

Review

Review on the Recent Development of Fatty Hydrazide as Corrosion Inhibitor in Acidic Medium: Experimental and Theoretical Approaches

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Abstract: In recent years, numerous research work has been conducted in order to find the most practical and cost-effective solution for corrosion issues in the oil and gas industry. Several studies have revealed that fatty hydrazide derivatives are the most suitable corrosion inhibitor for the application in the said industry. These compounds can also act as effective corrosion inhibitors in acidic medium with inhibition efficiency greater than 95%. This review summarizes and discusses the recent corrosion inhibitor development in acidic media from 2017 until 2021, focusing on fatty hydrazide derivatives. The significant findings and mechanisms of inhibition have been elucidated. In addition, intake on the computer simulation studies of fatty hydrazide inhibition properties is also included in this review. Finally, some suggestions for future research on corrosion inhibitors have been recommended.

Keywords: corrosion inhibitors; fatty hydrazide derivatives; mild steel; acidic medium; computational simulation



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1. Introduction

Corrosion has become one of the most protracted problems in the oil and gas industries. Corrosion is encountered in all production and transportation facilities and has become a potential natural hazard to the industry [1]. The presence of contaminants causes severe corrosion in the inner wall of pipelines. Continuous effects of corrosion can reduce the thickness of the walls, reducing the strength of pipelines, and lead to leakage accidents [2]. The price of failure due to internal corrosion is enormous in terms of direct costs, such as repair/replacement and lost production, and indirect costs, such as environmental and impact on the downstream industries [3]. A report released by NACE International in 2016 estimated that the global cost of corrosion to be approximately USD 2.5 trillion, excluding the cost of corrosion failure consequences on the safety and the environment. However, the report also stated that these damage costs could be reduced to 15% and 35% by implementing excellent control and management practice, respectively [4].

Mild steel is the most economical construction material used in pipelines for the oil and gas industry. Although many corrosion-resistance alloys have been introduced, mild steel is still the best choice in terms of economic perspective [3]. Corrosion in the oil and gas pipelines occurs when steel comes in contact with an aqueous environment, mainly water. Though, studies show that early stages of crude oil production from a newly discovered field are usually dry with no water formation or low water cuts. Unfortunately, as oil and gas fields mature, the amount of produced water increases naturally or due to recovery processes, and so does damage due to corrosion attacks. Nowadays, reservoirs

produce various amounts of water, CO₂, H₂S, and other high-impurity products, which are inherently corrosive. These characteristics can change from one reservoir to the next and can change from one reservoir segment to another. Besides, the combination of high-water cuts, salts, acidity, temperature, and pressure pose more additional problems and eventually lead to more corrosive conditions in pipelines [4]. Therefore, corrosion management strategies primarily in pipeline applications have become more challenging in modern days.

Over the years, there has been rapid progress in the scientific exploration of corrosion mitigation strategies. One of the most practical and cost-effective method for corrosion control in the oil and gas industry is the use of corrosion inhibitors. Corrosion inhibitors can protect the surface of metals and retard corrosion action when added to the corrosive environment, even in small concentrations [5].

2. Selection and Mechanism of Corrosion Inhibitors

Industrially, it has been established that corrosion inhibitors are the most cost-effective solution in managing corrosion in the oil and gas pipeline systems [3]. Normally, corrosion inhibitors are added continuously or intermittently in small amounts to the corrosive medium to provide the required control against corrosion in the production system. In addition, it is proven that a small amount of corrosion inhibitor can drastically reduce the corrosion rate when added into the corroding medium such as metal steel [6]. Inhibitors protect the surface of metals used in oil and gas industries from corrosion, including temporary protection during storage and transport, either by merging with them or reacting with the impurities in the environment that may cause pollution. Therefore, many studies have proved that corrosion inhibitor is an effective method in mitigating corrosion and reducing the corrosion rates to acceptable limits [7].

Generally, corrosion inhibition occurs on the metal surface via adsorption. However, the reaction mechanism of inhibitors can also be classified as adsorption, passivation, film precipitation, and elimination of oxygen. Therefore, even if corrosion inhibition generally occurs by adsorption, it is not the only possible mechanism. The adsorption activities of inhibitors depend on the physicochemical properties of metal, inhibitor, and the medium involved. There are three types of adsorptions, known as physisorption, chemisorption, or both [6]. Physisorption refers to the electrostatic force attraction between inhibitor and metal surface. This interaction occurred due to the presence of electrically charged metal and inhibitor molecules in the medium, during which corrosion occurred. This interaction resulted in a weaker type of adsorption than the other [8]. Meanwhile, chemisorption occurs due to the sharing or transferring of electrons between metal and the inhibitor molecules, resulting in the formation of coordinate bonds [9]. Olajire et al. [10] stated that the most effective inhibitors are those that have the ability to absorb chemically (chemisorption) into the metallic substrate and form a protective film on the metal surface.

Corrosion inhibitors can be further classified depending on their mode of action, such as anodic, cathodic, and mixed type. Anodic inhibitors control the anodic reaction by forming a protective layer or barrier of oxide film on the metal surface, causing resistance to corrosion, thereby reducing the corrosion rate. This inhibitor type also alters the anodic reaction in a chemical cell by increasing the potential of the anode, thus slowing down the corrosion reaction. Meanwhile, cathodic inhibitors reduce corrosion by slowing down the reduction rate of the electrochemical corrosion cell. This is performed by blocking the cathodic sites by precipitation. Finally, mixed inhibitors retard both the anodic and cathodic processes by adsorbing on the metal surface to form a protective film that causes the formation of precipitates on the surface, indirectly blocking both anodic and cathodic sites. Therefore, mixed inhibitors have more advantages because they can control both the cathodic and anodic corrosion reactions [11–13].

The chemistry of corrosion inhibitors varies, with some molecular structures being more effective than others in different physical and chemical environments. For example, some are more effective at restricting corrosion caused by CO₂, while others are for corrosion from H₂S. In addition, each inhibitor reacts differently to temporal and spatial changes

in conditions, such as temperature, pH, salinity, and solids in the fluid [14]. In addition, the corrosion control system for each inhibitor will also vary with different fluid compositions, production rates, environmental conditions, and flow regimes. Because of that, corrosion inhibitors are not selected in the same way for different production methods [3,4].

Hence, few factors need to be considered in order to select the most suitable corrosion inhibitors for each operating system. These include the cost, availability, and the effect on the environment and its species [15]. Furthermore, some requirements need to be fulfilled for inhibitors to meet the competitive requirements of the industry. Some of the requirements are the pour point in which the inhibitors must be below $-30\text{ }^{\circ}\text{C}$ (optimal) so that it can remain in liquid form for storage. The solubility and dispersion properties of inhibitors must be based on the purpose of the inhibitors. Additionally, the corrosion inhibitors must have a low emulsion tendency to avoid secondary problems during the application. Lastly, laboratory tests should be conducted to evaluate the performance of the inhibitors before purchasing and usage in the operating well [16].

3. Organic Corrosion Inhibitors

Generally, organic inhibitors contain heteroatoms such as O, N, and S, heterocycles, phenyl rings, π -bonds, hyperconjugations, and polar functional groups [17]. Some of the examples of organics inhibitors are alcohol, amine, amides, amine salts, carboxylates, ethers, heterocyclic nitrogen, hydrazides, phosphate, polymers, sulfonates, and others with polar groups nature [18]. These functionalities act as the active center for adsorption and allow the organic inhibitors to be adsorbed on the metal surface by displacing the water molecule on the surface, forming a thin film, which reduces the metal dissolution and provides protection to the metal. In addition, the availability of non-bonded (lone pair) and π -electron in organic inhibitor typically help facilitate electron transfer from inhibitor molecule to the metal, forming a coordinate covalent bond involving electron transfer from inhibitors to the metal surface [15]. The adsorption of organic corrosion inhibitors can occur in the form of physical, chemical, or mixed type depending on the nature of organic molecules, metal surface, the chemical composition of corrosive medium, and the solution temperature [19]. In fact, the efficiency of organic inhibitors largely depends on the nature of the medium, metal surface state, and the structure of inhibitors [20]. Some factors contribute to the action of organic inhibitors, including the chain length, size of the molecule, bonding, aromatic/conjugate, strength of bonding to the substrate, cross-linking ability, and solubility in the environment [15]. Among the alternative corrosion inhibitors, organic inhibitors are considered an excellent choice for controlling and mitigating corrosion due to their superior inhibition capabilities in acidic and neutral mediums [21]. Moreover, it is known to be more effective than inorganic corrosion inhibitors for the protection of steel in acidic media [1]. A study by Kadhum et al. [22] in 2021 revealed that considerable improvements in corrosion resistance of up to 80% were observed when using organic compounds as corrosion inhibitors. Recent review studies by Reza et al. [23] and Yang [24] also discussed various types of organic corrosion inhibitors for mild steel application, which show excellent performance up to 90% in the acidic environment. Other beneficial properties of organic compounds include high inhibition effectiveness, cost-effectivity, ease of application and synthesis, and being more environmentally friendly than inorganic compounds [25,26].

4. Fatty Hydrazides Derivatives as Effective Corrosion Inhibitors

Recently, many researchers have reported that nitrogen-containing compounds such as fatty hydrazide and its derivatives demonstrated to be effective inhibitors for metal corrosion in acidic mediums. Their versatile molecular structure containing electron-donating groups, heteroatoms, π -electrons, and lone pair increases their ability to mitigate corrosion in an acidic medium [27]. Besides, the presence of heteroatoms acts as the active adsorption site to form a protection layer on the metal surface and facilitates more donor-acceptor interaction with the inhibitor's molecules [28]. Moreover, it is proven that these nitrogen-

containing compounds, such as fatty hydrazide, are more environmentally friendly and possess biodegradable characteristics. Furthermore, many studies on corrosion inhibitors have found that hydrazides of fatty acids are more efficient inhibitors than cyclic amines, hydrazides, and aromatic amines [29]. Moreover, hydrazide derivatives are well known for their effectiveness as anticancer, antibacterial, anti-inflammatory, analgesic, and antioxidant properties [27,30]. Numerous studies have been conducted using fatty hydrazides as corrosion inhibitors in the past years. Most of the studies focus on the application of metal steel in a 1.0 M HCl solution. It can be concluded that almost all adsorption isotherms of these inhibitors followed Langmuir and mixed-type inhibitors, with efficiency ranging from 71% to 97%. Kumar Singh et al. [31] investigated the influence and inhibition effects of two new hydrazide derivatives, namely N'-(thiophene-2-ylmethylene) nicotinic hydrazone (TNH) and N'-(pyrrol-2-ylmethylene) nicotinic hydrazone (PNH) for the application in 1.0 M HCl of mild steel using electrochemical, weight loss, field emission-scanning electron microscope (FESEM), atomic force microscope (AFM), and quantum chemical calculation methods. Their results showed that both compounds were good inhibitors, and the inhibition efficiency was reported to increase with concentration. Comparing both compounds, PNH had better efficiency than TNH due to the presence of pyrrole rings in the structure. The adsorption process of TNH and PNH both obeyed the Langmuir adsorption isotherm showing both physisorption and chemisorption onto the mild steel surface.

In 2018, a continuous study by Kumar Singh et al. [32] reported two new hydrazide derivatives namely N'-(4-Hydroxybenzylidene) nicotinic hydrazone (HBNH) and N'-(4-methylbenzylidene) nicotinic hydrazone (MBNH) for mild steel in 1.0 M HCl. The same analysis method was used as previously, including electrochemical, weight loss, FESEM, AFM, quantum chemical calculation, and molecular dynamics simulation methods. Findings indicated that both inhibitors showed good inhibition efficiency, with MBNH being higher than HBNH. Besides, the inhibition efficiency was found to increase with increasing concentrations. Moreover, the polarization proved that both inhibitors suppress anodic and cathodic reactions acting as mixed type inhibitors that obeys Langmuir adsorption isotherm.

Chaitra et al. [33], in 2018 evaluated the inhibition effect of newly synthesized heterocyclic aromatic compounds, 3-(cyano-dimethyl-methyl)-benzoic acid thiophen-2-ylmethylenehydrazide (CBTH) and 3-(cyano-dimethyl-methyl)-benzoic acid furan-2-ylmethylenehydrazide (CBFH) using gravimetric, electrochemical, and morphological techniques, correlated with the quantum chemical for mild steel corrosion in HCl acidic medium. The study revealed that both inhibitors showed the highest inhibition efficiency of 87.1% and 85.3% at optimized concentration of 2.0 mM. It is also revealed that both inhibitors followed Langmuir isotherm, acting as cathodic and anodic inhibitors. Overall, the synthesized hydrazone derivatives showed good inhibition properties against mild steels corrosion in 0.5 M HCl medium.

The inhibition efficiency of two newly synthesized sulfonohydrazide derivatives, namely N'-{(E)-[4-(dimethylamino) phenyl] methylidene} benzenesulfonohydrazide (MBSH), and N'-{(E)-[4-(dimethylamino) phenyl] methylidene}-4-methylbenzenesulfonohydrazide (MpTSH) for XC38 carbon steel in 1.0 M HCl was studied by Ichchou et al. [34] using electrochemical measurements and theoretical calculations. Figure 1 shown the synthesis pathway of the new sulfonohydrazides corrosion inhibitors.

Both inhibitors were found to be good corrosion inhibitors for carbon steel applications in HCl solution with maximum efficiency of 93.1% and 90.7% for MpTSH and MBSH, respectively. MpTSH showed better performance due to higher values of E_{HOMO} , electron affinity, softness, electrophilicity, number of electrons transferred and lower values of ET, energy gap, E_{LUMO} , ionization energy, electronegativity, dipole moment, and hardness, compared to MBSH. All in all, both inhibitors displayed a mixed type behavior that followed Langmuir adsorption isotherm. Moreover, their inhibition efficiency increased with their concentration but decreased with increasing temperature.

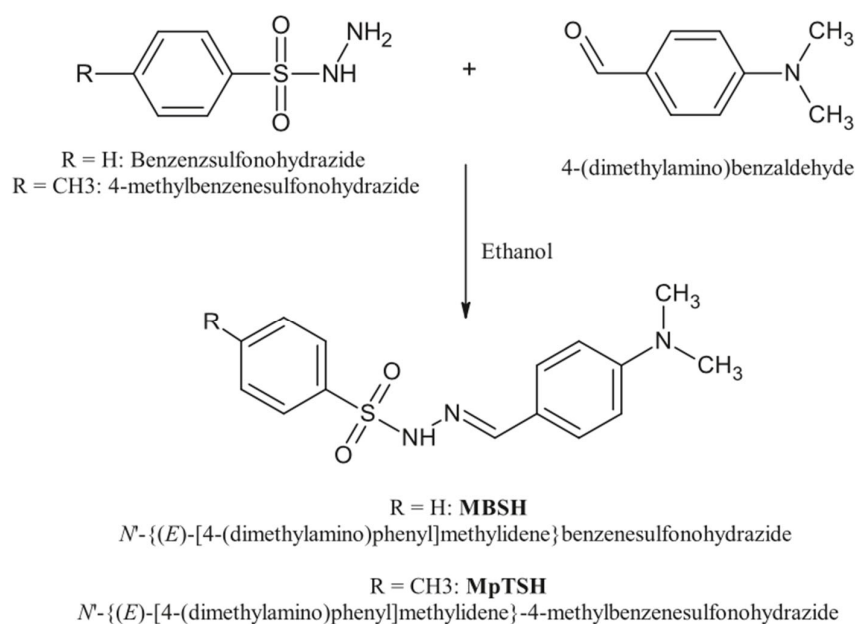


Figure 1. The synthetic pathways of the newly synthesized MBSH and MpTSH corrosion inhibitors (Ichchou et al., 2019). Reproduced with permission from [34].

Arshad et al. [35] synthesized hydrazide derivatives; PA1 {(E)-N'-(4'-Hydroxy-3-methoxybenzylidene) isonicotino hydrazide}, PA2 {(E)-N'-(Pyridin-4'-ylmethylene) isonicotino hydrazide}, and PA3 {(E)-N'-(Pyridin-3'-ylmethylene) isonicotino hydrazide} for corrosion protection activities on mild steel in 1.0 M HCl using experimental, theoretical, and surface analysis. The study revealed that PA1 had the highest potential as a corrosion inhibitor with an inhibition efficiency of 90–95% among the synthesized compounds. The SEM surface analysis on the MS electrode surface in the absence and presence of PA1 revealed that in the presence of PA1, the surface appeared smooth compared to without PA1. This is because the PA1 adsorbed film has formed on the MS surface and protects the surface from corrosion. It is also shown in the thermodynamic and kinetic parameters that PA1 had the strongest adsorption of parallel alignment than the others on the surface of metal steel. Meanwhile, the parametric analysis showed chemisorption nature of interaction that further supported the experimental results.

In another study, Mohd et al. [36] described the corrosion inhibitor study of N-cinnamalidene palmitohydrazide (CPH) on mild steel in 1.0 M HCl solution via Tafel polarization, electrochemical impedance spectroscopy, and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX). In this study, the reported corrosion inhibitor showed a maximum inhibition efficiency of 95% at 200 mg L^{−1}. Furthermore, the inhibition efficiency of CPH increased with increasing inhibitor concentration and temperature, and the adsorption obeyed Langmuir adsorption isotherm. The Tafel polarization study also revealed that CPH functions as a mixed type inhibitor with a predominant anodic control. Moreover, the impedance spectroscopy analysis showed that a charge transfer process mainly controlled the corrosion of mild steel in HCl solution by forming a protective film on the metal-solution interface.

Basiony et al. [37] synthesized a new cationic Gemini surfactant from hydrazide derivative, namely N,N'-((ethane-1,2-diylbis(oxy))bis(2-oxoethane-2,1-diyl))bis(N,N-dimethyl-4-((E)-(2-((E)-octadec-9-enoyl)hydrazineylidene)methyl)benzenaminium) dichloride and investigated its corrosion inhibition ability using various spectroscopy analysis. The results showed that the synthesized inhibitor exhibited a maximum efficiency of 94% at 1.0 mM. However, the efficiency decreased to 64% with increasing temperature. The inhibitor acted as a mixed type inhibitor while following the Freundlich isotherm model. Finally, the

enrichment of GI-surfactant with the centers of high electron density increased the charge transfer resistance (R_{ct}) of X-65 steel and dropped the corrosion rate.

The inhibition performance of two synthesized hydrazone propanehydrazide (HYD-1) and N-cyclohexylidene-2-(6-methoxynaphthalen-2-yl) propanehydrazide (HYD-2) on mild steel in aggressive acidic medium was investigated by Chaouiki et al. [38] using weight loss measurements, electrochemical techniques, and scanning electron microscope coupled with energy-dispersive X-ray spectroscopy (SEM-EDX). This study revealed that both hydrazone derivatives, HYD-1 and HYD-2, exhibited a high inhibition performance of 96% and 84%, respectively, at an optimal concentration of 50 mM. In addition, both inhibitors displayed the combination of chemisorption and physisorption and obeyed the Langmuir isotherm model. The inhibition efficiency also started to increase with their concentrations. HYD-1 showed better performances than HYD-2 due to its functional properties such as molecular size and electron-donating groups. Furthermore, the study on SEM revealed that the surface of metal steel in the presence of HYD-1 shows a smoother surface than the surface with the absence of HYD-1 (Figure 2).

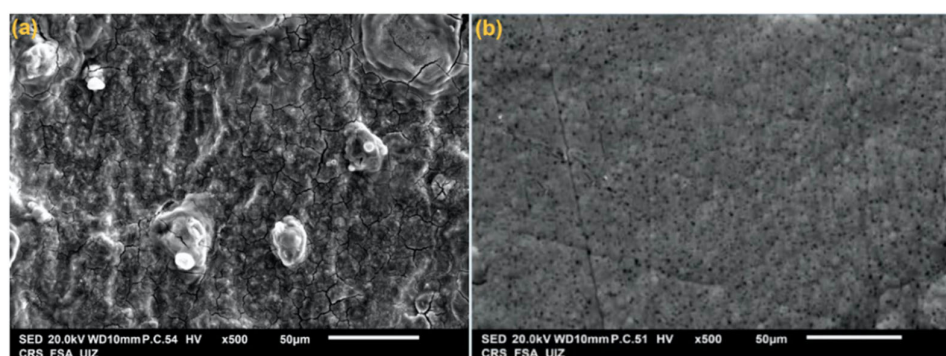


Figure 2. SEM photograph of mild steel specimen in the (a) absence and (b) presence of HYD-1 corrosion inhibitor (Chaouiki et al., 2020) [38].

Abdel Hameed et al. [39] tested five new sulfur-containing heterocyclic derivatives of sulfanyl pyridazine type compounds namely, (6-phenyl-pyridazin-3-ylsulfanyl)-acetic acid (1), (6-phenyl-pyridazin-3-ylsulfanyl)-acetic acid hydrazide (2), (6-Phenyl-pyridazin-3-ylsulfanyl)-acetic acid (2,4-dihydroxy-benzylidene)-hydrazide (3), (6-Phenyl-pyridazin-3-ylsulfanyl)-acetic acid (2-hydroxy-naphthalen-1-ylmethylene)-hydrazide compound (4), and (6-Phenyl-pyridazin-3-ylsulfanyl)-acetic acid (4-dimethylamino-benzylidene)-hydrazide (5), for the application of carbon steel in 1.0 M HCl at various concentrations and temperatures. The study was conducted using gravimetric, gasometric, atomic absorption spectroscopy (AAS), thermometric, and acidimetric techniques. Results showed that corrosion inhibition efficiency increased with increasing inhibitors concentration with compound 3 having the highest inhibition efficiency (93%) due to chelation with the steel metal surface. The order of inhibition efficiency increased as followed: $C1 < C2 < C4 < C5 < C3$. The inhibition was found to be physicochemical adsorption while the adsorption obeyed the Langmuir isotherm.

A study by Preethi Kumari et al. [40] reported the corrosion inhibitor, namely N'-[(4-methyl-1H-imidazole-5-yl) methylidene]-2-(naphthalen-2-yloxy) acetohydrazide (IMNH), and its anticorrosion behavior on mild steel in 1.0 M HCl medium via potentiodynamic polarization and electrochemical impedance spectroscopy techniques. IMNH showed good anticorrosion activity compared with other reported hydrazide derivatives by adsorbing onto the surface, forming a protective barrier predominantly through chemisorption. Besides, the inhibition efficiency of IMNH was found to increase with temperature and concentrations. Moreover, it was confirmed that the synthesized molecule acts as a mixed type, obeying Langmuir adsorption isotherm. Furthermore, the scanning electron microscopy (SEM), atomic force microscopy (AFM), and energy-dispersive X-ray spectroscopy (EDX) studies confirmed the formation of a protective film on the mild steel surface.

Shetty et al. [41] evaluated the anticorrosion performance of 4-hydroxy-N'-[3-phenylprop-2-en-1-ylidene] benzo- hydrazide (HBH) on 6061 Al-15%(v) SiC(P) composite (Al-CM) in 0.5 M HCl media. Overall, their study concluded that the new HBH compound can be a good potential inhibitor for corrosion control. The inhibition efficiency of HBH was found to increase with increased concentration and decrease with increased temperature. The results from electrochemical measurement and specimen morphology revealed that the adsorption of HBH over the Al-CM surface was through physisorption that obeyed Langmuir isotherm model. Meanwhile, the potentiodynamic polarization study showed that the HBH acted as a mixed type inhibitor. The electrochemical impedance spectroscopy (EIS) also revealed that the increase in the adsorption tendency of HBH onto the metal surface was due to an increase in the polarization resistance.

On the other hand, Muthamma et al. [27] studied the corrosion behavior of new hydrazide derivative corrosion inhibitor N-[(3,4-dimethoxyphenyl)methyleneamino]-4-hydroxy-benzamide (DMHB) for mild steel in 0.5 M H₂SO₄ and 0.5 M HCl medium, respectively. This investigation was performed using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques supplementing with surface characterization using scanning electron microscope (SEM) and atomic force spectroscopy (AFM). The results indicated that the inhibition efficiency of DMHB increased with an increase in concentration and showed maximum inhibition efficiency of 86% in 0.5 M H₂SO₄ and 81% in 0.5 M HCl, respectively, in a concentration of 30 mM at 303 K. This maximum inhibition was obtained relatively at lower concentration comparing to other previously reported related compounds, therefore, confirming its potential as a good corrosion inhibitor. Moreover, DMHB was reported to act as mixed type inhibitive action, followed Langmuir's isotherm model. Therefore, it was concluded that DMHB is a potential corrosion inhibition for mild steel application in both the acid media.

The adsorption effect of a new inhibitor, p-Toluenesulfonylhydrazide (p-TSH), on copper corrosion in 0.5 M HCl solution was studied by Laggoun et al. [42] using weight loss, electrochemical methods, morphological characterization, and quantum chemical calculations. The result indicated that p-TSH reduced the corrosion rate of copper as its concentration increased in acidic solutions, provided that the adsorption mechanism of the inhibitor obeyed the Langmuir isotherm. Furthermore, the compound acted mainly as a cathodic inhibitor with inhibition efficiency exceeding 93% reaching 5 mM p-TSH. The scanning electron microscopy analysis suggested the possible adsorption of p-TSH molecules on the Cu(111) surface with positive protection of the copper surface by the inhibitor for several days (48 h and 12 days). Therefore, p-TSH is a good inhibitor against copper corrosion in naturally aerated 0.5 M HCl.

Ajmal et al. [43] has discovered the inhibition performance of fatty hydrazides derivatives, namely oleic acid dihydrazides (OAH), and found out that the studied hydrazides shows high efficiency and proven to protect the metal surface by forming metal-inhibitor complexes via the adsorption of the organic adsorbate on the sample surface. The formation of the protective film of OAH inhibitor on the steel was also confirmed by SEM, XPS, Raman spectroscopy, and FTIR spectra.

In the latest study by Al-Baghdadi et al. [44] in 2021, new hydrazide derivatives, terephthalohydrazide, and isophthalohydrazide were investigated for their application as corrosion inhibitors for mild steel in a corrosive environment. The investigation findings revealed that terephthalohydrazide and isophthalohydrazide could control and reduce corrosion through adsorption mechanism showing remarkable inhibition efficiencies of 96.4% and 97.2%, respectively, at the optimum concentration of 0.5 mM. Both terephthalohydrazide and isophthalohydrazide molecules were adsorbed on the mild steel surface, and the process of adsorption followed chemical adsorption that obeyed the Langmuir adsorption isotherm. The results indicated that increase in temperature increased the corrosion rates and decreased the inhibition efficiencies of the investigated corrosion inhibitors. The scanning electron microscopy also revealed a protective layer formed on the mild steel surface in a 1.0 M HCl environment for both inhibitors.

Fouda et al. [30] reported the inhibition of three newly synthesized hydrazide derivatives, namely 8-Hydroxy-*N'*-((2-methoxynaphthalen-1-yl)methylene)-2,3-dimethyl-8*H*-pyrimido [1,2-*b*] [1,2,4]triazine-7-hydrazide (H1), *N'*-((2-Methoxynaphthalen-1-yl)methylene)-8-oxo-4*a*,5-dihydro-8*H*-pyrimido [1,2-*b*] [1,2,4]triazine-7-hydrazide (H2), and 6-Hydroxy-*N'*-((2-methoxynaphthalen-1-yl)methylene)-2-oxo-2*H*-chromene-3-hydrazide (H3) on C-steel in 1.0 M HCl solution using weight loss, potentiodynamic polarization (PDP), and electrochemical impedance spectroscopy (EIS) techniques. It was revealed that all three synthesized hydrazide derivatives gave high inhibition efficiency reaching maximum efficiencies of 91.7 to 96.5% at 2.0 mM at 45 °C. The high inhibition efficiency of all synthesized inhibitors was associated with the constitution of the protective layer on the C-steel surface, which increased with increasing concentration and temperature. The polarization curves of these three derivatives belonged to mixed type inhibitors, while the adsorption on the carbon steel surface followed the Temkin adsorption isotherm.

In another study by Fouda et al. [45], three newly compounds of carbohydrazide derivatives, namely: 5-amino-*N'*-((2-methoxynaphthalen-1-yl)methylene)isoxazole-4-carbohydrazide (H4), 2,4-diamino-*N'*-((2-methoxy-naphthalene-1-yl)methylene)pyrimidine-5-carbohydrazide (H5), and *N'*-((2-methoxynaphthalen-1-yl)methylene)-7,7-dimethyl-2,5-dioxo-4*a*,5,6,7,8,8*a*-hexahydro-2*H*-chromene-3-carbohydrazide (H6) were also examined to study the efficiency of the new corrosion inhibitors for carbon steel application in 1.0 M HCl solution. The same method analysis was used to detect the corrosion efficiency as previously. The study revealed that the percentage of inhibition for carbon steel corrosion rises with the increase of H4, H5, and H6 concentrations. The percentage of inhibition also increased with increasing temperatures. The maximum inhibition efficiency ranged from 81.5 to 95.2% in 2.0 mM concentration at room temperature. Furthermore, the results indicated that these compounds act as mixed type inhibitors and reduced the corrosion rate of carbon steel by forming a stable, protective film on the metal surface lowering the cathodic hydrogen evolution reaction. Therefore, the Temkin isotherm was the most acceptable model to describe the carbohydrazide derivative molecule adsorption on the surface of carbon steel. Overall, the inhibition efficiency followed the order of H6 > H4 > H5.

Ahmed et al. [46] evaluated the performance of ethanedihydrazide (EH) as a corrosion inhibitor for iron in sodium chloride (3.5% wt) solutions via electrochemical impedance spectroscopy (EIS), cyclic potentiodynamic polarization (CPP), scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX) techniques. The findings revealed that the presence of 500 µM EH was found to inhibit the corrosion of iron. Furthermore, the surface investigations demonstrated that the chloride solution without EH caused severe corrosion (Figure 3a). Meanwhile, the coexistence of EH within the chloride solution greatly minimized the acuteness of chloride, particularly pitting corrosion. Prolonging the exposure time from 1 to 48 h prevented iron corrosion in NaCl solutions and increased the inhibition efficiency of EH, particularly at high concentrations. Thus, it is proven that the availability of EH decreases the occurrence of pitting and the effect of inhibition profoundly increased with an increase in EH concentration up to 1.0 mM and further to 5.0 mM.

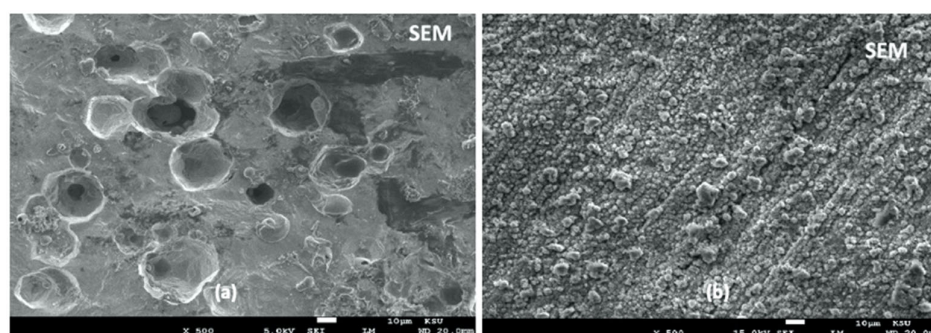


Figure 3. SEM surface analysis for the iron surface that was immersed in (a) 3.5% NaCl and (b) 3.5% NaCl + EH solutions for 48 h before measurement (Ahmed et al., 2021) [46].

Last but not least, in a recent study by Kumar Singh et al. [47], new environmentally benign corrosion inhibitors, hydroxy acetophenone derivatives, namely, *N'*-(1-(2-hydroxyphenyl) ethylidene) acetohydrazide (ATOH), *N'*-(1-(2-hydroxyphenyl) ethylidene) benzohydrazide (BZOH), 2-(1-(2-hydroxyphenyl)ethylidene) hydrazine-1-carbothioamide (TSCOH), and *N'*-(1-(2-hydroxyphenyl)ethylidene) hydrazinecarbothiohydrazide (TCBOH) were investigated for their protection ability against corrosion of mild steel in 1.0 M HCl medium. The study was evaluated using various electrochemical experimental techniques, including electrochemical impedance spectroscopy and potentiodynamic polarization coupled with microscopic techniques, such as scanning electron microscopy, atomic force microscopy, and x-ray photoelectron spectroscopy. Overall, the study revealed that all the newly synthesized inhibitors (ATOH, BZOH, TSCOH, and TCBOH) were proven to improve the mild steel corrosion resistance extensively by adsorbing themselves in the best suitable orientation. The Tafel polarization results showed that the derivatives compound simultaneously restricted the cathodic and anodic reactions, proving their mixed type nature. Most importantly, the theoretical result proved that all the newly inhibition compounds are non-toxic and have high solubility in an acidic medium.

All in all, various fatty hydrazide derivatives have been studied as corrosion inhibitors for corrosion mitigation in mild steel using multiple experimental techniques such as electrochemical, weight loss, FESEM, AFM, SEM-EDX, AAS, XPS, Raman spectroscopy, FTIR spectra, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques, gravimetric, gasometrical, thermometric, and acidimetric techniques. Table 1 summarizes the fatty hydrazide derivatives used as a corrosion inhibitor for various steel samples. These techniques help evaluate the ability to mitigate corrosion via corrosion inhibitors by comparing the inhibition efficiency of each corrosion inhibitor before and after each test. These instrumentations also help investigate the mechanism of fatty hydrazides as corrosion inhibitors in mitigating corrosion. Overall, it is revealed that the relation of chemical bonds between the hydrazides and metals influenced the inhibition mechanism, protection layer and the inhibition efficiency of fatty hydrazides. The addition of active sites such as nitrogen compounds further increases the interaction with the metal surface, causing stronger adsorption toward the metal surface and increasing the inhibition efficiency. However, it is seen that these fatty hydrazides were only applied in hydrochloric acid medium and not in highly organic acid conditions with the presence of high CO₂ and H₂S environments. Therefore, more studies with various conditions should be conducted to test the efficiency of fatty hydrazides in more extreme conditions.

Table 1. Fatty hydrazide derivatives used as a corrosion inhibitor for various steel samples.

Name of Corrosion Inhibitors	Metal and Acid Solution	Adsorption Isotherm and Type of Inhibitor	Inhibition Efficiency (303 K)	Ref.
<i>N'</i> -(thiophene-2-ylmethylene) nicotinic hydrazone (TNH) and <i>N'</i> -(pyrrol-2-ylmethylene) nicotinic hydrazone (PNH)	Mild steel 1.0 M HCl	Langmuir Mixed type	TNH: IE _w = 91.3% IE _{EIS} = 94.7% PNH: IE _w = 93.7% IE _{EIS} = 96.4%	Kumar Singh et al., (2017) [31]
<i>N'</i> -(4-Hydroxybenzylidene) nicotinic hydrazone (HBNH) and <i>N'</i> -(4-methylbenzylidene) nicotinic hydrazone (MBNH)	Mild steel 1.0 M HCl	Langmuir Mixed type	HBNH: IE _w = 90.0% IE _{EIS} = 95.5% MBNH: IE _w = 94.2% IE _{EIS} = 96.6%	Kumar Singh et al., (2018) [32]

Table 1. Cont.

Name of Corrosion Inhibitors	Metal and Acid Solution	Adsorption Isotherm and Type of Inhibitor	Inhibition Efficiency (303 K)	Ref.
3-(cyano-dimethyl-methyl)-benzoic acid thiophen-2-ylmethylene-hydrazide (CBTH) and 3-(cyano-dimethyl-methyl)-benzoic acid furan-2-ylmethylene-hydrazide (CBFH)	Mild steel 1.0 M HCl	Langmuir Mixed type	CBTH: IE _{EIS} = 87.1% CBFH: IE _{EIS} = 85.3%	Chaitra et al., (2018) [33]
<i>N'</i> -(E)-[4-(dimethylamino) phenyl] methylidene] benzenesulfonohydrazide (MBSH), and <i>N'</i> -(E)-[4(dimethylamino) phenyl] methylidene]-4-methylbenzenesulfonohydrazide (MpTSH)	XC38 Carbon Steel 1.0 M HCl	Langmuir Mixed type	MBSH: IE _{EIS} = 91.9% MpTSH: IE _{EIS} = 94.5%	Ichchou et al., (2019) [34]
(E)- <i>N'</i> -(4'-Hydroxy-3-methoxybenzylidene) isonicotino hydrazide (PA1), (E)- <i>N'</i> -(Pyridin-4'-ylmethylene) isonicotino hydrazide (PA2), and (E)- <i>N'</i> -(Pyridin-3'-ylmethylene) isonicotino hydrazide (PA3)	Mild steel 1.0 M HCl	Langmuir Mixed type	PA1: IE _{EIS} = 96.7% PA2: IE _{EIS} = 81.1% PA3: IE _{EIS} = 71.3%	Arshad et al., (2019) [35]
<i>N</i> -cinnamalidene palmitohydrazide (CPH)	Mild steel 1.0 M HCl	Langmuir Mixed type	IE _w = 88% IE _{EIS} = 95%	Mohd et al., (2019) [36]
<i>p</i> -Toluenesulfonylhydrazide (<i>p</i> -TSH)	Copper Steel 0.5 M HCl	Langmuir Mixed type	IE _w = 90.6% IE _{EIS} = 93.0%	Laggoun et al., (2019) [42]
<i>N,N'</i> -((ethane-1,2-diylbis(oxy))bis(2-oxoethane-2,1-diyl)) bis(<i>N,N</i> -dimethyl-4-((E)-(2-((E)-octadec-9-enoyl)hydrazineylidene)methyl) benzenaminium) dichloride	X-65 Steel 1.0 M HCl	Freundlich	IE _{EIS} = 94.7%	Basiony et al., (2020) [37]
Hydrazone propanehydrazide (HYD-1) and <i>N</i> -cyclohexylidene-2-(6-methoxynaphthalen-2-yl) propanehydrazide (HYD-2)	Mild Steel 1.0 M HCl	Langmuir Mixed type	HYD-1: IE _w = 95% IE _{EIS} = 94% HYD-2: IE _{EIS} = 84%	Chaouiki et al., (2020) [38]
(6-phenyl-pyridazin-3-ylsulfanyl)-acetic acid (1), (6-phenyl-pyridazin-3-ylsulfanyl)-acetic acid hydrazide (2), (6-Phenyl-pyridazin-3-ylsulfanyl)-acetic acid (2,4-dihydroxy-benzylidene)-hydrazide (3), (6-Phenyl-pyridazin-3-ylsulfanyl)-acetic acid (2-hydroxy-naphthalen-1-ylmethylene)-hydrazide compound (4) and (6-Phenyl-pyridazin-3-ylsulfanyl)-acetic acid (4-dimethylamino-benzylidene)-hydrazide (5)	Carbon Steel 1.0 M HCl	Langmuir Mixed type	1: IE _w = 83.3% IE _{EIS} = 80.3% 2: IE _w = 87.7% IE _{EIS} = 85.7% 3: IE _w = 94.2% IE _{EIS} = 91.1% 4: IE _w = 90.1% IE _{EIS} = 89.2% 5: IE _w = 91.5% IE _{EIS} = 94.6%	Abdel Hameed et al., (2020) [39]
<i>N'</i> - [(4-methyl-1 <i>H</i> -imidazole-5-yl) methylidene]-2-(naphthalen-2-yloxy) acetohydrazide (IMNH)	Mild steel 1.0 M HCl	Langmuir Mixed type	IE _w = 88.3% IE _{EIS} = 88.1%	Preethi Kumari et al., (2020) [40]
4-hydroxy- <i>N'</i> -[3-phenylprop-2-en-1-ylidene] benzo-hydrazide (HBH)	Al-CM 0.5 M HCl	Langmuir Mixed type	IE _w = 83.2% IE _{EIS} = 85.7%	Shetty et al., (2020) [41]
<i>N</i> -[(3,4-dimethoxyphenyl) methyleneamino]-4-hydroxy-benzamide (DMHB)	Mild steel 0.5 M H ₂ SO ₄ 0.5 M HCl	Langmuir Mixed type	H ₂ SO ₄ : IE _w = 86.6% IE _{EIS} = 84.2% HCl: IE _w = 81.5% IE _{EIS} = 81.5%	Muthamma et al., (2020) [27]
Oleic acid hydrazide (OAH)	API X70 steel in Indian oilfield-produced water	Mixed type	IE _{EIS} = 87.7%	Ajmal et al., (2020) [43]

Table 1. Cont.

Name of Corrosion Inhibitors	Metal and Acid Solution	Adsorption Isotherm and Type of Inhibitor	Inhibition Efficiency (303 K)	Ref.
Terephthalohydrazide (TPH), and Isophthalohydrazide (IPH)	Mild steel 1.0 M HCl	Langmuir Mixed type	TPH: IE _w = 97.02% IE _{EIS} = 96.4% IPH: IE _w = 96.4% IE _{EIS} = 97.2%	Al-Baghdadi et al., (2021) [44]
8-Hydroxy- <i>N'</i> -(2-methoxynaphthalen-1-yl)methylene)-2,3-dimethyl-8 <i>H</i> -pyrimido [1,2- <i>b</i>][1,2,4]triazine-7-hydrazide (H1), <i>N'</i> -(2-Methoxynaphthalen-1-yl)methylene)-8-oxo-4 <i>a</i> ,5-dihydro-8 <i>H</i> -pyrimido [1,2- <i>b</i>][1,2,4]triazine-7-hydrazide (H2), and 6-Hydroxy- <i>N'</i> -(2-methoxynaphthalen-1-yl)methylene)-2-oxo-2 <i>H</i> -chromene-3-hydrazide (H3)	Carbon steel 1.0 M HCl	Temkin Mixed type	H1: IE _w = 92.6% IE _{EIS} = 93.1% H2: IE _w = 85.3% IE _{EIS} = 85.2% H3: IE _w = 95.1% IE _{EIS} = 94.6%	Fouda et al., (2021) [30]
5-amino- <i>N'</i> -(2-methoxynaphthalen-1-yl)methylene)isoxazole-4-carbohydrazide (H4), 2,4-diamino- <i>N'</i> -(2-methoxynaphthalen-1-yl)methylene)pyrimidine-5-carbohydrazide (H5) and <i>N'</i> -(2-methoxynaphthalen-1-yl)methylene)-7,7-dimethyl-2,5-dioxo-4 <i>a</i> ,5,6,7,8,8 <i>a</i> -hexahydro-2 <i>H</i> -chromene-3-carbohydrazide (H6)	Carbon steel 1.0 M HCl	Temkin Mixed type	H4: IE _w = 88.3% IE _{EIS} = 93.1% H5: IE _w = 85.3% IE _{EIS} = 85.3% H6: IE _w = 95.1% IE _{EIS} = 95.2%	Fouda et al., (2021) [45]
Ethanedihydrazide (EH)	Iron in NaCl (3.5% wt)	Mixed type	IE _w = 87.4% IE _{EIS} = 80.9%	Ahmed et al., (2021) [46]
<i>N'</i> -(1-(2-hydroxyphenyl) ethylidene) acetohydrazide (ATOH), <i>N'</i> -(1-(2-hydroxyphenyl) ethylidene) benzohydrazide (BZOH), 2-(1-(2-hydroxyphenyl)ethylidene) hydrazine-1-carbothioamide (TSCOH) and <i>N'</i> -(1-(2-hydroxyphenyl)ethylidene) hydrazinecarbothiohydrazide (TCBOH)	Mild steel 1.0 M HCl	Tefel Mixed type	ATOH: IE _w = 85.5% IE _{EIS} = 85.5% BZOH: IE _w = 85.9% IE _{EIS} = 85.7% TSCOH: IE _w = 86.6% IE _{EIS} = 86.5% TCBOH: IE _w = 92.4% IE _{EIS} = 92.4%	Kumar Singh et al., (2021) [47]

5. Molecular Modelling Study on Corrosion Inhibitors

5.1. Understanding the Basic Molecular Modelling on Corrosion Inhibitor

The theoretical understanding of the organic corrosion inhibitor was actively studied in the recent years via molecular modelling. Molecular modelling such as density functional theory (DFT) and molecular dynamics (MD) simulation is a powerful technique used to study the molecular interaction and adsorption towards the metal surface [48–51]. The molecular modelling method is conducted to obtain the equilibrium properties of a system by reaching the most stable state of the inhibitor molecule. DFT calculation provides relatively fast and reliable electronic properties in order to predict the performance of corrosion inhibitors [52]. The electronic properties will give information on whether the inhibitor molecule prefers to be adsorbed or desorbed from the metal surface. MD simulation is a computer simulation that acts as a bridge between microscopic length and time scales with the laboratory's microscopic world. An advantage of MD simulation is the possibility of directly determining each component's transport properties within a complex chemical environment under different thermodynamic conditions [53,54]. MD simulation, the trajectory of each atom that describe each configuration of atoms within a

small-time interval in real-time is possible to be simulated by repeating the measurement of the potential energy, force and acceleration from the position and velocity of each atom. The potential energy that acts on an atom can be obtained from two categories which are bonded (bonds, angles, and dihedrals) and non-bonded (van der Waal and Columbic) interactions [55]. The position of each atom as a function of time can be predicted by calculating their acceleration via the integration of Newton's law of motion [56]. Thus, the corrosion inhibitor molecules' behavior towards the metal surface can be studied at a molecular level by positioning the corrosion solution next to the metal surface in a most stable state by MD simulation.

5.2. Parameter Derived from the Molecular Modelling Study on the Corrosion Inhibitor

Several parameters such as electronic properties, molecular interaction, and the orientation of the inhibitor molecules from the DFT calculation and MD simulation can be derived to investigate the inhibition efficiency of the corrosion inhibitor.

The electronic properties can elucidate the adsorption and corrosion inhibition behavior of an inhibitor molecule. The parameters studied in DFT calculation explaining the inhibitor efficiency are the highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), dipole moment (μ), number of transferred electron (ΔN), electronegativity (χ), softness (σ), ionization potential (I), and electron affinity (A) [20]. The adsorption of an inhibitor on a metal surface is based on the interaction between the heteroatom electrons and the π -electrons with the metal atoms d-orbital vacancies [57]. A high value of E_{HOMO} increases the donating tendency of the inhibitor molecule to the vacant orbitals, hence increasing its adsorption on the metal surface. Meanwhile, for ΔE , a low energy difference value increases the reactivity of the inhibitor molecule, enhancing the inhibition efficiency [58]. The softness, σ of the inhibitor molecules also correlates with the ΔE value. The lower the ΔE value, the higher the σ of the molecules, the greater their reactivity [59]. In 2010, Obot et al., [60] reported a high correlation (0.999) between the dipole moment and corrosion inhibition efficiency stating that the adsorption strength increases at a high value of dipole moment. Meanwhile, ΔN is the number of electrons transferred from the inhibition molecule to the metal atom. Lukovitt et al., [61] stated that if the ΔN value is lower than 3.6, the electron releasing ability on metal surface increases thus increasing the inhibition efficiency. The ionization energy, I , and electron affinity, A , are used to identify the inhibitor molecule's electronegativity value, χ in explaining the inhibitor efficiency. The high χ value indicates that the inhibitor molecule has the reducing power and higher tendency to donate electrons to the metal surface [20].

On the other hand, the parameters derived in investigating the inhibitor efficiency from MD simulation are adsorption energy (E_{ads}), binding energy (E_{bind}), and inhibitor molecular orientation. Adsorption energy is defined as the decreasing of energy when two materials are combined under the adsorption process in which an atom, ion, or molecule (adsorbate) is attached to the surface of a solid (adsorbent) [62]. The adsorption energy can be expressed as follows:

$$E_{\text{ads}} = E_{\text{total}} - (E_{\text{metal+solution}} + E_{\text{inhibitor}})$$

where E_{total} is the total energy of the whole system, $E_{\text{(metal+solution)}}$ is the energy of the metal and the aqueous phase, and $E_{\text{inhibitor}}$ is the energy of the inhibitor molecule. The greater the negative energy value of E_{ads} , the stronger the strength of adsorption, the higher the corrosion inhibitor efficiency [63]. Meanwhile, the binding energy also explains the adsorption strength of the inhibitor on the metal surface. In the corrosion inhibitor perspective, the binding energy is the energy required for the inhibitor molecule to desorb from the metal surface due to bond dissociation [55]. Hence the greater value of the binding energy will increase the attraction force between the inhibitor molecule and the metal surface increasing the inhibition efficiency. Lastly, for the inhibitor molecule orientation, the planar conformation favors the inhibition efficiency leading to a high interaction and large

occupation of the metal surfaces [20]. Thus, all the parameters derived from molecular modelling are able to explain the inhibition efficiency of the corrosion inhibitor molecule and can be applied in corrosion studies.

5.3. Recent Studies of Molecular Modelling on Corrosion Inhibition Application

In recent years, molecular modelling method has become an important tool in developing and designing more suitable organic corrosion inhibitors used in the protection of metal surfaces in the pipelines. An in-depth study on the electronic properties and behavior of organic corrosion inhibitor in protecting metal surfaces alongside experimental procedures produces a crucial understanding on the corrosion inhibition mechanism. Fouda et al. [45], examined the inhibition efficiency of three compounds of carbohydrazide derivatives (H4, H5, and H6) on carbon steel in 1.0 M HCl experimentally and theoretically. The substituents of the inhibitor molecules were varied with different electron-donating atoms (N, O) and groups (CH₃, OH). The order of efficiency measured experimentally was H6 > H4 > H5 which showed good agreement with the molecular simulation based on their adsorption energies properties and the tendency of donating electrons to the carbon steel surface. Tables 2 and 3 indicate the calculated simulation results of total energy, adsorption energy, rigid adsorption energy, and deformation energies in vacuum and acid solutions, respectively.

Table 2. Simulation results (total energy, adsorption energy, rigid adsorption energy, and deformation energies) in vacuum (Fouda et al., 2021) [45].

Structure	CS-H4	CS-H5	CS-H5
Total energy	−244.22	−267.41	−246.99
Adsorption energy	−321.15	−291.12	−323.92
Rigid adsorption energy	−229.01	−199.66	−232.17
Deformation energy	−92.14	−94.46	−91.75
Inh: dE_{ad}/dN_i	−321.15	−291.12	−323.92

Table 3. Simulation results (total energy, adsorption energy, rigid adsorption energy, and deformation energies) in acid solutions (Fouda et al., 2021) [45].

Structure	CS-H4	CS-H5	CS-H5
Total energy	−4019.83	−4002.17	−4028.35
Adsorption energy	−4096.76	−4025.88	−4105.29
Rigid adsorption energy	−4183.44	−4107.05	−4184.89
Deformation energy	86.68	81.17	79.60
Inh: dE_{ad}/dN_i	−323.65	−212.26	−340.60
H ₂ O: dE_{ad}/dN_i	−8.73	−7.60	−11.69
H ₃ O ⁺ : dE_{ad}/dN_i	−151.74	−154.70	−147.92
Cl [−] : dE_{ad}/dN_i	−144.41	−155.94	−152.37

Basiony et al., [37] synthesized the Gemini cationic surfactant based on hydrazide moiety (GI-surfactant) and studied their adsorption as X-65 steel acid corrosion inhibitor. The quantum chemical calculation and monte Carlo (MC) simulation were computed to study the adsorption properties of the GI-surfactant molecule. The HOMO and LUMO revealed that the (−C=N−NH−) attached to the benzene ring represents the nucleophilic center. At the same time, LUMO is focused on the ethereal groups (spacer), which represents the electrophilic center. The quantum chemical descriptors suggest the tendency of the GI-surfactant molecule to suppress the corrosion on X-65 steel.

The MC simulation data from the study revealed the interaction of the GI-surfactant molecule with the Fe(110) surface in the most stable state. The adsorption energy of GI-surfactant was higher than that of water and chloride ion, indicating that it can substitute/replace water and aggressive ions gradually forming a protective adsorbed layer shield. The molecular orientation of the inhibitor molecule also lies flat and parallel to the

Fe(110) surface allowing the active centers to react effectively with the metal surface thus leads to higher protection affinity.

In 2020, Ferkous et al. [64] studied 2-(2-methoxybenzylidene) hydrazine-1-carbothioamide (MBHCA) in 1.0 M HCl solution. The experimental results showed that the inhibition efficiency of MBHCA reached a maximum value of 97.8% at 200 ppm. The quantum calculations explained that the HOMO orbitals are localized at the hydrazine and carbothioamide groups. On the other hand, the LUMO was localized at the aromatic ring, indicating that the imine group plays an important role as active sites for the interaction of MBHCA with a steel surface. Meanwhile, Monte Carlo simulations showed that the MBHCA was quickly and firmly adsorbed onto the iron surface with the negative adsorption energy.

Other than that, Kumar Singh et al., [47] synthesized an environmentally benign corrosion inhibitors, hydroxy acetophenone derivative namely, *N'*-(1-(2-hydroxyphenyl) ethylidene) acetohydrazide (ATOH), *N'*-(1-(2-hydroxyphenyl) ethylidene) benzo hydrazide (BZOH), 2-(1-(2-hydroxyphenyl) ethylidene) hydrazine-1-carbothioamide (TSCOH), and *N'*-(1-(2-hydroxyphenyl) ethylidene) hydrazine carbothiohydrazide (TCBOH), and studied their corrosion inhibition mechanism via DFT and MD simulation techniques. The HOMO is expanded over the whole molecule for both ATOH and BZOH molecules, while the LUMO is on a phenylic group for BZOH and -CH₃ for ATOH. For TSCOH and TCBOH molecules, the HOMO was distributed on -(C=S)-NH₂ and -(C=S)-N-NH₂, respectively. All the parameters calculated by DFT analysis revealed that the order of corrosion inhibition efficiency is TCBOH > TSCOH > BZOH > ATOH. For MD simulation, the molecules adsorbed almost flat orientation on the Fe surface indicated the stronger coordination for an adsorbate system. The determined Eads values are -473.1, -475.4, -477.9, and -489.4 kJ mol⁻¹ for ATOH, BZOH, TSCOH, and TCBOH, respectively, indicating that TCBOH with the highest negative value of adsorption energy has the highest inhibition efficiency. Thus, the results from the experiment have a good agreement with the DFT and MD simulation results where the order of inhibition efficiency is TCBOH > TSCOH > BZOH > ATOH.

In 2020, El-Lateef et al. [65] synthesized and studied the inhibition efficiency of salicylidene isatin hydrazine sodium sulfonate (SHMB) experimentally and via computer simulation. The experimental and computer simulation results show the agreement where the protonated SHMB molecule (presence of Ni²⁺) has a higher inhibition efficiency compared to neutral SHMB. The results from the DFT analysis acquired that SHMB is likely to inhibit steel corrosion in the protonated form than in the neutral forms. In MD simulation, protonated SHMB was also found to have a better inhibition efficiency towards Fe (110) metal surface than neutral SHMB with a higher negative value of interaction energy ($E_{interaction}$) and binding energy ($E_{binding}$).

Belghiti et al., [66] also investigated the corrosion efficiency of the 'Cis (E) and Trans (Z)' conformations of three families of azines, namely: [1, 2- bis (pyrrole-2-ylidenemethyl) hydrazine (HZ1), 1, 2-bis (thiophene-2-idenemethyl) hydrazine (HZ2), and 1, 2-Bis (furyl-2-lidenemethyl) hydrazine (HZ3)] experimentally and theoretically by DFT analysis and MD simulation technique. Based on the comparative study by the standard deviation in DFT analysis, the crystal geometry of HZ1 agrees more with the Trans than with the Cis geometric monomer. While in the MD simulation, the results show that the adsorption of both conformers (Z-HZi and E-HZi) on the Fe (111) surface takes nearly parallel to the surface to maximize its contact with the Fe-surface, as shown as the MDs (Figure 4). The adsorption energy is also calculated, and the value follows the order: HZ2-Trans > HZ1-Trans > HZ3-Trans. This same trend is observed with respect to quantum chemical parameters that are well correlated with corrosion inhibition performance. The distance between the Fe atom and heteroatoms of azines was also studied, representing the metal-inhibitor complex's strength where a shorter distance indicates stronger interactions while a longer distance indicates weaker interactions. The results from radial distribution function (RDF) analysis show that the trend follows the order: HZ2-Trans < HZ1-Trans ≤ HZ3-Cis < HZ3-Trans < HZ2-Cis < HZ1-Cis (Figure 5), which confirms that the E-conformers has the strongest interaction with the Fe-surface than

Z-conformers. This is consistent with the observed experimental trend of inhibitory efficacy of E-conformers inhibitors.

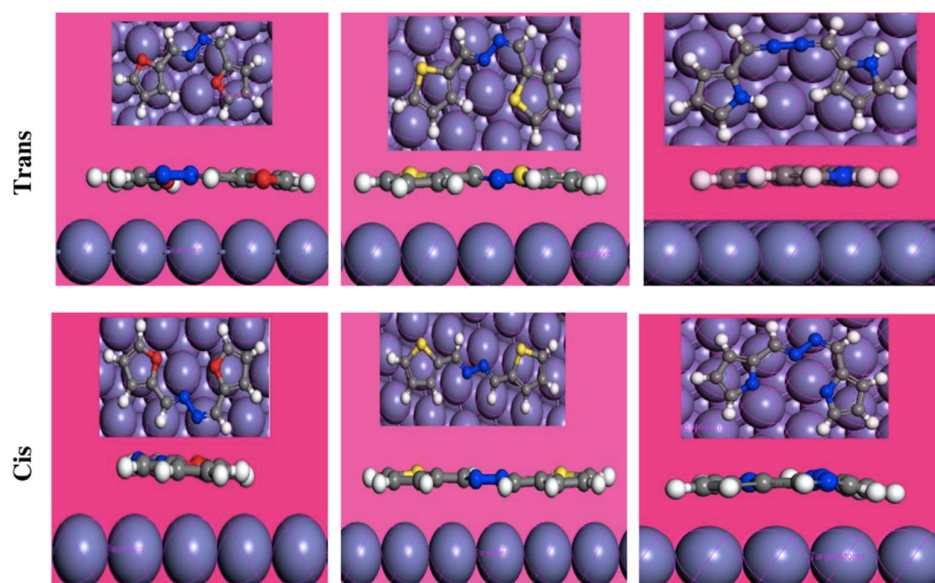


Figure 4. Side and top views of most stable adsorption configurations for (Fe (111))/(E&Z)-HZi/Gas phase) systems at 308 K (Belghiti et al., 2019) [66].

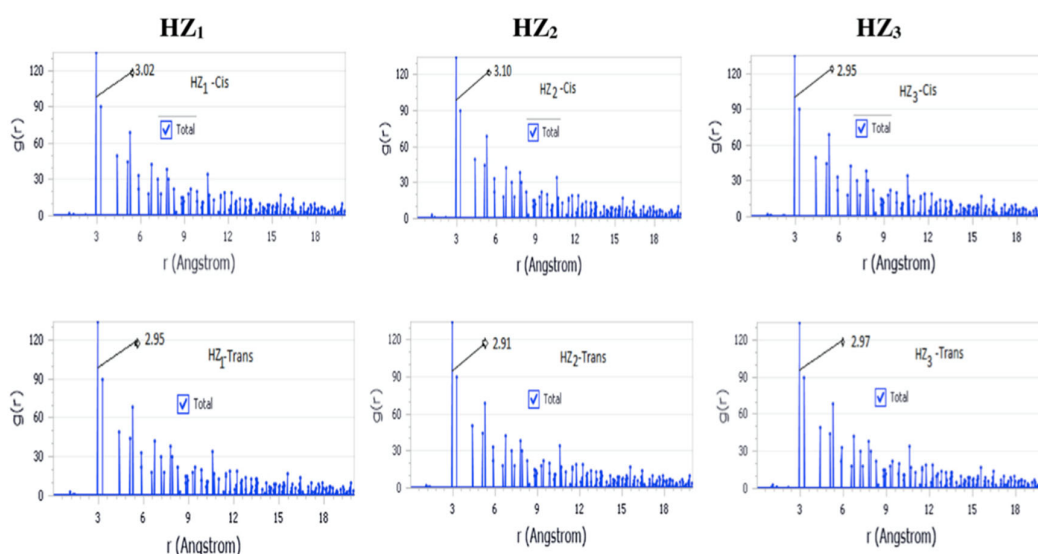


Figure 5. Radial Distribution ($g(r) \sim r$) Functions for (Fe (111))/(E&Z)-HZi/Gas phase) systems at 308 K (Belghiti et al., 2019) [66].

Another study is by Boudina et al. [67] where they investigate the corrosion inhibition properties of two compounds, namely, 1,2-dibenzylidenehydrazine (C1) and 1,2-bis(1-phenylethylidene) hydrazine (C2) experimentally and C1 exhibiting the highest inhibition efficiency than C2. Then, the DFT and MD simulations were used to study the mechanism of inhibition action. The quantum chemical calculation parameters revealed that C1 has a better chemical reactivity towards the metal surface than the C2 molecule. The selected energy parameters ($E_{interaction}$ and $E_{binding}$) were also calculated by MD simulation. The energy value calculated also proved that the C1 molecule has a better corrosion inhibition action on the Fe (110) surface, which agrees well with the experimental.

In conclusion, computer simulations such as DFT analysis and MD simulation are well-established theoretical approaches applied extensively in corrosion inhibition research.

These methods provide more information on the interaction modes of the CI molecules, such as molecular orientation, ability to donate and accept electrons, and adsorption properties on the metal surface. These methods were also helpful in the modify and development of new complex CI molecules. After a detailed review of the DFT analysis, all the hydrazide derivative CI molecules can donate and accept electrons and have a good adsorption property towards the metal surface. In the MD simulation, all the hydrazide derivatives inhibitors were adsorbed on the metal surface on the parallel orientation and high negative value of E_{ads} , which favor the inhibition efficiency. All the literature also proved the ability of DFT analysis and MD simulation technique in predicting inhibition efficiency with a good agreement with the results from experimental. The CI molecules, DFT and MD simulation parameters, and the results from DFT and MD for several Hydrazide derivatives CI molecules are presented in Table 4.

Table 4. Hydrazide derivatives CI, DFT, and MD simulation parameters and results.

Name of Corrosion Inhibitors	Metal and Acid Solution	DFT and MD Parameters	ΔE (eV) from DFT and Orientation and E_{ads} (kJ/mol) from MD Simulation	Ref.
8-Hydroxy- <i>N'</i> -(2-methoxynaphthalen-1-yl)methylene)-2,3-dimethyl-8 <i>H</i> -pyrimido [1,2- <i>b</i>][1,2,4]triazine-7-hydrazide (H1), <i>N'</i> -(2-Methoxynaphthalen-1-yl)methylene)-8-oxo-4 <i>a</i> ,5-dihydro-8 <i>H</i> -pyrimido [1,2- <i>b</i>][1,2,4]triazine-7-hydrazide, and 6-Hydroxy- <i>N'</i> -(2-methoxynaphthalen-1-yl)methylene)-2oxo-2 <i>H</i> -chromene-3-hydrazide 5-amino- <i>N'</i> -(2-methoxynaphthalen-1-yl)methylene)isoxazole-4-carbohydrazide (H4), 2,4-diamino- <i>N'</i> -(2-methoxynaphthalen-1-yl)methylene)pyrimidine-5-carbohydrazide (H5), and <i>N'</i> -(2-methoxynaphthalen-1-yl)methylene)-7,7-dimethyl-2,5-dioxo-4 <i>a</i> ,5,6,7,8 <i>a</i> -hexahydro-2 <i>H</i> -chromene-3-carbohydrazide (H6)	Carbon steel 1.0 M HCl	DFT: Material studio Dmol6 DFT software, GGA basis set RPBE. MD: -	DFT: $\Delta E = 1.80274$ (H1), 1.77942 (H2), 1.86997 (H3) MD: Planar orientation $E_{ads} = -218.075$ (H1), -207.526 (H2), -221.927 (H3)	Fouda et al., (2021) [30]
	Carbon steel 1.0 M HCl	DFT: Material studio Dmol6 DFT software, GGA basis set RPBE. MD: -	DFT: $\Delta E = 1.95288$ (H1), 2.17013 (H2), 1.39953 (H3) MD: Planar orientation $E_{ads} = -321.14876$ (H1), -291.1181 (H2), -323.92464 (H3)	Fouda et al., (2021) [45]
<i>N,N'</i> -(ethane-1,2-diylbis(oxy))bis(2-oxoethane-2,1-diyl) bis (<i>N,N</i> -dimethyl-4-((<i>E</i>)-(2-((<i>E</i>)-octadec-9-enoyl)hydrazineylidene)methyl)benzenaminium) dichloride	X-65 Steel 1.0 M HCl	DFT: Diatomic differential overlap (NDDO) Hamiltonian type in Material Studio 6.0 (MS 6.0). MD: Fe (110) (74.47, 74.47, 33.01) Å COMPASS.	DFT: $\Delta E = 6.026$ MD: Planar orientation $E_{ads} = -1389.3$ (without HCl solution), -14,074.3 (with HCl solution)	Basiony et al., (2020) [37]

Table 4. Cont.

Name of Corrosion Inhibitors	Metal and Acid Solution	DFT and MD Parameters	ΔE (eV) from DFT and Orientation and E_{ads} (kJ/mol) from MD Simulation	Ref.
2-(2-(methoxybenzylidene)hydrazine-1-carbothioamide (MBHCA)	Mild steel 1.0 M HCl	DFT: Dmol3 module in Material Studio 2017™ with DFT-B3LYP functional set. MD: Fe (001) (22.93, 22.93, 34.39) Å COMPASS	DFT: $\Delta E = 3.996$ (Gas), 4.212 (Aqueous) MD: Planar orientation $E_{ads} = -1389.3$ (without HCl solution), $-14,074.3$ (with HCl solution)	Ferkous et al., (2020) [64]
<i>N'</i> -(1-(2-hydroxyphenyl)ethylidene) acetohydrazide (ATOH), <i>N'</i> -(1-(2-hydroxyphenyl)ethylidene) benzohydrazide (BZOH), 2-(1-(2-hydroxyphenyl)ethylidene) hydrazine-1-carbothioamide (TSCOH), and <i>N'</i> -(1-(2-hydroxyphenyl)ethylidene) hydrazinecarbothiohydrazide (TCBOH)	Mild steel 1.0 M HCl	DFT: 6–31 g(d,p), 6–311 + g(d,p) and 6–311 ++g(2df,2pd) basis set by G09W package. MD: Fe (110) (17.3, 17.3, 345.1) Å COMPASSII NVT	DFT: Aqueous- $\Delta E = 4.8883$ (ATOH), 4.7084 (BZOH), 4.4706 (TSCOH), 4.3598 (TCBOH). MD: Planar orientation $E_{ads} = -473.1$ (ATOH), -475.4 (BZOH), -475.4 (TSCOH), -477.9 (TCBOH).	Kumar Singh et al., (2021) [47]
4-sodium sulfonate-2-hydroxy-3-((2-oxoindolin-3-ylidene)hydrazineylidene)methyl benzene sulfonate (SHMB), and Protonated 4-sodium sulfonate-2-hydroxy-3-((2-oxoindolin-3-ylidene)hydrazineylidene)methyl benzene sulfonate (SHMBH)	Carbon steel 1.0 M HCl	DFT: B3LYP combined with 6–31 + G(d,p) basis set using Gaussian 09. MD: Fe (110) (22, 26, 45) Å	DFT: $\Delta E = 0.13551$ (SHMB), 0.1259 (SHMBH) MD: Planar orientation $E_{ads} = -123.451$ (SHMB), -129.784 (SHMBH)	El-Lateef et al., (2020) [65]
Cis and Trans 1,2- <i>bis</i> (pyrrole-2-ylidenemethyl) hydrazine (HZ ₁), 1,2- <i>bis</i> (thiophene-2-ylidenemethyl) hydrazine (HZ ₂), and 1,2- <i>bis</i> (furyl-2-ylidenemethyl) hydrazine (HZ ₃),	Mild steel 2.0 M H ₃ PO ₄	DFT: B3LYP combined with 6–31 ++ G(2d,2p) basis set using Gaussian 09 W. MD: Fe (111) (35, 35, 40) Å COMPASS	DFT: $\Delta E = 3.7418$ (HZ _{1(cis)}), 3.7023 (HZ _{1(trans)}), 3.6196 (HZ _{2(cis)}), 3.7418 (HZ _{2(trans)}), 3.6682 (HZ _{3(cis)}), 3.6487 (HZ _{3(trans)}) MD: Planar orientation $E_{ads} = -98.725$ (HZ _{1(cis)}), -74.845 (HZ _{1(trans)}), -234.70 (HZ _{2(cis)}), -163.263 (HZ _{2(trans)}), -98.093 (HZ _{3(cis)}), -96.274 (HZ _{3(trans)})	Belghiti et al., (2019) [66]
1,2-dibenzylidenhydrazine (C1), and 1,2- <i>bis</i> (1-phenylethylidene) hydrazine (C2)	Mild steel 1.0 M HCl	DFT: Material Studio 6.0 at DFT/GGA level using BOP functional and DNP basis set. MD: Fe (110) (24.82, 24.82, 35.69) Å COMPASS NVT	DFT: $\Delta E = 2.836$ (C1), 3.178 (C2) MD: Planar orientation $E_{ads} = -573.52$ (C1), -407.06 (C2)	Boudina et al., (2018) [67]
(<i>E</i>)-2-(4-(2-(methyl(pyridine-2-yl)amino)ethoxy)benzylidene)-hydrazine-1-carboxamide (MPAH)	Mild steel 1.0 M HCl	DFT: B3LYP combined with 6–31 + G(d,p) basis set using Gaussian 09. MD: Fe (110) (24.82, 24.82, 25.14) Å COMPASS NVT	DFT: $\Delta E = 2.394$ MD: Planar orientation $E_{ads} = -476.29$	Chafiq et al., (2020) [68]

6. Conclusions

Over the years, there has been rapid progress in the scientific exploration of corrosion mitigation strategies. One of the most practical and cost-effective methods for corrosion control in the oil and gas industry is corrosion inhibitors. Corrosion inhibitors can protect the surface of metals and retard corrosion action when added to the corrosive environment. Recent findings agree that organic inhibitors, mainly fatty hydrazide derivatives, are very effective for metal steel in an acidic medium. Many scientists have investigated various hydrazide derivatives and proved their effectiveness in mitigating corrosion. Most studies on hydrazide derivatives show excellent inhibition efficiency up to 97% in an acidic medium. Not only that, but fatty hydrazides are also known to be more environmentally friendly, biodegradable and less toxic than synthetic organic inhibitors since they are produced using green technology from a renewable source. Besides, it is revealed that most of the hydrazide derivatives showed mixed type inhibitors and followed Langmuir adsorption isotherm, while only one study followed Temkin adsorption isotherm. These types of adsorption isotherm depend on the physisorption or chemisorption of the inhibitors on the metal surface, and based on the studies, it is observed that most of the fatty hydrazide derivatives have proven to have chemisorption interaction with the metal surfaces. Moreover, as most of the inhibitors are adsorption inhibitors, the inhibition efficiency increases with concentration and temperatures. Finally, the computer simulation study (DFT and MD) has significantly contributed to the formulation of new corrosion inhibitors due to its ability to predict the efficiency and mechanism of corrosion inhibitors. In addition, all theoretical studies via DFT and MD agree with the experimental observation of the adsorption properties of the corrosion inhibitors. However, it should be noted that most of the cited fatty hydrazide inhibitors are in higher concentrations. Therefore, future studies must focus on developing a highly effective fatty hydrazide inhibitor at a lower concentration for future cost reduction. Moreover, the previous studies were typically conducted using HCl and not in weak organic acid environments. Thus, future works should be undertaken in different acidic conditions.

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