 7) and with carbon dioxide saturation (pH 4). Mass loss methods and electrochemical tests were used. In a medium with pH 4 saturated with CO_2 , the inhibition efficiency values (IE%) did not reach 34%. For the pH 7 condition, an inhibition efficiency of up to 89% was observed. The values corroborated with the quantum chemistry and Density Functional Theory (DFT) calculations, showing that the histidine molecule is responsible for the excellent inhibition potential. A Fourier transform infrared spectroscopy (FTIR) study and a thermogravimetric study (TGA) of the amino acid were also carried out. The substrate surface was analyzed by scanning electron microscopy and atomic force microscopy.

Keywords: Corrosion Inhibitor, Amino Acids, Carbon Steel.

1. Introduction

Corrosion poses a significant economic threat in industrial settings due to the myriad physical-chemical interactions between materials and the environment. This phenomenon is particularly intense in the oil and gas industry, where pipelines and extraction equipment are constantly exposed to corrosive elements such as chlorinated media and CO₂. The structural failures and leaks result in large financial losses and require an urgent need for effective corrosion mitigation strategies^{1,2}.

While traditional approaches rely on coatings and corrosion inhibitors containing harmful elements, concerns regarding toxicity and environmental impact have increased interest in organic corrosion inhibitors. Among these, amino acids have emerged as promising candidates due to their non-toxic nature, environmental safety, and inhibitory effectiveness attributed to the presence of N, O, and S heteroatoms in their molecular structures³⁻⁷.

The adsorption mechanisms, which can be chemical or physical, show how organic the molecules that feature N, S, P, and O heteroatoms, together with functional groups, phenyl rings, and π electrons, have a particular affinity for the steel surface⁸. This affinity is facilitated by the ability of these groups and molecular structures to interact with the active sites on the metal surface. Through chemical interactions, such as coordinate bonds and hydrogen, and physical interactions, such as Van der Waals interactions and π - π interactions, these molecules can firmly adsorb to the steel surface, forming a protective layer. This layer, in turn, prevents or slows down corrosive processes, thus protecting against metal degradation. Understanding these adsorption mechanisms is essential for the development of organic corrosion inhibitors. Consequently, amino acids provide ideal properties as effective substances for protecting metallic materials in corrosive environments^{4,9-20}.

In this context, L-histidine, an essential amino acid characterized by a positively polarized imidazole side chain, presents a compelling avenue for corrosion inhibition. Its imidazole group, with readily available nitrogen atoms possessing free electron pairs, exhibits promising inhibitory properties in aqueous media. However, despite the potential of L-histidine as a corrosion inhibitor, its effectiveness in environments with varying pH levels, particularly those saturated with CO₂, remains underexplored.

Therefore, this study aims to address this gap by investigating the inhibitory properties of L-histidine on the corrosion of AISI 1018 carbon steel exposed to a 3.5 wt% NaCl solution, both

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in environments without and with CO_2 saturation. In the first environment, the working solutions, NaCl with L-histidine, were exposed to ambient air aerated with oxygen at pH 7, while in the second environment, deaeration occurred through N₂, immediately followed by CO_2 saturation, until reaching pH 4. This allowed for a comparative analysis of histidine as a corrosion inhibitor in environments without and with CO_2 saturation, considering the influence of the different pH levels characteristic of these environments. NaCl solutions were used due to their importance as the primary source of chloride ions in seawater, where pipelines used in the oil and gas industry are submerged.

Analysis of L-histidine efficiency involved mass loss measurements, potentiodynamic polarization (PP) curves, and electrochemical impedance spectroscopy (EIS). Consequently, addressing the central questions of this study was based on evaluating corrosion potential, electrical current density, polarization resistance, charge transfer, and inhibition efficiency measurements. Additionally, information about the metallic substrate surface and its protection by the amino acid was obtained through scanning electron microscopy and atomic force microscopy. Finally, quantum chemical calculations were performed using the DFT method at the computational level B3LYP/6-311++G(d,p), employing pH-dependent structures.

The significance of this research lies in its potential to provide insights into the efficacy of L-histidine as a corrosion inhibitor in complex industrial environments. By evaluating its performance against corrosion parameters such as corrosion potential, electrical current density, charge transfer resistance, and inhibition efficiency, it will be possible to contribute to developing more sustainable and effective corrosion reduction strategies. Furthermore, the utilization of quantum chemical calculations using the DFT method represents an approach to understanding the pH-dependent structures of L-histidine and its interaction with the metallic substrate. This integration of experimental and computational techniques enables a deeper insight into the underlying mechanisms governing the inhibitory action of L-histidine, thus paving the way for future advancements in corrosion inhibition research.

In summary, this study not only addresses the imminent need for environmentally friendly corrosion inhibitors but also presents a significant possibility to advance understanding of the corrosion inhibition mechanisms of L-histidine in challenging industrial environments.

2. Experimental

2.1. Preparation of samples and solutions

The working electrodes used in this study were AISI 1018 carbon steel cylinders, with chemical composition obtained by optical emission spectroscopy (% by weight): C 0.197, Mn 0.84, Si 0.19, and Fe balance. This material was used to manufacture the working electrodes, soldered with copper wire and embedded in epoxy resin with an exposed area of 0.5 cm². To prepare the surface of the substrate, sandpaper numbers 220, 320, 400, and 600 were used. The reference electrode was made of Hastelloy alloy, while the counter electrode was manufactured using a platinum

plate with an area of 2.45 cm². The conventional reference electrode (Ag/AgCl or saturated calomel) typically employed in electrochemical assays proves unsuitable for this system, as the inhibitor infiltrates the porous tip, contaminating the internal solution²¹.

The inhibitor-free reference solution was prepared with 3.5 wt% NaCl. The remaining solutions were formulated by adding different concentrations of L-histidine (250, 500, and 1000 ppm) to 3.5 wt% NaCl. It is essential to note that all solutions were prepared using distilled, deionized water at room temperature. The amino acid L-histidine, whose molecular formula is shown in Figure 1, is a product of SIGMA-ALDRICH, boasting a purity level of 99%.

For the solution with pH 4: 3.5 w.t.% NaCl solution was added to a beaker without and with the addition of L-histidine (in the three concentrations: 250, 500 and 1000 ppm), N₂ was bubbled until reaching an oxygen concentration of 0.7 mg/L, verified by an O₂ sensor, soon after, the solution was saturated with CO_2 , effectively reducing the O₂ concentration below 0.3 mg/L and reaching a pH of 4, monitored with a pH meter.

For the solution with pH 7: 3.5 wt.% NaCl solution was added to a beaker without and with L-histidine (in the three concentrations: 250, 500, and 1000 ppm), and the pH was checked with a pH meter. The values of the NaCl solution varied at a value of 6.85 ± 0.35 . The pH values are in the range of 7.25 ± 0 , 25 for the solution with the addition of L-histidine.

2.2. Amino acid characterization: L-histidine

L-histidine was characterized using vibrational spectroscopy in the Fourier Transform Infrared Region (FT-IR), conducted with a spectrophotometer (Spectrum Frontier; Perkin-Elmer Corp.). This equipment has an attenuated total reflectance accessory (ATR) featuring a zinc selenide (ZnSe) crystal surface. The spectra were obtained with 32 scans spanning from 4000 to 550 cm⁻¹, employing a resolution of 4 cm⁻¹ in a transmittance model²². Thermogravimetric analysis of the L-histidine sample was performed using TGA/SDTA851E equipment from the Mettler Toledo brand. The analysis occurred under an inert nitrogen atmosphere with a 50 ml/ min flow rate. The experiment utilized a heating rate of 10°C/min, covering temperatures from 30°C to 800°C, and employed a semi-open alumina crucible. The equipment essentially comprises a scale that enables continuous sample weighing based on temperature²³.

2.3. Weight loss measurements

The gravimetric test was conducted over 48 hours for both studied media, following the ASTM G31-72^{24,25} standard. The AISI 1018 carbon steel samples, each with an area of



Figure 1. Structure of L-histidine.

14,76 cm², were immersed in a 3.5 wt% NaCl solution, both with and without the addition of inhibitors across the three concentrations. The immersion time was 48 h, and right after, the specimens were treated by the previously mentioned standard. All assays were carried out in triplicate.

Before and after the corrosive attack, the samples were weighed using an analytical balance (accuracy ± 0.0001 mg) to obtain weight loss values in g/cm².h²⁶. After this test, the samples were taken to scanning electron microscopy (SEM).

2.4. Electrochemical tests

The electrochemical measurements were performed in a conventional three-electrode cell. The polarization curves and the electrochemical impedance test were generated using a potentiostat/galvanostat model PGSTAT302N, linked to the NOVA 2.1.4 software. After the open circuit potential (OCP) stabilization lasting 3600 seconds, both tests were carried out.

For potentiodynamic polarization, these measurements were carried out using in the range -200 to +200 mV versus E_{ocp} at a scan rate of 10 mV·s⁻¹. The objective of this test is the qualitative analysis of the cathode and anode branches for the L-histidine solution without and with CO₂ saturation.

The electrochemical impedance test measurements were conducted within a frequency range of 100 kHz to 6 MHz, with a sinusoidal signal amplitude of 10 mV^{27,28}.

2.5. Surface analysis – Scanning electron microscopy (SEM) and atomic force microscopy (AFM)

The surface characterizations of the samples were carried out after an immersion test for 48 hours without and with CO_2 saturation. They were analyzed using a scanning electron microscope (SEM), specifically the Quanta 450-FEG (FEI), and an atomic force microscope. Atomic Force Microscopy (AFM) measurements were acquired in intermittent contact mode using an Asylum MFP-3D BIO system, employing tips with a radius of curvature of less than 20 nm and a resonance frequency of 75 kHz.

For each medium (pH 4 and 7), three samples of the AISI 1018 substrate were used for the investigation. These included a sample polished with 6, 3, and 1 μ m diamond paste, a sample immersed in a NaCl solution, and a sample immersed in a NaCl solution of L-histidine at a concentration of 1000 ppm²⁹.

2.6. Quantum chemical calculations

The L-histidine molecule was geometrically optimized using the exchange-correlation hybrid functional B3LYP^{30,31} and the 6-311++G (d,p) basis set. The molecular geometry was calculated in the gas phase and using water as an implicit solvent using the IEF-PCM³²⁻³⁴ solvation model available in Gaussian 09 for the microstates in pH = 7 and pH = 4. From the optimized geometry from both the gas phase and water media, the Frontier Molecular Orbitals (FMO) were computed at B3LYP/6-311++G(d,p) level of theory and the isosurface for both Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) were rendered using the trial version of the ChemCraft program. To understand the behavior of the histidine molecule as a corrosion inhibitor, the energy values of the FMO were used to compute the quantum reactivity descriptors: the HOMO-LUMO energy gap (ΔE_{gap} , (a))³⁵, the ionization potential (I, (b))³⁶, the electron affinity (A, (c))³⁶, the electronegativity (χ , (d))^{37,38}, the global hardness (η , (e))^{39,41}, the global softness (S, (f))⁴², the global electrophilicity index (ω , (g))⁴³, the global nucleophilicity index (ε , (h))⁴⁴, and the fraction of electrons transferred (ΔN , (i))⁴⁵. For the fraction of electrons transferred, the carbon steel electrode can be considered as an iron (Fe) metallic bulk. The following parameters were used: $\chi_{Fe} = 7.0$ eV and $\eta_{Fe} = 0$ since the ionization potential (I) is equal to the electron affinity (A) for the bulky metallic surface⁴⁵. Table 1 calculates all quantum reactivity descriptors necessary for this work.

3. Results and Discussion

3.1. Characterization

3.1.1. FTIR

The infrared spectrum of the amino acid L-histidine is illustrated in Figure 2 vibrations characteristic of the C–H and NH– bonds of the imidazole ring are evident at wavelengths of 3011 cm⁻¹ and 2705 cm⁻¹, respectively. Aliphatic C–H chains are observed at 2855 cm⁻¹. The peak at 1630 cm⁻¹ may be associated with the asymmetric stretching of the carboxylate group, along with the asymmetric deformation of the NH₃ group. Bands located at 1585, 1449, 1341, and 623 cm⁻¹ correspond to the C=C bonds, symmetric stretching of the NH₃ bonds, symmetric COO⁻ group, and CN⁻ bond, respectively^{1,22,46}.

Table 1. Quantum reactivity descriptor equations.

(a) - $\Delta E_{GAP} = E_{LUMO} - E_{HOMO}$
(b) - $I = -E_{HOMO}$
(c) - $A = -E_{LUMO}$
$(d) - \chi = \frac{I+A}{2}$
$(e) - \eta = \frac{I - A}{2}$
$(f) - S = \frac{1}{\eta}$
(g) - $\omega = \frac{\chi^2}{2\eta}$
(h) - $\varepsilon = \frac{1}{\omega}$
(i) - $\Delta N = \frac{\chi_M - \chi_{inh}}{2(\eta_M + \eta_{inh})}$



Figure 2. FTIR analysis of L-histidine.

From the spectrum, it is evident that there are vibrations characteristic of the NH_3^+ group at wavelengths of 3011 cm⁻¹, 2855 cm⁻¹, 2705 cm⁻¹, and 1630 cm⁻¹. Additionally, vibrations associated with the COO⁻ group appear at 1585 cm⁻¹ and 1449 cm⁻¹ wavelengths, reflecting the asymmetric and symmetric stretching of C(=O)₂, respectively. These vibrations are attributed to the amino acid as they are present in its isoelectronic or zwitterionic form Figure 3. Assignments confirm the presence of multiple functional groups^{47,48}.

3.1.2. TGA

The study of thermal stability holds significant importance in material characterization. The thermogravimetric analysis investigates the changes in mass a sample undergoes due to physical processes (such as sublimation, evaporation, and condensation) or chemical transformations (such as degradation, decomposition, and oxidation) about time or temperature. The substance's total mass or mass fraction is continuously monitored, and the resulting data is represented on a thermal decomposition curve, commonly referred to as a thermogram. The primary processes measured encompass evaporation, sublimation, decomposition, oxidation, reduction, and gas adsorption^{46,49}.

From the analysis of the TGA and DTG curve, Figure 4, it can be observed that two different mass loss events occur, a decomposition in more than one step (mult-step decomposition), the first event involving two mass losses between temperatures of 270°C and 400°C and a second decomposition at temperatures ranging between 400 and 800°C.

The first event presents mass losses of approximately 15.66% and 19.98% and peak DTG temperatures of 285.5°C and 340.5°C. The second event presents a mass loss of 44% and a peak DTG temperature of approximately 714.8°C. Therefore, we can infer that the sample has thermal stability up to 270°C.

3.2. Weight loss measurements

The data obtained from the gravimetric test are presented in Table 2, the inhibition efficiency (IE) was calculated from Equation 2. Where C_{Ro} represents the corrosion rate in the absence of an inhibitor, and C_{Ri} is the corrosion rate in the presence of an inhibitor.

$$IE = \left(1 - C_{Ri} / C_{Ro}\right) x 100 \tag{1}$$



Figure 3. The structural formula of the amino acid between positive and negative charges (isoelectronic or zwitterionic).



Figure 4. L-histidine TGA curves.

There is little variation in IE with increasing concentration in both media. However, the Inhibition Efficiency for the pH 7 medium is greater at the three concentrations of L-histidine compared to the pH 4 medium. This behavior was also observed for other organic inhibitors.

3.3. Electrochemical tests

3.3.1. Potentiodynamic polarization

The figure 5 shows the potentiodynamic polarization curves obtained after 3600 s of immersion in a 3.5 %wt.

Concentration (ppm) –	pH 4		рН 7		
	CR (mm/y)	IE (%)	CR (mm/y)	IE (%)	
Blank	1.4196 ± 0.123		0.8888 ± 0.091		
250	0.9398 ± 0.088	33.33	0.1306 ± 0.076	83.10	
500	0.9260 ± 0.095	34.86	0.1183 ± 0.084	87.03	
1000	0.8826 ± 0.057	34.61	0.1022 ± 0.096	88.32	

 Table 2. Gravimetric results of AISI 1018 carbon steel after 48 h of immersion in 3.5 w.t.% NaCl without and with different inhibitor concentrations, in pH 4 and pH 7 medium.



Figure 5. Polarization curves of AISI 1018 steel in solution 3.5 wt% NaCl without and with L-histidine (250, 500, and 1000 ppm), at pH7 (a) and pH4 (b).

NaCl solution with and without L-histidine in the two media studied.

Figure 5a depicts the cathodic and anodic curves in the pH 4 medium. In this medium, it was not possible to observe a reduction in current densities in either branch, and the corrosion potential only showed more positive values when compared to the sample without inhibitor, for concentrations of 500 and 1000 ppm. It is also observed that at pH 4, the L-histidine curves at the three concentrations exhibit changes in the anodic branches compared to the blank, resulting in a modification in the mechanism and higher values of current densities. It can be concluded that, in a CO_2 -saturated environment, the change in the process mechanism implies that the material surface remains unblocked due to the non-adsorption of L-histidine molecules⁵⁰⁻⁵². In Figure 5b, the anodic current densities are lower for samples with inhibitors compared to the control system (blank), revealing the anodic behavior of the inhibitors. It is also observed that the presence of L-histidine in the solution does not alter the process mechanism but acts as an adsorption inhibitor, resulting in lower current density values in the anodic branch. Consequently, this delays the anodic reaction, obstructing active sites. However, it can be concluded that there was no increase in L-histidine molecules at the metal/solution interface with the increase in inhibitor concentration. Therefore, at this pH, the reduction in density can be attributed to the adsorption of inhibitory molecules at active corrosion sites^{1,53,54}.

3.3.2. Electrochemical impedance spectroscopy

Data on L-histidine inhibition were derived from the electrochemical impedance spectroscopy test and are illustrated by Nyquist graphs in Figure 6. The inhibition efficiency (IE) was calculated using Equation 6 based on the charge transfer resistance values presented in Table 3.

IE =
$$(\frac{R_I - R_0}{R_I})$$
x 100 (2)

Where, $R_0 \in R_I$ represent the charge transfer resistance values without and with the inhibitor, respectively, obtained from Nyquist plots.

In the medium with CO_2 at pH 4, the arc is inductive at a low-frequency range and was related to the local adsorption of OH⁻ on the steel surface, forming intermediate product FeOH_{ads}, as illustrated in Figure 6a. For all three concentrations, the curves remain nearly identical, indicating that increasing the amount of histidine in an acidic medium does not lead to an enhancement in inhibition^{55,56}. It was also observed in this medium that a change in the mechanism occurred when the medium was saturated with CO_2 , corroborating the results of potentiodynamic polarization.

In Figure 6b, the curves exhibit depressed capacitive semicircles, indicating a distinct charge transfer process at the electrode/solution interface. The semicircle diameters in the inhibitor solution are greater than those in the reference solution. This capacitive loop is in a higher frequency range (attributed to double-layer relaxation and charge transfer). The diameter of these semicircles is linked to resistance against polarization and increases with the concentration of L-histidine. However, no significant growth was observed for the concentration of 1000 ppm when compared to the concentration of 500 ppm, aligning with the values obtained from linear polarization and mass loss tests^{11,28,54,57}.

Concentration (ppm) –	pH 4		рН 7		
	$R_{ct}(\Omega cm^2)$	IE%	$R_{ct} (\Omega cm^2)$	IE%	
BLANK	205 ± 8.14		336 ± 7.86		
250	$234{\pm}4.73$	12.68	895 ± 11.52	62.46	
500	232 ± 5.34	11.81	1119 ± 16.89	69.97	
1000	235 ± 3.71	13.12	1181 ± 10.48	71.55	

Table 3. Parameters obtained by EIS for corrosion of AISI 1018 carbon steel in 3,5 WT. % NaCl without and with L-histidine (250, 500, and 1000 ppm), in pH 4 and pH 7.



Figure 6. Nyquist plots for AISI 1018 carbon steel at 3.5 wt% NaCl without and with L-Histidine (250, 500, and 1000 ppm) at pH7 (a) and pH4 (b).

Soon, in the medium without CO_2 at pH 7, the inhibition efficiency increases with the rise in histidine concentration. However, for the medium with CO_2 at pH 4, the efficiency does not continue to increase with the addition of histidine; the trend remains essentially the same for all concentrations, and the efficiency values are presented in Table 3.

3.4. Surface analysis

3.4.1. Scanning electron microscopy

After 48 hours of the mass loss test, images of the substrate surface were obtained using scanning electron microscopy (SEM). Figure 7 displays representative images: (a) sample submerged in solution 3.5 wt% NaCl (b) sample submerged in solution 3.5 wt% NaCl (b) sample submerged in solution of L-histidine-1000 ppm (pH 7), (d) NaCl with the addition of L-histidine-1000 ppm with CO₂ saturation (pH 4). The samples without inhibitor (white) showed surfaces with corrosion products. However, after adding L-histidine at 1000 ppm (pH 7), the sample presented a well-preserved surface. However, at pH 4, it is possible to observe a greater amount of corrosion product than the surface of the sample at pH 7.

3.4.2. Atomic force microscopy

Atomic force Microscopy (AFM) was used to evaluate the surface topography of AISI 1018 carbon steel. Four samples were used, shown in Figure 8. a) a sample with a surface polished with diamond paste, b) a sample immersed in a 3.5% by weight NaCl solution, c) a sample immersed in a NaCl solution with the addition of L-histidine-1000 ppm (pH7), d) a sample immersed in NaCl solution with the addition of L-histidine-1000 ppm (pH4). The samples remained in solution for 48 hours before being analyzed in the AFM.

According to 3D standards, the polished sample showed a roughness profile of 8.34. The height profile of this specimen revealed slight fluctuations (Figure 8a). After immersion in solution 3.5 wt% NaCl, a severely corroded surface was obtained (Figure 8b), due to the corrosion attack and the surface accumulation of corrosion products, a height profile with sharp peaks was acquired. However, in the presence of 1000 ppm of L-histidine with pH 7, a relatively flat surface was observed, with slight deteriorations that demonstrate a substantial reduction in the corrosion rate of the steel (Figure 8c). For the surface of the sample in the presence of 1000 ppm of L-histidine at pH 4 (Figure 8d), the surface presented a profile with roughness greater than at pH 7 but lower than the sample without the inhibitor. The height profile recorded for the sample at pH 7 was much closer to the polished sample.

The Ra value measurements for the polished, severely corroded, and inhibited samples without CO₂ (pH 7) and with CO₂ (pH4) were approximately 8.34 nm, 185.9 nm, 24.86 nm, and 117.27 nm, respectively. These results can be understood by the surface adsorption of L-histidine, which forms a passive inhibitory layer between the carbon steel and the corrosive solution. The influence of organic inhibitors on reducing the surface roughness of metallic substrates has also been identified in previous studies⁵⁸⁻⁶³.

3.5. Quantum chemical calculations

Figure 9 displays the microspecies distribution at varying pH levels, a crucial calculation for determining the molecular structure of histidine in experimental environments. The main objective is to understand the inhibition capabilities of the molecule in a neutral medium and saturated medium with CO₂. At neutral pH, the predominant microspecies is the zwitterion structure (Structure 3), while at pH 4, it shifts to Structure 6. Quantum chemical calculations, using the DFT method at the B3LYP/6-311++G(d,p) computational level, utilized the pH-dependent structures. Figure 10 shows



Figure 7. SEM images of the surface of AISI 1018 carbon steel, (a and b) in 3.5 wt% NaCl without and with CO_2 saturation, (c and d) with the addition of L-histidine without and with CO_2 saturation (pH 7 and pH4).



Figure 8. Atomic force microscopy (AFM) images of AISI 1018 steel, (a) polished sample, (b) sample in solution 3.5 wt% NaCl, (c) Sample in solution de 3.5 wt% NaCl with L-histidine-1000ppm (pH7); (d) Sample in solution 3.5 wt% NaCl with L-histidine-1000ppm (pH4).



Figure 9. Microspecies distribution with different values of pH for the histidine molecule.

the optimized geometry for histidine in the gas phase and water, revealing differences due to dielectric effects. In the gas phase, the structure maintains the carboxylic acid and amino group, whereas it aligns with the zwitterion structure in water. The water molecules stabilize histidine through additional hydrogen bonds, impacting reactivity. Bond lengths in the carboxylate group also vary across phases. In water, the resonance effect increases stability and reduces reactivity compared to the gas phase geometry.

From the optimized geometry in both gas-phase and water media (both neutral and acidic environments), Frontier Molecular Orbitals (FMO) were computed at the B3LYP/6-311++G(d,p) level of theory, as shown in Figure 11. In the gas phase and neutral media geometries, the Highest Occupied Molecular Orbital (HOMO) is predominantly spread over the imidazole ring, carboxylic group, and the C-C σ -bond from the ethyl group. Only the gas phase geometry exhibits a portion of the HOMO spread over the amino group. This similarity in HOMO distribution suggests both molecules should interact similarly with the iron bulk, as the electronic density available for donation to the empty d-orbitals on the metallic surface is almost identical. The acid media geometry displays a different HOMO distribution, with the molecular orbital primarily spread over the carboxylic group and a small part distributed in the imidazole group. The disparity in HOMO distribution between neutral and acidic media is crucial in determining corrosion inhibition power. In the neutral media, the HOMO is mainly spread over the imidazole ring, while in the acid media geometry, the HOMO is primarily spread over a group strongly stabilized by resonance effects. Consequently, it is expected that the HOMO for the neutral media geometry would be more reactive than the acid media geometry.

The LUMO exhibits distinct characteristics across the three simulated geometries. In the gas-phase structure, the LUMO primarily spans the imidazole ring, while in the neutral media structure, it is mainly over the ammonium cation. In the acid media geometry, the LUMO is mainly spread over the imidazole ring, indicating a change in the molecule's ability to accept electronic density with alterations (a) Gas phase



Figure 10. Optimized molecular geometries at B3LYP/6-311++G(d,p) computational level for the histidine molecule (a) in the gas phase (b) in the water as an implicit solvent (pH 7) (c) in water as an implicit solvent (pH4).

in the chemical environment. This trend is reflected in the energy values of HOMO and LUMO, as shown in Table 4.

The HOMO energy values are nearly identical for the gas phase and neutral media structures, with only a difference of

Quantum Reactivity Descriptor	Gas phase	Water (neutral media)	Water (acid media)	Histidine ¹⁷	Histidine ¹⁶	Histidine ¹⁶	Histidine9
HOMO energy (E_{HOMO} /eV)	-6.8268	-6.7014	-7.19504	-6.367	-6.72725	-6.71337	-6.700
LUMO energy (E_{LUMO}/eV)	-0.7606	-0.2952	-1.41237	-0.272	-0.88955	-0.31538	-0.094
Energy gap (ΔE_{Gap} / eV)	6.0663	6.4062	5.7827	6.095	5.83770	6.39799	6.600
Ionization Potential (I / eV)	6.8268	6.7014	7.1950	6.3670	6.72725	6.71337	6.700
Electron Affinity (A / eV)	0.7606	0.2952	1.4124	0.2720	0.88955	0.31538	0.094
Electronegativity (χ/ eV)	3.7937	3.4983	4.3037	3.3195	3.80840	3.51438	3.397
Global Hardness (η/ eV)	3.0331	3.2031	2.8913	3.0475	2.91885	3.19900	5.200
Global Softness (σ/eV1)	0.3297	0.3122	0.3459	0.3281	0.34260	0.31260	0.303
Electrophilicity index (ɛ/eV)	2.3725	1.9104	3.2030	1.8079	2.4845	1.9304	1.747
Nucleophilicity index (@/eV ⁻¹)	0.4215	0.5235	0.3122	0.5531	0.4025	0.5180	0.573
Fraction of electrons transferred (ΔN)	0.528544	0.546611	0.466272	0.5782	0.546722	0.544800	0.540

Table 4. The quantum reactivity descriptors were computed from the energy values of the HOMO and LUMO for the histidine molecule in the gas phase, in the water media, and a comparison with other work.

(a) Gas phase



Figure 11. Calculated Frontier Molecular Orbitals (FMO) at B3LYP/6-311++G(d,p) level of theory for the histidine molecule (a) in the gas phase (b) in the water as an implicit solvent (pH 7) (c) in water as an implicit solvent (pH 4).

0.1254 eV. However, in the acid media geometry, the HOMO energy shows a significant difference of 0.49364 eV compared to the water media structure. This suggests that histidine in acid media is less prone to donating electronic density to the metallic surface, whereas in neutral media, the tendency for this electron transfer is more probable. The increasing order of corrosion inhibition power based on HOMO energy values is as follows: acid media < gas phase < neutral media. The LUMO energy values show a higher difference between the gas phase and neutral structure, between the gas phase and acid media geometry, and between histidine in neutral and acid media. These differences indicate that pH influences the electronic properties of histidine, with a higher electrophilic character in acid media and a greater nucleophilic character in neutral media. The increasing order for corrosion inhibition based on LUMO energy values is neutral media < gas phase < acid media.

The HOMO-LUMO energy gap ($\Delta E_G ap$), considering both the molecule's susceptibility to donate or accept electronic density, is higher for the gas phase and neutral media structures, indicating lower chemical reactivity. The acid media geometry, with a lower energy gap, is expected to be more reactive, although its corrosion inhibition power depends on back donation from the metal to the molecule.

Comparisons with existing literature and calculations are made, showcasing agreement with some studies and differences with others. Despite variations in basis sets, the B3LYP method is deemed accurate^{9,16,17}.

The next set of quantum reactivity descriptors under evaluation includes ionization potential (I), electron affinity (A), and electronegativity (χ). These descriptors are directly linked to the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO). The results for the three simulated histidine molecules (gas-phase and water media for the neutral and acidic chemical environments) are as follows: a consistent trend in donating electronic density is observed between the gas-phase and neutral media structures, given their similar ionization potentials. However, histidine in the acidic media exhibits a notable difference, indicating a lower nucleophilic character. This order aligns with the corrosion inhibition power determined by HOMO values. Histidine in acidic media demonstrates a higher tendency to accept electronic density, as evidenced by its elevated electron affinity compared to histidine in neutral media and the gas phase. Consequently, the electronegativity of histidine in acidic media surpasses that of histidine in neutral media and the gas phase, reflecting its heightened electrophilic character in the acidic media geometry. Hence, the predicted order for corrosion inhibition aligns with the observations made for the LUMO.

The global hardness (η) and softness (S) are related to the HOMO-LUMO energy gap: the higher the energy gap, the higher the global hardness and the lower the global softness, which means a soft molecule is more reactive than a hard molecule. The global hardness of the histidine in water (neutral media) is higher than the histidine in the gas phase and the acid media due to the higher value of the energy gap. However, the values of the global softness are quite similar between the neutral media and the gas phase because the power to donate electronic density to the iron surface is almost the same as discussed before. The metallic surface is classified as soft since the global hardness (η_{Metal}) is zero. Hence, the histidine molecule has similar electrondonating power in the gas phase and water. Hence, the histidine molecule has excellent applicability as corrosion inhibition. The same tendency occurs in the electrophilic (ω) and nucleophilic index (ε). The histidine molecule shows different values for the electrophilic index when compared to the molecule in the gas phase and water media (for both neutral and acid chemical environments). The histidine in the acid media has greater electrophilic character due to the higher electron affinity (A), electronegativity (χ), and electrophilic index (ω), however, the nucleophilic index is higher for the histidine in the neutral media since this microstate has the higher nucleophilic character (electron-donating power). Finally, the fraction of transferred electrons shows how the charge transfer will occur from the inhibitor molecular or the metallic surface. If $\Delta N > 0$, the flow of the electrons occurs from the molecule to the surface, and if $\Delta N < 0$, the molecule will receive electronic density from the metal. It can be seen from Table 4 that the histidine in the gas phase and water media (neutral and acid environment) showed the value of the fraction of transferred electrons positive ($\Delta N > 0$), and the value is higher for the histidine in neutral media followed by the gas-phase structure. These results demonstrate that the histidine molecule can be used as a corrosion inhibitor in a neutral media, and the nucleophilic character is responsible for the great performance of this molecule as a corrosion inhibitor. Although some of the values of quantum reactivity descriptors for the acid media structure were better than in comparison with the neutral media structure, since the value of the fraction of transferred electrons showed a positive value, the charge transfer between the organic molecule and the

metallic surface will occur more strongly as the nucleophilic power of the molecule increases. Therefore, histidine in a neutral medium should be more efficient in inhibiting corrosion. The histidine in acid media should be a suitable corrosion inhibitor. However, when the concentration of this molecule increases, the probability of the back donation from the metal will decrease; hence, it is expected that the corrosion inhibition power for the histidine in acid media will decrease with the increase in the number of molecules.

4. Conclusions

Through analysis of the results, it was possible to conclude that L-histidine in a medium without saturation with CO₂ exhibits good inhibition efficiency and can be utilized as a corrosion inhibitor for AISI 1018 carbon steel in a 3.5 wt% NaCl solution. The spectra from chemical analysis via FTIR reveal the presence of species commonly found in corrosion inhibitors, such as oxygen and nitrogen atoms, as well as groups of aromatic rings, which are likely adsorbed onto the sample surface, thereby elucidating the inhibitory properties. Gravimetric mass loss tests indicated that in the presence of L-histidine at pH 7, the corrosion rate was significantly lower than at pH 4, with 89% and 34% efficiencies, respectively. Electrochemical tests suggest that the corrosion mechanism remains unchanged in the presence of L-histidine without CO₂ saturation. However, in an L-histidine medium with CO₂, the mechanism undergoes modification. These findings are consistent with the calculations from quantum chemistry and Density Functional Theory (DFT), The histidine molecule was electronically characterized by the Frontier Molecular Orbitals and the quantum reactivity descriptors in the gas phase and water as an implicit solvent (pH =7 for the neutral media and pH = 4 for the acid media). Despite the chemical environment, the nucleophilic character of the histidine molecule should be responsible for its great potential as a corrosion inhibitor, and the corrosion inhibition efficiency should increase when the concentration of histidine molecule in a neutral media increases, which does not occur in a medium with saturation of CO₂ (pH 4). SEM images demonstrate that L-histidine is adsorbed onto the surface of the carbon steel, serving as a protective barrier against the progression of the corrosive process on the substrate, with higher quantities observed at pH 7 and lower quantities at pH 4.

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6. Referências

- Fawzy A, Abdallah M, Zaafarany IA, Ahmed SA, Althagafi II. Thermodynamic, kinetic and mechanistic approach to the corrosion inhibition of carbon steel by new synthesized amino acids-based surfactants as green inhibitors in neutral and alkaline aqueous media. J Mol Liq. 2018;265:276-91. http:// doi.org/10.1016/j.molliq.2018.05.140.
- 2. Gharbi K, Chouicha S, Andrew M. Field test investigation of the performance of corrosion inhibitors: a case study. J Pet Explor

Prod Technol. 2021;11(10):3879-88. http://doi.org/10.1007/s13202-021-01287-y.

- Finšgar M, Jackson J. Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: a review. Corros Sci. 2014;86:17-41. http://doi.org/10.1016/j.corsci.2014.04.044.
- Bobina M, Kellenberger A, Millet JP, Muntean C, Vaszilcsin N. Corrosion resistance of carbon steel in weak acid solutions in the presence of l-histidine as corrosion inhibitor. Corros Sci. 2013;69:389-95. http://doi.org/10.1016/j.corsci.2012.12.020.
- Yang K, Wang X, Lynch I, Guo Z, Zhang P, Wu L. Green construction of MBI corrosion-resistant interfaces modified NZVI@MOFs-regulated 3D PAN cryogel film to enhance Cr(VI) removal. Separ Purif Tech. 2024;333:125902. http:// doi.org/10.1016/j.seppur.2023.125902.
- Rached S, Habsaoui A, Mzioud K, Lachhab R, Haida S, Errahmany N, et al. Valorization of the green corrosion inhibitor Marrubium vulgare L.: electrochemical, thermodynamic, theoretical & surface studies. Chem Data Collect. 2023;48:101099. http:// doi.org/10.1016/j.cdc.2023.101099.
- Li D, Zhao X, Liu Z, Liu H, Fan B, Yang B, et al. Synergetic anticorrosion mechanism of main constituents in *Chinese Yam* peel for copper in artificial seawater. ACS Omega. 2021;6(44):29965-81. http://doi.org/10.1021/acsomega.1c04500.
- Souza ECCA, Ripper BA, Perrone D, D'Elia E. Roasted Coffee Extracts as Corrosion Inhibitors for Mild Steel in HCL Solution. Mater Res. 2016;19(6):1276-85. http://doi.org/10.1590/1980-5373-mr-2015-0740.
- Zhang L, Zhang S, He Y, Yang R, Ma L, Xia Y, et al. Histidine and histidine dimer as green inhibitors for carbon steel in 3wt% sodium chloride solution; Electrochemical, XPS and quantum chemical calculation studies. Int J Electrochem Sci. 2018;13(2):2136-53. http://doi.org/10.20964/2018.02.76.
- Ismail KM. Evaluation of cysteine as environmentally friendly corrosion inhibitor for copper in neutral and acidic chloride solutions. Electrochimica Acta. 2007;52(28):7811-19. http:// doi.org/10.1016/j.electacta.2007.02.053.
- El Ibrahimi B, Jmiai A, El Mouaden K, Oukhrib R, Soumoue A, El Issami S, et al. Theoretical evaluation of some α-amino acids for corrosion inhibition of copper in acidic medium: DFT calculations, Monte Carlo simulations and QSPR studies. J King Saud Univ Sci. 2018;32(1):163-171. http://doi.org/10.1016/j. jksus.2018.04.004.
- Zhang QH, Hou BS, Li YY, Zhu GY, Lei Y, Wang X, et al. Dextran derivatives as highly efficient green corrosion inhibitors for carbon steel in CO2-saturated oilfield produced water: experimental and theoretical approaches. Chem Eng J. 2021;424:130519. http://doi.org/10.1016/j.cej.2021.130519.
- Thangakani JA, Rajendran S, Sathiabama J, Rathish RJ, Santhanaprabha S. Corrosion inhibition of carbon steel in well water by L-cysteine-Zn2+ system. Port Electrochem Acta. 2017;35(1):13-25. http://doi.org/10.4152/pea.201701013.
- Infante MR, Pérez L, Pinazo A, Clapés P, Morán MC, Angelet M, et al. Amino acid-based surfactants. C R Chim. 2004;7(6-7):583-92. http://doi.org/10.1016/j.crci.2004.02.009.
- Ashassi-Sorkhabi H, Ghasemi Z, Seifzadeh D. The inhibition effect of some amino acids towards the corrosion of aluminum in 1 M HCl + 1 M H 2 SO 4 solution. Appl Surf Sci. 2005;249(1-4):408-18. http://doi.org/10.1016/j.apsusc.2004.12.016.
- Kaya S, Tüzün B, Kaya C, Obot IB. Determination of corrosion inhibition effects of amino acids: quantum chemical and molecular dynamic simulation study. J Taiwan Inst Chem Eng. 2016;58:528-35. http://doi.org/10.1016/j.jtice.2015.06.009.
- Fu JJ, Li SN, Wang Y, Cao LH, Lu LD. Computational and electrochemical studies of some amino acid compounds as corrosion inhibitors for mild steel in hydrochloric acid solution. J Mater Sci. 2010;45:6255-65. http://doi.org/10.1007/s10853-010-4720-0.
- Singh P, Bhrara K, Singh G. Adsorption and kinetic studies of L-leucine as an inhibitor on mild steel in acidic media. Appl

Surf Sci. 2008;254(18):5927-35. http://doi.org/10.1016/j. apsusc.2008.03.154.

- Zhang QH, Li YY, Lei Y, Wang X, Liu HF, Zhang GA. Comparison of the synergistic inhibition mechanism of two eco-friendly amino acids combined corrosion inhibitors for carbon steel pipelines in oil and gas production. Appl Surf Sci. 2022;583:152559. http://doi.org/10.1016/j.apsusc.2022.152559.
- El-Baradie KY, El-Wakiel NA, El-Ghamry HA. Synthesis, characterization and corrosion inhibition in acid medium of 1 -histidine Schiff base complexes. Appl Organomet Chem. 2015;29(3):117-25. http://doi.org/10.1002/aoc.3255.
- Vasques RB, Levy MM, Rodrigues MS, Almeida FWQ No, Silva LP, et al. A theoretical and experimental study of phosphate ester inhibitors for AISI 1018 in carbon dioxide - saturated 3.5 wt % NaCl solution. Mater Corros. 2021;72(8):1417-32. http:// doi.org/10.1002/maco.202112365.
- Martin Britto Dhas SA, Natarajan S. Growth and characterization of two new NLO materials from the amino acid family: l-Histidine nitrate and l-Cysteine tartrate monohydrate. Opt Commun. 2008;281(3):457-62. http://doi.org/10.1016/j. optcom.2007.09.049.
- Pereira JEM. Análise térmica e Espectroscopia Raman à temperatura ambiente de cristais L-histidina. [Trabalho de Conclusão de Curso]. Fortaleza: Centro de Ciências, Universidade Federal do Ceará; 2012.
- Saxena A, Prasad D, Haldhar R. Investigation of corrosion inhibition effect and adsorption activities of Achyranthes aspera Extract for Mild Steel in 0.5 M H2SO4. J Fail Anal Prev. 2018;18(4):957-68. http://doi.org/10.1007/s11668-018-0491-8.
- Haldhar R, Jayprakash Raorane C, Mishra VK, Periyasamy T, Berisha A, Kim S-C. Development of different chain lengths ionic liquids as green corrosion inhibitors for oil and gas industries: experimental and theoretical investigations. J Mol Liq. 2023;372:121168. http://doi.org/10.1016/j. molliq.2022.121168.
- Solmaz R, Altunba E, Karda G. Adsorption and corrosion inhibition effect of 2-((5-mercapto-1,3,4- thiadiazol-2-ylimino)methyl)phenol Schiff base on mild steel. Mater Chem Phys. 2011;125(3):796-801. http://doi.org/10.1016/j.matchemphys.2010.09.056.
- Liang Y, Wang D, Wu Y, Lai Q, Xue L, Feng S. Perylenecontaining polysiloxane: an effective candidate for corrosion protection of iron surface. Appl Surf Sci. 2011;257(24):10576-80. http://doi.org/10.1016/j.apsusc.2011.07.053.
- Bonanos N, Steele BCH, Butler EP. Applications of impedance spectroscopy. In: Barsoukov E, Macdonald JR, editors. Impedance spectroscopy: theory, experiment, and applications. 2nd ed. New Jersey: John Wiley & Sons; 2005. p. 205-63. http://doi. org/10.1002/0471716243.ch4.
- Fouda AS, Ismail MA, Elewady GY, Abousalem AS. Evaluation of 4-amidinophenyl-2,2'-bithiophene and its aza-analogue as novel corrosion inhibitors for CS in acidic media: experimental and theoretical study. J Mol Liq. 2017;240:372-88. http://doi. org/10.1016/j.molliq.2017.05.089.
- Becke A D. Density-functional thermochemistry. I. The effect of the exchance-only gradient correction. Am Inst Phys. 1992;96:2155-60. https://doi.org/10.1063/1.462066.
- Lecklider T. Maintainng a heathy rhythm. EE Eval Eng. 2011;50(11):36-9.
- 32. Tomasi J, Cammi R. Remarks on the use of the apparent surface charges (asc) methods in solvation problems: iterative versus matrix-inversion procedures and renormalization of the apparent charges. J Comput Chem. 1995;16(12):1449-58. http://doi. org/10.1002/jcc.540161202.
- 33. Mennucci B, Cancès E, Tomasi J. Evaluation of solvent effects in isotropic and anisotropic dielectrics and in ionic solutions with a unified integral equation method: theoretical bases, computational implementation, and numerical applications. J Phys Chem B. 1997;101(49):10506-17. http://doi.org/10.1021/jp971959k.

- 34. Cancès E, Mennucci B, Tomasi J. A new integral equation formalism for the polarizable continuum model: theoretical background and applications to Isotropic and anisotropic dielectrics. J Chem Phys. 1997;107(8):3032-41. http://doi. org/10.1063/1.474659.
- Pearson RG. Physical and Inorganic Chemistry Hard and Soft Acids and Bases. J Am Chem Soc. 1963;85(C):353.
- Koopmans T. Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen Eines Atoms. Physica. 1934;1(1-6):104-13. http://doi.org/10.1016/S0031-8914(34)90011-2.
- Chermette H. Chemical reactivity indexes in density functional theory. J Comput Chem. 1999;20(1):129-54. http://doi. org/10.1002/(SICI)1096-987X(19990115)20:1<129::AID-JCC13>3.0.CO;2-A.
- Iczkowski RP, Margrave JL. Electronegativity. J Am Chem Soc. 1961;83(17):3547-51. http://doi.org/10.1021/ja01478a001.
- Pearson RG. Recent advances in the concept of hard and soft acids and bases. J Chem Educ. 1987;64(7):561-7. http://doi. org/10.1021/ed064p561.
- Janak JF. Proof that ∂E∂ni=ε in density-functional theory. Phys Rev B Condens Matter. 1978;18(12):7165-8. http://doi. org/10.1103/PhysRevB.18.7165.
- Von Szentpály L. Studies on electronegativity equalization. Part 1. Consistent diatomic partial charges. J Mol Struct THEOCHEM. 1991;233(C):71-81. http://doi.org/10.1016/0166-1280(91)85055-C.
- 42. Yang W, Parr RG. Hardness, softness, and the fukui function in the electronic theory of metals and catalysis. Proc Natl Acad Sci USA. 1985;82(20):6723-6. http://doi.org/10.1073/ pnas.82.20.6723. PMid:3863123.
- Parr RG, Szentpály LV, Liu S. Electrophilicity index. J Am Chem Soc. 1999;121(9):1922-4. http://doi.org/10.1021/ja983494x.
- Chattaraj PK, Sarkar U, Roy DR. Electrophilicity index. Chem Rev. 2006;106(6):2065-91. http://doi.org/10.1021/cr040109f. PMid:16771443.
- 45. Obot IB, Macdonald DD, Gasem ZM. Density functional theory (DFT) as a powerful tool for designing new organic corrosion inhibitors: Part 1: An overview. Corros Sci. 2015;99:1-30. http://doi.org/10.1016/j.corsci.2015.01.037.
- 46. Vinayagamoorthy R, Irudayaraj AA, Raj AD, Karthick S, Jayakumar G. Comparative study of properties of L-Histidine and L-Histidine nickel nitrate hexahydrate crystals grown by slow evaporation. Mech Mater Sci Eng J. 2017;9:1-7. http:// doi.org/10.2412/mmse.83.74.689.
- 47. Wu J, Wu J, Lu L, Mei P. Design, characteristics, and theoretical analyses of 8-hydroxyquinoline derivatives with different heteroatoms as effective corrosion inhibitors. Mater Chem Phys. 2023;304:127929. http://doi.org/10.1016/j. matchemphys.2023.127929.
- Alnajjar AO, El-lateef HMA, Khalaf MM, Mohamed IMA. Steel protection in acidified 3. 5% NaCl by novel hybrid composite of CoCrO 3 / polyaniline : chemical fabrication, physicochemical properties, and corrosion inhibition performance. Constr Build Mater. 2022;317:125918. http://doi.org/10.1016/j. conbuildmat.2021.125918.
- Kalantar MAAM. Thermal analysis on the Milled Al B2 O3 +Si+WO3 System to Synthesize Al2 O3 -WxSiy-WxBy Powders. Mater Res. 2020;23(1):1-9.

- Yin C, Kong M, Zhang J, Wang Y, Ma Q, Chen Q, et al. Influence of hydroxyl groups on the inhibitive corrosion of gemini surfactant for carbon steel. ACS Omega. 2020;5(6):2620-9. http://doi.org/10.1021/acsomega.9b02989. PMid:32095685.
- Khadom AA. Modeling of corrosion reaction data in inhibited acid environment using regressions and artificial neural networks. Korean J Chem Eng. 2013;30(12):2197-204. http:// doi.org/10.1007/s11814-013-0170-0.
- Abdulazeez I, Al-Hamouz OCS, Khaled M, Al-Saadi AA. Inhibition of mild steel corrosion in CO2 and H2S-saturated acidic media by a new polyurea-based material. Mater Corros. 2020;71(4):646-62. http://doi.org/10.1002/maco.201911270.
- Amin MA, Khaled KF, Mohsen Q, Arida HA. A study of the inhibition of iron corrosion in HCl solutions by some amino acids. Corros Sci. 2010;52(5):1684-95. http://doi.org/10.1016/j. corsci.2010.01.019.
- Barreto LS, Santos AM, de Almeida TF, Silva DR, Cotting F, Capelossi VR. Application of a mix of vegetables residues as inhibitor for carbon steel. Mater Res. 2020;25:e20200440. http://doi.org/10.1590/1980-5373-mr-2020-0440.
- Lin X, Liu W, Wu F, Xu C, Dou J, Lu M. Applied surface science effect of O2 on corrosion of 3Cr steel in high temperature and high pressure CO2-O2 environment. Appl Surf Sci. 2015;329:104-15. https://doi.org/10.1016/j.apsusc.2014.12.109.
- Farelas F, Galicia M, Brown B, Nesic S, Castaneda H. Evolution of dissolution processes at the interface of carbon steel corroding in a CO 2 environment studied by EIS. Corros Sci. 2010;52(2):509-17. http://doi.org/10.1016/j.corsci.2009.10.007.
- Furtado LB, Leoni GB, Nascimento RC, Santos PHC, Henrique FJFS, Guimarães MJOC, et al. Experimental and theoretical studies of tailor-made schiff bases as corrosion inhibitors for carbon steel in HCl. Mat Res. 2023;26:e20220398. https://doi. org/10.1590/1980-5373-MR-2022-0398.
- Rabizadeh T, Asl SK. Casein as a natural protein to inhibit the corrosion of mild steel in HCl solution. J Mol Liq. 2019;276:694-704. http://doi.org/10.1016/j.molliq.2018.11.162.
- Li H, Zhang S, Tan B, Qiang Y, Li W, Chen S, et al. Investigation of Losartan Potassium as an Eco-Friendly Corrosion Inhibitor for Copper in 0.5 M H2SO4. J Mol Liq. 2020;305:112789. http://doi.org/10.1016/j.molliq.2020.112789.
- Jafari H, Ameri E, Vakili MH, Berisha A. Novel Silicon-based schiff-base as corrosion inhibitor for anti-corrosion behavior of API 5L Grade B in 1M HCl. Mater Chem Phys. 2024;311:128499. http://doi.org/10.1016/j.matchemphys.2023.128499.
- Jafari H, Ameri E, Hassan Vakili M, Berisha A. Effect of OH position on adsorption behavior of Schiff-base derivatives in corrosion inhibition of carbon steel in 1 M HCl. Electrochem Commun. 2024;159:107653. http://doi.org/10.1016/j. elecom.2023.107653.
- Jafari H, Akbarzade K, Danaee I. Corrosion inhibition of carbon steel immersed in a 1 M HCl solution using benzothiazole derivatives. Arab J Chem. 2019;12(7):1387-94. http://doi. org/10.1016/j.arabjc.2014.11.018.
- Jafari H, Ameri E, Rezaeivala M, Berisha A. 4,4'-(((2,2-Dimethylpropane-1,3-Diyl)Bis(Azanediyl)Bis(Methylene)Bis(2-Methoxyphenol) as New Reduced Form of Schiff Base for Protecting API 5L Grade B in 1 M HCl. Arab J Sci Eng. 2023;48:7359-72. http:// doi.org/10.1007/s13369-022-07281-8.