The Theoretical Investigations and Molecular Dynamic Stimulation of Isoniazid as a Corrosion Inhibitor

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

API5L Steel is known as one of the most useful materials on earth which is also subject to corrosion in certain environments. Many methods have been used to minimize its corrosion, but the use of inhibitors is widely accepted. The use of green inhibitors has gained wide usage because of their environmental friendliness. The theoretical investigations of isoniazid as corrosion inhibitor was carried out using Fourier transform infrared spectroscopy (FTIR), whereas theoretically, quantum chemical parameters and molecular dynamic simulations of the inhibitor were studied. The analyses of the experimental results showed that the expired drug (isoniazid) decreased the corrosion rate of API5L steel in a 0.5M H_2SO_4 medium. The inhibition efficiency decreased with a decrease in inhibitor concentration. FTIR results showed that the inhibition mechanism is physical through the functional groups present in the expired drug. Relying on quantum chemical parameters and molecular dynamic simulations results, the adsorption/binding strength of the concerned inhibitor molecule on API5L steel surface follows a good order. The computed adsorption/binding energy values (Eads) for the various isolated concentrations from the inhibitor indicate the adsorption process to be non-covalent (physiosorption) which is in good agreement with the literature.

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1. INTRODUCTION

Corrosion of metals is a fundamental academic and industrial concern that has received a considerable amount of attention. Acid solutions are generally used for the removal of rust and scale in several industrial processes [1]. The API- 5L- X65 steel is a high-strength low-alloy (HSLA) steel that is mostly used as a construction material for pipelines, pumps, off-shore rigs, tanks, agitators [2,3]. The low cost of API- 5L -X-65 steel relative to the higher-performing steels grade is among the reasons, while it is utilized in several applications. In the industrial sector, a major challenge is usually faced by pipeline steels, where they are affected by corrosion consequent to their exposure to a corrosive environment, such as HCl [4]. The existence of high concentrations of corrosive agents such as CO_2, H_2S, and Cl^- in acidic gas exploration fields, along with the high pressure of the gas being transported and high gas flushing velocity, place natural gas pipelines at risk for corrosion [5-8].

Organic inhibitors have been reported to be relatively eco-friendly, non-toxic, readily available, and sustainable. Their ability to resist decomposition with time as compared to most of the green inhibitors is among the reason why they are the most effective and efficient types of inhibitors. These inhibitor molecules have heterocyclic compounds with polar functional groups (e.g., Nitrogen, Sulfur, Oxygen, and Phosphorus) and/or conjugated double bonds with different aromatic systems [2]. Metals are usually protected by inhibitors when the inhibitors adsorb themselves to the substrate and then form a passive layer, thus protecting the metal [9]. Inorganic inhibitors have been put to use in many industrial processes for corrosion protection, but due to some reasons, such as cost, toxicity, preference is given to organic inhibitors [10,11,12,2]. Also, there are organic green inhibitors (natural products), but they are yet to be produced at commercial level. The use of plant extract as corrosion inhibitors has been in existence for a long time and several types of research have been conducted. Green inhibitors from plant extract have been reported to display high inhibition efficiency levels in addition to their low cost and availability [13]. However, the debate is that the plant kingdom is likely to diminish slowly if plant materials are used as corrosion inhibitors that are metals will be offered protection at the detriment of the plant kingdom. Furthermore, the problem of using some plant inhibitors is their instability that is they are readily biodegradable [2]. The use of TMT and IMI as corrosion inhibitors has been widely studied and the result has revealed that they offer good protection for steel in water [2].

Generally, corrosion inhibition is performed by adsorption of molecules on the metal-solution interface [14,15]. Molecular structure determines the efficiency of corrosion inhibitors. Through the decades, distinctive techniques for corrosion reduction or prevention had been reported by many scientists and engineers [16]. Some Quantum chemical parameters such as E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), the energy gap (ΔE), hardness (η), Softness (S), dipole moment (μ), electron affinity (EA), ionization potential (IE), the absolute electronegativity (χ), electrophilicity index (ω) and the fraction of electron transferred (ΔN) using B3LYP/6-31G(d,p) basis set, can be calculated [17]. The corrosion inhibition characteristics of two vinyl imidazole derivatives on mild were studied using Density Function Theory (DFT), and it was affirmed that the ability to inhibit the corrosion process could be established [17].

In this present research, the corrosion behavior of API5L X65 steel in 0.5M H_2SO_4 containing various concentrations of isoniazid corrosion inhibitor was studied.

2. MATERIALS AND METHODS

2.1 Preparation of Steel Samples

The steel samples were cut into test coupons - dimension of length 2 cm x 2 cm x 0.78 cm using a shear cutter. The dimensions were measured using Digital Vernier Caliper. Each coupon was polished on a grinding machine mounted with silicon carbide (SiC) emery paper of grit size between 60 and 1200. This was done to obtain a mirror-like surface suitable for the polarization test. Table 1 displays the chemical composition of the tested steel.

2.2 Preparation of Reagents

Analytical chemicals, such as isoniazid, H_2SO_4, and Distilled water were obtained. Thereafter, 0.5

M concentration of H_2SO_4 environments were prepared using H_2SO_4 and distilled water. Various grams of 0.2, 0.4, 0.6, and 0.8 g of the prepared inhibitor were introduced into different plastic beakers containing 150 ml of the prepared H_2SO_4.

2.3 Surface Analysis

The surface morphology of the API steels consequent to the reaction of the environment with the steel's surface was analyzed with optical microscopy. The API5L-X65 steel immersed in 0.5M H_2SO_4 for 1,200 seconds from the electrochemical test at normal conditions was used for the study. Sample in the absence of inhibitor (considered as blank or control) and those exposed at optimum grams of the inhibitor were subjected to optical microscopic analysis.

2.4 Scanning electron microscope (SEM)

The microstructure of the steel was examined before and after exposure to the corroding media by a Joel-JSM 7600F scanning electron microscope (SEM) as presented in Plate 1.

2.5 Fourier Transform Infrared (FT-IR) Analysis

FTIR Instrument of model: Cary 630 FTIR Spectrophotometer (Agilent Technologies) was used to identify the major functional groups present in Isoniazid and corrosion product of inhibited API5L steel in 0.5M H_2S0_4 solution. Each coupon was separately dipped in 100 mL of 0.5M H_2SO_4 of acid-inhibitor concentration respectively for 10 days after which they were removed, then taken for analysis. The analysis was done by scanning the sample through a wave number range of 399.278160 – 4000.497120 cm^{-1}[18].

3. RESULTS AND DISCUSSION

3.1 Chemical Composition

The elemental composition of the API-5L-X65 steel used for this research is shown in Table 1.

Table 1 represents the elemental composition of the as-received API5L steel used for the research. It is observed that the steel is deficient in sufficient alloy components required to resist corrosion tendencies, like Chromium and Nickel. The percentage carbon composition is 0.13%, which belongs to the class of low carbon steel and that makes it to be ductile and malleable. However, the amount of alloying elements content is less than 2%, which makes it plain carbon steel. Therefore, it is vulnerable to corrosion in a chloride environment [19,2].

3.2 Scanning Electron Microscopy Evaluation

Plate 1 (a-c) displays the micrograph of the API5L-X65 steel before immersion and after immersion in a 0.5M H_2SO_4 environment with and without inhibitor (isoniazid). Plate 1a is displaying the morphology of the API5L-X65 steel sample, which has not been immersed into the corrosive environment. Hence, it is as received without any formation of corrosion product on the surface. It is observed from the micrograph in plate 1(b and c) that there was a formation of a non-tenacious corrosion product on the control sample surface after immersion in 0.5M H_2SO_4 environment with inhibitor (isoniazid). The non-tenacious corrosion product formed as a result of the reaction of the steel with the aggressive environment. Thus, increasing the rate at which the steel corrodes [20]. Plate 1b represents the micrograph of the API steel immersed in the 0.5M H_2SO_4 environment, containing 0.8 g of inhibitor. It was observed that the inhibitor adsorbed and was uniformly dispersed on the steel surface, thereby acting as a protective barrier between the steel surface and the corrosive environment. This led to a reduction in the corrosion rate of the steel.
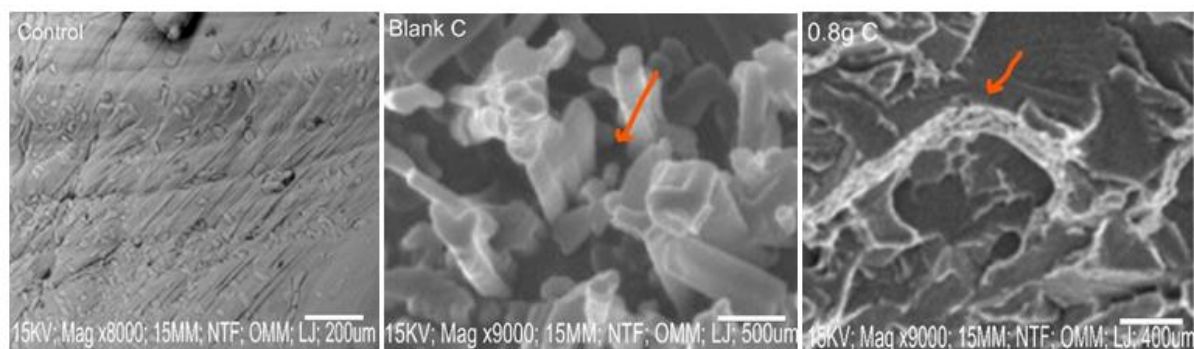
3.2.1 Fourier transform infrared spectroscopy (FTIR)

The functional groups present within the adsorption film that results during the adsorption process were investigated using the FTIR technique. The FTIR spectra of the studied isoniazid and API5L Steel surfaces after corrosion with and without inhibitor are shown in Fig. 1a -1b, FTIR spectra recorded for the corroded environment are depicted in Fig. 1a. An absorption peak at 3454.62, 3385.18 cm−1 is assigned for linked -OH groups [21].

The peak at 1622.19, 1548.89 cm−1 are attributed to the stretching vibration of C=O groups. Peaks at 1504.53 cm−1 correspond to asymmetric stretching of N=O, 1410.01-1346.36 cm−1 are attributed to the alkane bending of C–H groups. The stretching mode of the C–N group was confirmed by the peaks present at the wavenumbers 1201.69, 1122.61, and 999.16 cm−1, all these were absent in Fig. 1b (which is the undissolved inhibitor in 0.5M of H_2SO_4).

Table 1. Elemental composition of API5L steel

Element	C	Mn	Si	Cu	P	S	Cr	Ni	Fe
Metal (wt %)	0.13	1.35	0.25	0.012	0.02	0.002	0.024	0.014	Bal.

(a) (b) (c)

Plate 1 (a-c). Scanning electron micrographs of API5L Steel samples before and after immersion in 0.5M H_2SO_4 Environment with and without inhibitor (isoniazid), Plate a, b, and c respectively
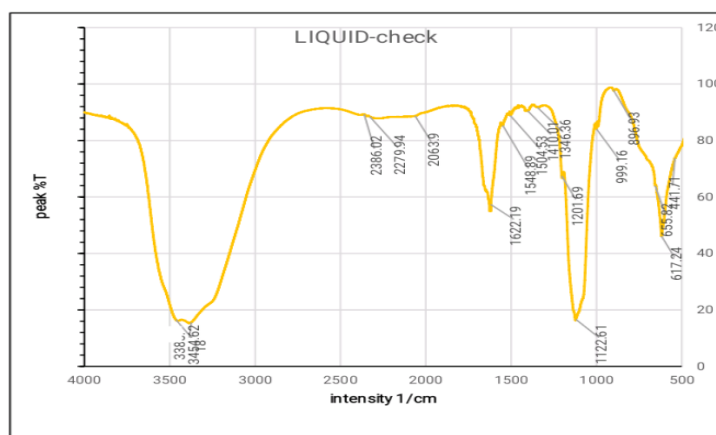

Fig. 1a. Fourier transform infrared spectroscopy (FTIR)

Fig. 1b. Fourier transform infrared spectroscopy (FTIR)

On the other hand, in Fig. 1a, C–N stretch at 873.78, 844.85, 578.66, 503.44, 675.11, 1141.9, and 748.41 cm⁻1 were absent, suggesting that these bonds were used for the adsorption of the inhibitor onto the surface of the API5L Steel [21].

3.2.2 Quantum chemical calculations

Fig. 2(a - b) shows the optimized structure, total electron density, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) of Isoniazid compounds utilized in this study. The regions of high HOMO density are the sites at which electrophilic attack and represent the active centers, with the utmost ability to bond to the metal surface, whereas the LUMO orbital can accept the electrons in the p-orbital of the metal using antibonding orbitals to form feedback bonds from the API5L steel [22].

The fraction of electron transferred was found to be 6.500 Ev. It was reported that if ΔN is less than 3.6, inhibition efficiency increases with increasing values of the electron-donating ability of the molecules, while values of fraction electron (ΔN) greater than 3.6 indicate a decrease in inhibition efficiency with an increase in the electron-donating ability of the inhibitor. The earlier case is found to apply to all the studied molecules since their ΔN values are all less than 3.6 [23].

3.2.3 Molecular dynamics (MD) simulation

The optimized structure of the inhibitor molecule was used for the simulation. Adsorption of a single molecule of the chemical from isoniazid sourced from literature onto the Fe (110) surface provides access to the adsorption energetics and its effect on the inhibition efficiency of the molecule. Thus, the adsorption energy, Eads, between each chemical molecule of Isoniazid obtained from literature compound molecule and Fe (110) surface was calculated using equation 16 [24].
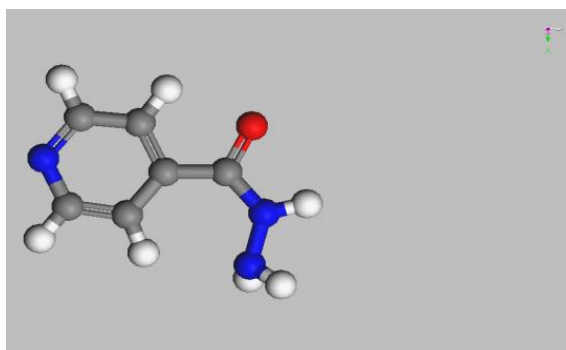

Fig. 2a. Electronic properties of Isoniazid: Optimized Molecule of Isoniazid. (atom legend: white H, light gray C and dark gray O). The isosurfaces (larger lobes) depict the electron density difference; the darker regions show electron accumulation, whereas the lighter regions show electron loss [21]
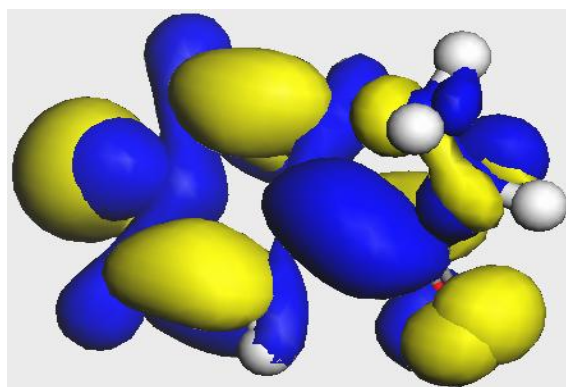

Fig. 2b. Electronic properties of Isoniazid: Structure indicating the HOMO and LUMO (Frontier Molecular Orbital (FMOs))

Table 2. Computed quantum chemical parameters (Electronic and Structural) of the studied inhibitor molecules

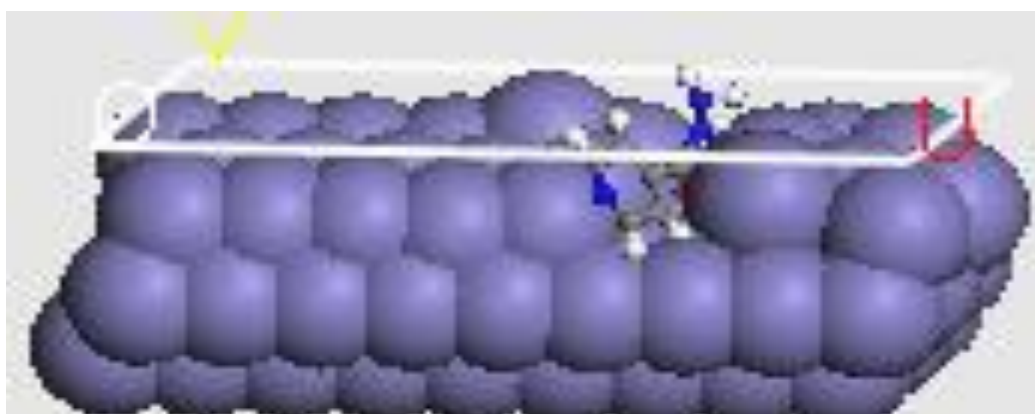| Quantum parameters	Isoniazid molecule
E_{HOMO} (eV)	-6.500Ev
E_{LUMO} (eV)	-1.060Ev
Energy gap, ΔE (eV)	7.560Ev
Binding energy	-19598.005553 kcal/mol
Ionization potential, I (eV)	6.500Ev
Electron affinity, A (eV)	1.060Ev
Electronegativity, χ inhib(eV)	1.28 Ev
Electronegativity χ of Fe	1.83
Absolute(Global) hardness, η	2.72 Ev
Global softness (σ)	0.3677 eV
Electron transfer (ΔN)	-0.01011
Global electrophilicity index (ω)	0.30118
The initial molecule-metal interaction energy ($\Delta \psi$)	0.00278
HOMO	36
LUMO	37

Fig. 3. Molecular dynamic stimulation

Table 3. Calculated adsorption parameters for the Interaction of the studied molecules with the Fe (110) surface using material studio

Parameters/ Molecules	Isoniazid
Total Potential Energy (kcal/mol)	-1575.603683 kcal/mol
Energy of Molecule (kcal/mol)	-313253.4986kcal/mol
Energy of Fe (110) Surface (kcal/mol)	0.000
Adsorption Energy (kcal/mol)	-19598.005553 kcal/mol

$$E_{ads} = E_{total} - (E_{mol} - E_{Fe}) \qquad (1)$$

Where E_{mol}, E_{Fe}, and E_{total} correspond to the total energies of the molecule, Fe (110) slab, and the adsorbed Mol/ Fe (110) couple in a gas phase.

4. CONCLUSION

1. This study has revealed that extracts of isoniazid effectively inhibit API5L steel corrosion in 0.5 M H_2SO_4. The result of

Fourier transforms infrared spectroscopy (FTIR) indicated that the corrosion reaction was inhibited by the adsorption of the phytochemicals onto the corroding API5L steel metal surface. The E_{HOMO} (-6.500Ev) and E_{LUMO} (-1.060Ev), Energy gap, (ΔE= 7.560 eV) are parts of other related molecular and thermodynamic properties which portrait good corrosion inhibition efficiency of the inhibitor on the API5L steel surface.

2. Since electron transfer (ΔN = -0.01011) is less than 3.6, the inhibition efficiency was found to increase with increasing values of the electron-donating ability of the inhibitor. The magnitude of the obtained adsorption energy from Density Functional Theory (DFT) which is -19598.005553 kcal/Mol confirms strong physiosorption of the molecules onto the API5L Steel surface.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

CONSENT AND ETHICAL APPROVAL

It is not applicable.

ACKNOWLEDGEMENTS

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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