



An Overview of Molecular Dynamic Simulation for Corrosion Inhibition of Ferrous Metals

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Abstract: Molecular dynamics (MD) simulation is a powerful tool to study the molecular level working mechanism of corrosion inhibitors in mitigating corrosion. In the past decades, MD simulation has emerged as an instrument to investigate the interactions at the interface between the inhibitor molecule and the metal surface. Combined with experimental measurement, theoretical examination from MD simulation delivers useful information on the adsorption ability and orientation of the molecule on the surface. It relates the microscopic characteristics to the macroscopic properties which enables researchers to develop high performance inhibitors. Although there has been vast growth in the number of studies that use molecular dynamic evaluation, there is still lack of comprehensive review specifically for corrosion inhibition of organic inhibitors on ferrous metal in acidic solution. Much uncertainty still exists on the approaches and steps in performing MD simulation for corrosion system. This paper reviews the basic principle of MD simulation along with methods, selection of parameters, expected result such as adsorption energy, binding energy and inhibitor orientation, and recent publications in corrosion inhibition studies.

Keywords: corrosion inhibitor; ferrous metal; molecular dynamics simulation; adsorption energy; binding energy

1. Introduction

The use of computational method for studies of metal corrosion inhibition has progressively increased due to time, cost and environmental considerations as well as the inadequacy of conventional methods to provide notable insight on metal surface-inhibitor interaction. The performance of corrosion inhibitors in inhibiting metallic corrosion are conventionally evaluated using experimental procedures such as weight loss method, electrochemical impedance spectroscopy, potentiodynamic polarization and cyclic voltammetry. These methods are sufficient to obtain physical and electrochemical properties of the corrosion inhibitor, yet require the usage of chemicals and are time consuming. Computational studies of metal corrosion inhibition using molecular dynamic (MD) simulation provides significant insight into the mechanism and interaction between a metal surface and inhibitor molecules with minimum cost. While MD was first introduced in 1956 by Berni Alder, the use of MD simulation for metal corrosion inhibition application was never until reported 17 years ago in 2003 by Bartley et al., who studied copper corrosion inhibition using alkyl ester compounds [1–3]. Since then, the use of MD for simulating metal surface-inhibitor interaction had gained the attention of scientists and researchers all over the globe and had progressed vastly in the field of corrosion science.



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Copyright: © 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/). Ferrous metals are iron-based metals such as mild steel, stainless steel and cast iron that account for 80% of all metallic materials [4]. These metals are commonly used for transportation, construction and manufacturing industries, owing to their high durability, great tensile strength and relatively low cost. The major drawback of ferrous metals especially low carbon steel is its low corrosion resistance [5,6]. The corrosion and oxidation resistance of steel can be improved by adding alloy elements such as nickel and chromium, yielding high alloy steel such as duplex stainless steel [7]. However, the price of stainless steel is almost four times higher (2314 USD/tonne) compared to mild steel (614 USD/tonne) as of April 2020 [8]. For most cases with economical concern, using lower-cost material with proper corrosion protection is preferable.

Corrosion inhibitors (CIs) have been used extensively to prevent corrosion of ferrous metals [9–13]. Inorganic CIs underlying mechanism are electron sharing and/or filmforming action. However, toxic inorganic CIs such as chromates and nitrites are banned due to health and environmental concern. Hence, the scientific community is devoting major efforts to develop organic CIs that are environmentally benign. The inhibition mechanism of organic CIs can be generally explained by the adsorption of the inhibitor compounds on the metal surface by displacing water molecules. This occurs physically and/or chemically, depending on the nature, chemical structure and electron distribution of the inhibitor molecules. Typical organic CIs contain heteroatoms such as nitrogen, oxygen, sulphur and phosphorus with lone pairs of electrons which act as the active sites of adsorption. The adsorbed inhibitors form a thin layer of molecules which shields the active sites of corrosion reaction [14]. The key to further understand the mechanism of the inhibition lies in knowing the atomic and molecular level information on the metal inhibitor interface. MD simulation is capable of identifying this information that can help us understand the detailed mechanism of the inhibition. Other than the corrosion field, MD simulation also offers numerous advantages in various sectors such as renewable energy generation, food technology, medicine, and pharmaceutical [15–18]. A broad list of reviews of MD simulation application for corrosion sector as well as other sectors had been published in the literature [14,19–22]. In this context, numerous works have shown that MD simulation is a promising method to obtain the molecular level information of a system. Thus, in this paper, the basic principle of MD simulation along with the methods, parameters and applications in corrosion inhibition are reviewed. This review also focuses on the selection of parameters such as the force field, time step and ensemble in performing an MD simulation for corrosion studies, which to the best of our knowledge, has not been discussed in any review article found in the literature. The scope of this review is limited to recent studies of ferrous metals corrosion inhibition using CIs in acidic solution.

2. Corrosion of Ferrous Metals in Acidic Solution

2.1. Corrosion Mechanism

Corrosion is the deterioration of a metal as a result of interactions or chemical reaction with the surrounding environment. It is an electrochemical reaction which occurs due to anodic and cathodic reaction. In the case of ferrous metal corrosion, the anodic reaction is the oxidation of iron that can be expressed as follows:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \tag{1}$$

The generated electrons are consumed in cathodic reactions, which in an acidic environment is predominantly hydrogen evolution as shown in Equation (2) [23]. In an aerated condition where dissolved oxygen is present in the solution, a reaction in Equation (3) is also possible.

$$2H^+ + 2e^- \to H_2 \tag{2}$$

$$4H^+ + O_2 + 4e^- \to 2H_2O \tag{3}$$

Along with anodic and cathodic reactions, electron flows through the metal from anodic site to cathodic site and an ionic flows through the solution in which cations (positively charged ions) move from anode to cathode, and vice versa [24]. As the cations and anions interact between the anode and cathode, a precipitate of insoluble ferrous hydroxide is likely to form (Equation (4)). In excess oxygen, ferrous hydroxide is rapidly oxidized to ferric hydroxide (Equation (5)). The rust that is usually found on the surface of metal is the dehydrated form of ferric hydroxide, which is ferric hydroxide (Equation (6)). Figure 1 illustrates the processes of a ferrous metal corrosion system in acidic solution:

$$2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2 \tag{4}$$

$$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3 \tag{5}$$

$$2Fe(OH)_3 \to Fe_2O_3 + 3H_2O \tag{6}$$



Figure 1. Electrochemical process of ferrous metal corrosion in acidic solution.

2.2. Corrosion Inhibition of Ferrous Metal

A corrosion inhibitor (CI) is a substance that can reduce the corrosion rate of metal effectively. A wide range of CIs that include inorganic and organic (natural and synthetic) CIs has been discovered in the past decade [25]. Inorganic inhibitor compound is typically a compound that lacks carbon-hydrogen bonds. Zinc nitrate and sodium molybdate are examples of efficient inorganic inhibitors for steel and nickel respectively [26,27]. The understood mechanism of inorganic CIs is due to electron sharing and film-forming action [26,27]. On the other hand, the inhibition capability of organic CIs is believed to be due to the presence of heteroatoms such as oxygen, nitrogen, sulfur and phosphorus that exist as polar functional groups (hydroxyl, amine, methoxy, and carboxyl groups) in the compounds [14,25]. Generally, organic CIs inhibit corrosion by adsorbing physically and/or chemically on the interface of metal, forming several monolayers that block ions from reacting with the metal. The protective layer retards anodic, cathodic, or both reactions depending on the type of CI used. Nowadays, organic CI is preferred over inorganic CI due to sustainability, environmental, health and economical concerns [25].

In the perspective of ferrous metal corrosion inhibition in acidic solution, the inhibition starts as the heteroatoms in the structure of organic CI get protonated and adsorbed on the negatively charged iron surface due to electrostatic interaction [28]. This is known as physical adsorption or physisorption. At this stage, the inhibitor ions are not in direct contact with the iron atoms, but rather "bridged" by a layer of water molecules or negative ions from acid such as chloride from hydrochloric acid [29,30]. This kind of adsorption is relatively weak, reversible, nearly temperature-independent and has low adsorption energy (typically 20 kJ/mol) [31]. During the later stages of interaction, the neutral form of CI molecules begins to move towards the iron surface and start to share their free electron pairs (p electrons) from the heteroatoms and π electrons from the double and triple bonds,

respectively, with the vacant d-orbital of the iron atoms [29]. This chemical interaction forms a strong chemical bond which is recognized as chemical adsorption or chemisorption. It is characterized as a slow, irreversible, temperature-dependent and has high adsorption energy (equal or more than 40 kJ/mol).

The adsorption strength is significantly affected by a plethora of variables related to the inhibitor such as the molecular weight, electron density, asymmetry, polarity, hydrophobicity and solubility. As the performance of a CI is significantly affected by the adsorption strength, it is crucial to take all parameters into consideration. Conventional experimental method alone is not capable of considering molecular level parameters into account. Hence, the use of a computational tool such as MD along with experimental approaches such as gravimetric analysis, electrochemical impedance spectroscopy, potentiodynamic polarization and cyclic voltammetry has therefore been of considerable benefit.

3. Molecular Dynamics Simulation of Ferrous Metal Corrosion Inhibition

3.1. Basics of Molecular Dynamics Simulation

Molecular dynamics (MD) simulation is a method used to compute the trajectory or transport properties of a macromolecular structure. In simpler words, it determines how atoms or molecules move within a specified time frame by conducting calculations computationally. The goal of MD simulation may vary depending on one's interest, but typically it is conducted to obtain the equilibrium properties of the system [14]. In the context of a corrosion system, for instance, an inhibitor molecule surrounded with water molecules that mimic a corrosive solution positioned next to the iron atoms that represent the metal surface, the MD simulation is intended to reach the most stable state (lowest energy at equilibrium) of the inhibitor molecule. Based on the result, one can determine whether the inhibitor molecule prefer to be adsorbed or desorbed from the metal surface. Aside from that, the strength of the adsorption can also be obtained in terms of energy which can be used to screen inhibitor molecules before conducting a real experiment.

The underlying principle behind an MD simulation is simple and straightforward. Given the initial positions (coordinates) and velocity of all atoms in a system, the force acting on each atom by all other atoms in the system in terms of potential energy can be obtained. The potential energy that acts on an atom can be categorised into two; bonding potentials (bonds, angles and dihedrals) and non-bonding potentials (van der Waal and Columbic). Upon knowing the potential energy, the force can be derived from the energy function. This stage of computing the force is the utmost importance in getting a reliable and accurate simulation result [32]. Finally, Newton's law of motion is integrated in order to calculate the acceleration of each atom, enabling the prediction of the new position of each atom as a function of time [33]. Again, the new potential energy, force and acceleration can be obtained from the updated position and velocity of each atom. As this step is repeated, it is possible to simulate the trajectory of each atom that describes each configuration of the atoms within a small time interval in real-time. The overall step in MD simulation is illustrated in Figure 2.



Figure 2. Computational flow of molecular dynamics simulation.

3.2. Steps in Performing a Molecular Dynamics Simulation for Corrosion Studies

3.2.1. Construction of a Corrosion System

The first step of performing an MD simulation for corrosion system is constructing the components of the interaction model. A corrosion system typically consists of two components; an inhibitor molecule and a metal surface. Typically, the inhibitor molecule is sketched and its geometry is optimized to obtain an accurate geometry. In real condition, the inhibitor does not exist in isolated space of vacuum, but as an aqueous phase in the corrosive solution [32]. Besides, the degree of inhibitor adsorption is greatly influenced by the surroundings as an unbounded inhibitor is more vigorous in interacting with metal surface compared to inhibitor surrounded by solvent molecules [14]. Hence, to ensure that the simulation resembles actual scenario as close as possible, the simulation should be performed in the presence of water molecules and ions, typically ranging from 200 to 600 total molecules combined [34–36]. In addition, the proportion of water molecules to the ions should also roughly resemble the actual concentration of the solution. For instance, 1 M of hydrochloric acid (HCl) is composed of 55.5 mol of water molecules (H₂O), 1 mol of hydronium ions (H_3O^+) and 1 mol of chloride ions (Cl^-) , which makes the ratio of water to hydrogen chloride is 55.5:1 or roughly 500:9. Thus, it can be deduced that the most suitable composition of 1M HCl aqueous phase is 500 H₂O, 9 H₃O⁺ and 9 Cl⁻. The aqueous phases used for several acidic solutions in recently reported studies are summarized in Table 1.

Acid Solution	Aqueous Phase	Reference
HC1		
0.1 M	556 H_2O , 1 H_3O^+ and 1 Cl^-	[37]
0.5 M	491 H_2O , 9 H_3O^+ and 9 Cl^-	[38]
1.0 M	500 H ₂ O	[39]
	H_2O , H_3O^+ and Cl^-	[40]
	233 H_2O , 15 H_3O^+ and 15 Cl^-	[41]
	$350 \text{ H}_2\text{O}$, $10 \text{ H}_3\text{O}^+$ and 10 Cl^-	[42]
	491 H ₂ O, 9 H ₃ O ⁺ and 9 Cl ⁻	[43,44]
	500 H_2O , 5 H_3O^+ and 5 Cl^-	[45]
	533 H_2O , 5 H_3O^+ and 5 Cl^-	[46]
	H ₂ O	[47]
15% (4.86 M)	500 H ₂ O	[48]
H_2SO_4		
0.5 M	H ₂ O	[49]
	400 H ₂ O	[50]
1.0 M	500 H ₂ O, 20 H ₃ O ⁺ and 10 SO_4^{2-}	[51]
HClO ₄		
0.1 M	400 H ₂ O, 15 H ₃ O ⁺ and 15 ClO ₄ ⁻	[52]

Table 1. Aqueous phase of acidic solution in MD simulation.

The second component resembles the metal surface which is composed of iron atoms in the case of ferrous metal. In normal temperature and pressure, iron exists as body-centred cubic (bcc) structure with (110), (100), (211), (311), (111), (321) and (210) as the most densely packed surfaces as depicted in Figure 3. Typically, a Fe(110) surface is used as the adsorption site for simulation of corrosion inhibitor adsorption because it contributes the largest area of the Fe crystal and is the most thermodynamically stable facet among the others [53–58]. Contrarily, Zhu et al. [59] demonstrated the use of Fe(100) surface as the adsorption site for 2-aminobenzimidazole derivative inhibitor. The order of surface energy of the iron surface is Fe(110) < Fe(100) < Fe(111), which makes Fe (110) to be the most stable, followed by Fe(100) and Fe(111) facets [60]. Regardless of the type of ferrous metal (carbon steel, alloy steel or stainless steel) studied experimentally, pure iron atoms instead of a mixture of iron with alloying elements are usually used for theoretical studies [11,38,61–63]. Table 2 shows the implementation of several Fe surfaces for different types and grade of ferrous metal in corrosion inhibition studies in acid solution.



Figure 3. Top view of most densely packed surfaces of bcc structure, reproduced from [53], with permission from Elsevier, 2007.

Ferrous Metal	Fe Lattice	Reference
	Mild steel	[40,41,43,45,51,52,64,65]
	Fe LatticeMild steelCarbon steelC35E steelN80 steelQ235 steelXC48 steelX80 steelAISI 304 stainless steelMild steelCarbon steelQ235 steel	[44,66]
	C35E steel	[42]
$E_{2}(110)$	N80 steel	[48]
Fe (110)	Q235 steel	[39,49,50]
	XC48 steel	[67]
	X80 steel	[46]
	AISI 304 stainless steel	[38]
$E_{2}(100)$	Mild steel	[47]
Fe (100) Carbon steel		[59]
Fe (001)	Q235 steel	[68]

Table 2. Fe surfaces used to resemble several types and grades of ferrous metals in MD simulation.

3.2.2. Specifying Boundary Condition

Simulating a bulk of system with an infinite number of molecules is computationally expensive. As the positions, velocities and forces of each atom need to be recomputed in every time step, the calculation time required for a large number of molecules (>10000) using average performance computers is infinite [69]. Constructing a smaller system in an enclosed simulation box is a less expensive option, but the forces acting on atoms near the "walls" of the box and atoms in the center differs significantly due to boundary effect. To solve this issue, periodic boundary condition (PBC) can be implemented to the system, which replicates the simulation box in all directions as images. These images behave exactly like the original simulation box and have the same number, position and momentum of atoms. PBC is always employed for the simulation of corrosion inhibitor adsorption onto the metal surface to avoid any arbitrary boundary effects [70–74].

3.2.3. Simulation Tool

To perform any computational simulation, it is necessary to use a tool or module that is usually embedded in the simulation software. Forcite or Forcite Plus is an advanced tool in Materials Studio Software (BIOVIA Materials Studio 2017, 17.1.0.48, San Diego, CA, USA), to compute classical simulation that utilizes molecular mechanics or molecular dynamics [75]. It can be used to calculate energy, optimize geometry or determine the trajectory of a system. Forcite module has been extensively used for a broad range of properties determination in countless types of system such as the interaction property of nanoform zinc oxide with Covid19, the mechanical properties of polyvinyl chloride/highdensity polyethylene composite, the mechanism of Schiff base as an anticancer drug and a lot more [76–78]. On top of that, Forcite is the most frequently used module for corrosion inhibition studies using MD simulation reported in the literature [45,79–82].

3.2.4. Selection of Ensembles

An ensemble is a collection of microscopic states (position and velocity of atoms at a timestep) that have the same thermodynamic state such as energy, E, volume, V, temperature, T, pressure, P and number of particles, N. The most common ensembles for MD simulation are microcanonical ensemble (constant N,V,E), canonical ensemble (constant N,V,T) and isothermal-isobaric ensemble (constant N,P,T). Canonical ensemble or NVT ensemble is usually used for the determination of adsorption energy in a corrosion system [11,49,83–85]. With the implementation of this ensemble, the number of particles, volume and temperature of the system are conserved in every step of calculation or integration.

3.2.5. Choosing Time Step

MD simulation works by integrating Newtonian equation to compute the state of a system (velocity and position) by given the initial state of the system. Any mistake in specifying the numerical integrator will produce biased results and errors in calculation. Hence, it is crucial to select the proper time step to obtain a reliable result. As the integration in MD simulation computes the movement of atomic-scale system with chemical bonds, the scale of time step should match the scale of the fastest vibrational frequency of the chemical bonds which is on the order of fractions of femtosecond (fs). Ideally, the time step should be set as large as possible in order to simulate for a longer time span, with less integration step. The relationship of the time step with the integration step and length of the simulation is expressed as follows:

$$Integration step = \frac{length of simulation (fs)}{time step (fs)}$$
(7)

However, large time step will cause "exploding"; a phenomenon where the total energy increases rapidly with time, which causes atomic collision [86]. On the other hand, small time steps will cause unnecessary calculations which extend the calculation time. Therefore, the time step should be set optimum value, at least ten times lower than the highest frequency of the system [87]. For the simulation of compounds with hydrogen bonds (such as corrosion inhibitor molecules) that has the highest vibrational frequency among other chemical bonds, the ideal time step is 1–2 fs [39,88].

3.2.6. Selection of Force Field

A force field is a set of mathematical expression that is used to calculate the forces in terms of the potential energy of the interacting atoms in a simulation system. It is considered as the soul of MD as the selection of force field affects directly towards the accuracy of the simulation results [89]. The Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field is extensively used relative to other force fields for the simulation of corrosion inhibitor adsorption [11,90–92]. It is originally designed to describe forces for organic liquids and polymers, and then extended further for the application of organic compounds with H, C, N, O, S, P and metals [93]. Due to the broad coverage of COMPASS force field, it is a suitable force field to be used for a corrosion system, which typically contains organic compounds (inhibitor molecule) and metal atoms.

3.3. *Parameters Derived from Molecular Dynamics Simulation of Corrosion Inhibition* 3.3.1. Adsorption Energy

Adsorption energy or interaction energy resembles the amount of energy released or absorbed as 1 mole of adsorbate molecules is adsorbed on the adsorbent. The information of adsorption energy is crucial to understand the underlying mechanism of the adsorption. The main factors that affect the energy include the electronegativity, valence of adsorbate, and the coordination of active sites (adsorbent) [94]. In view of corrosion inhibition, the inhibitor molecule is regarded as the adsorbate, while the metal surface is referred as the adsorbent. It can be expressed as follows:

$$E_{ads} = E_{total} - \left(E_{metal + solution} + E_{inhibitor} \right)$$
(8)

where E_{ads} is the adsorption energy, E_{total} is the total energy of the whole system, $E_{metal + solution}$ is the energy of the metal and the aqueous phase and $E_{inhibitor}$ is the energy of the inhibitor molecule. A negative value of adsorption energy is an indication of an exothermic and spontaneous process. This means that the inhibitor is attracted towards the metal surface, causing adsorption of either physically, chemically or a combination of both. The greater the magnitude (more negative) of the energy released, the stronger the strength of adsorption, and hence the higher the corrosion inhibition efficiency [14].

3.3.2. Binding Energy

Binding energy is the energy required to separate a particle from a system. It can be viewed from several standpoints according to the distance and energy scale of the system of interest. Electron binding energy, atomic binding energy, bond dissociation energy, nuclear binding energy and gravitational binding energy are the types of binding energy for different systems. The adsorption of CIs on the metal surface is closely related to bond dissociation energy because the formation and dissociation of chemical bonds are ubiquitous in the process [94]. Hence in the perspective of corrosion inhibition, binding energy is the energy required to desorb the inhibitor molecule from the metal surface due to bond dissociation. It is regarded as the reciprocal of adsorption energy as expressed below:

$$E_{bind} = -E_{abs} \tag{9}$$

where E_{bind} is the binding energy. The greater the binding energy (more positive), the stronger the attraction force between the inhibitor and the metal surface, and hence the higher the inhibition efficiency.

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3.3.3. Inhibitor Molecule Orientation

The adsorption configuration of the inhibitor molecule on the metal surface is an important finding from MD simulation. Upon several calculation iterations done by the software, the most stable configuration of inhibitor with lowest energy level will be obtained. The final configuration of adsorption depends on the chemical structure and electron density of the inhibitor molecule [95]. Figure 4 shows the example of different possible configuration of sodium 2-quinoxalinecarboxylate on an iron substrate [96]. Typically, horizontal, flat or planar orientation as depicted in Figure 4b is preferred for better corrosion inhibition performance because it can cover a larger surface area of metal and has higher binding energy [14].



Figure 4. Adsorption configuration of sodium 2-quinoxalinecarboxylate on iron substrate; (**a**) vertical and (**b**) horizontal orientation, reproduced from [96], with permission from Elsevier, 2016.

3.4. Application of Molecular Dynamics Simulation for Corrosion Inhibition Studies of Ferrous Metal in Acidic Solution

The corrosion inhibition of ferrous metals in acidic media has been extensively investigated due to its exceptional industrial use [97]. As it is crucial to understand the mechanism of corrosion inhibition, MD simulation is normally performed alongside experimental procedures. Haque et al. carried out an experimental and an MD simulation to elucidate the inhibition of mild steel corrosion in 1 M hydrochloric acid (HCl) by two synthesized amino acid derivatives; hydroxyl-containing zwitterion (H-zwitterion) and sulfur-containing zwitterion (S-zwitterion) [54]. Two types of adsorption sites that represent the metal surface was used in the simulation for comparison purposes; neutral Fe (110) and α -Fe₂O₃ (110). The MD simulation results revealed that both inhibitors were adsorbed in a planar position with both surfaces (Figure 5a,b). However, S-zwitterion provided a greater extend of adsorption than the H-zwitterion based on the interaction and binding energy. This suggests that the presence of sulfur atom promotes bonding with the iron atoms. The adsorption model of S-zwitterion is illustrated in Figure 5c. Aside from that, it





Figure 5. Side view of (**a**) H-zwitterion; and (**b**) S-zwitterion adsorbed on α -Fe₂O₃ (110) surface; and (**c**) adsorption model of S-zwitterion, reproduced from [54], with permission from Elsevier, 2020.

Saranya and coworkers described the adsorption of three synthesized pyran derivatives; ethyl 2-amino-4-(4-hydroxyphenyl)-6-(*p*-tolyl)-4*H*-pyran-3-carboxylate (HP), ethyl 2-amino-4-(4-methoxyphenyl)-6-(*p*-tolyl)-4*H*-pyran-3-carboxylate (MP) and ethyl 2-amino-4-(4-hydroxy-3,5-dimethoxyphenyl)-6-(*p*-tolyl)-4*H*-pyran-3-carboxylate (HDMP) on Fe (110) surface in 1 M H₂SO₄ [51]. It is interesting to note that only the *p*-tolyl-pyran skeleton of all molecules preferred to adsorb completely on the iron surface with flat orientation. This phenomena can be explained by the non-planar geometry of the inhibitor molecules, which caused only the most electron-rich site to be adsorbed on the metal surface. The strongest adsorption property on Fe (110) surface was manifested by HDMP followed by MP and HP molecule. The presence of oxygen atoms, π electrons and electron-donating groups in the molecular structure can be attributed as the driving force for adsorption.

The inhibition effect of pentaglycidyl ether pentabisphenol A of phosphorus (PGEP-BAP) phosphorus polymer on carbon steel corrosion in 1 M HCl was investigated by Hsissou and coworkers [36]. According to the MD simulation result, it was revealed that the PGEPBAP molecule was adsorbed in a parallel position to the metal surface. The molecule surface with phosphorus and oxygen heteroatoms was oriented towards the iron atom. 1478 kcal/mol of adsorption energy was obtained from Monte Carlo simulation, but there was no quantification of interaction or binding energy reported from MD simulation.

El Arrouji et al. performed an experimental, Monte Carlo simulation and MD simulation to study the corrosion inhibition of two pyrazole derivatives which are (*E*)-N'-benzylidene-2-(3,5-dimethyl-1*H*-pyrazol-1-yl) acetohydrazide (DPP) and (*E*)-N'-(4-chlorobenzylidene)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)acetohydra zide (4-CP) on steel in 1 M HCl [41]. The Monte Carlo simulation suggested that 4-CP inhibitor exhibited stronger adsorption on Fe (110) surface with -109.18 kcal/mol adsorption energy compared to DPP inhibitor with -103.38 kcal/mol adsorption energy, respectively. This finding was in agreement with the experimental result, which showed that the inhibition efficiency

of 4-CP is relatively higher than DPP inhibitor. The lowest energy configuration of the inhibitor and Fe (110) surface obtained from MD simulation is shown in Figure 6. The site of the inhibitor molecules with oxygen and nitrogen heteroatoms were oriented towards the metal surface, but it is apparent that the orientation of the overall molecule was not completely parallel. This is probably due to the arrangement of heteroatoms, which is more concentrated at one side of the molecule instead of evenly distributed throughout the structure. No energy value was computed from the MD simulation.



Figure 6. Side view of (**a**) DPP; and (**b**) 4-CP adsorbed on Fe (110) in HCl, reproduced from [41], with permission from Elsevier, 2020.

An MD simulation study on the adsorption of quercetin-3-glucuronide, a major compound of *Lavandula mairei* (LM) ethanolic extract, on mild steel in 1 M HCl was reported by Berrissoul et al. [98]. The final configurations of the inhibitor and their respective interaction energy after equilibrium at different simulated temperatures (303, 313, 323 and 333 K) are reflected in Figure 7. It is apparent that the LM inhibitor was adsorbed in planar arrangement to the Fe (110) surface, which is due to the aromatic rings and oxygen atoms that are present in the inhibitor molecule. As the temperature was increased, it was found that the interaction energy of the LM inhibitor-Fe (110) system was becoming less negative. This indicates that the adsorption strength is weaker at elevated temperature, hence the LM inhibitor should be intended for lower temperature application to anticipate high performance.

Zhang et al. investigated the inhibition of mild steel corrosion in 15% HCl using the extract of aloe gel, which is composed of polysaccharides. For MD simulation purpose, four main monomers of the polysaccharide; glucose, mannose, galactose and fructose were used to resemble the extract. The final positions of the inhibitors were completely parallel to the Fe (110) surface, thanks to the planar geometry of the monomers. Based on the computed binding energy, fructose exhibited the strongest adsorption strength (598.35 kJ/mol), followed by mannose (593.96 kJ/mol), galactose (587.47 KJ/mol) and glucose (578.22 kJ/mol).



Figure 7. Side view of adsorbed LM molecule on Fe (110) and its interaction energy at different temperatures reproduced from [98], with permission from Elsevier, 2020.

The chemical structures, MD simulation parameters, and the results of the MD of several investigated organic corrosion inhibitors for various types of ferrous metal in acidic solution are summarized in Table 3. Generally, most studies had focused on the corrosion inhibition of mild steel, which is probably due to the extensive use in the industry relative to other ferrous metal and its poor resistance towards acid corrosion. With regard to the acidic media, the majority of the reviewed literature investigated corrosion inhibition in HCl solution, followed by H_2SO_4 . It seemed like there was less than a handful of studies that performed MD simulation in other acidic media such as perchlorate acid and ethanoic acid. In terms of the simulation result, after a detailed review, it can be inferred that most inhibitors were adsorbed on the metal surface in planar or parallel orientation. This configuration is preferred as the molecule can cover a larger surface of the metal and displace more water molecules and other corrosive species.

Table 3. Name and chemical structure of corrosion inhibitors for ferrous metals in acid solution, MD simulation parameters and MD results.

		MD Barram c'arra		
Name and Chemical Structure of Corrosion Inhibitor	Metal and Acid Solution	 Fe Surface Simulation Box Size Aqueous Phase Time Step and Simulation Time or Total Step Module, Force Field and Ensemble 	MD Result Orientation and Binding Energy (kJ/moL)	Ref.
Bis-phosphonic acid	XC48 steel 1 M HCl	Fe (110) 17.20 Å × 22.93 Å × 22.93 Å H ₂ O 0.1 fs, 50 ps COMPASS, NVT	Horizontal to Fe surface E _{binding} = 5027.03	[67]
Surfactant	Mild steel 15% HCl	Fe (110) 23.00 Å × 23.00 Å × 10.03 Å 500 H ₂ O 1 fs Forcite	Parallel to Fe surface E _{binding} = 1971.50	[47]
Amine derivative	Mild steel 1 M HCl	Fe (110) 24.82 Å × 24.82 Å × 38.10 Å 100 H ₂ O, 1 Cl ⁻ , 1 H ₃ O ⁺ 1.0 fs, 500 ps COMPASS	Flat position E _{binding} = 1562.3	[99]
Losartan potassium drug $\kappa^* \qquad \qquad$	Q235 steel 1 M HCl	Fe (110) 24.3 Å × 17.2 Å × 67.1 Å 500 H ₂ O 1.0 fs, 500 fs COMPASS, NVT	Horizontal orientation E _{binding} = 1120.89	[39]
Vanillin Schiff base	Mild steel 1 M HCl	Fe (110) 40.11 Å × 40.11 Å × 78.00 Å 150 H ₂ O, 15 Cl ⁻ , 15 H ₃ O ⁺ 1.0 fs, 100 fs COMPASS, NVT	Close to Fe surface E _{binding} = 1199.05	[100]
Bamboo leaves extract	Cold rolled steel 0.1 M Cl ₃ CCOOH	Fe (001) 31.53 Å × 31.53 Å × 15.30 Å 1.0 fs, 1000 ps COMPASS, NVT	Flat orientation E _{binding} = 1104.35	[101]
Cassava starch ternary graft copolymer $\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}$	Steel 1 M HCl	Fe (001) 31.53 Å × 31.53 Å × 15.30 Å 500 H ₂ O 1.0 fs, 1000 ps COMPASS, NVT	Flat orientation E _{binding} = 1072.90	[102]
Quinoxaline compound $\downarrow \downarrow $	Mild steel 1 M HCl	Fe (110) 24.82 Å × 24.82 Å × 25.28 Å 491 H ₂ O 1.0 fs, 200 fs COMPASS, NVT	Distributed over Fe surface E _{binding} = 903.70 kJ/mol	[103]

Table 3. Cont.				
Name and Chemical Structure of Corrosion Inhibitor	Metal and Acid Solution	 MD Parameters Fe Surface Simulation Box Size Aqueous Phase Time Step and Simulation Time or Total Step Module, Force Field and Ensemble 	MD Result Orientation and Binding Energy (kJ/moL)	Ref.
Amino acid HO N S derivatives	Mild steel 1 M HCl	Fe (110), α-Fe2O3 (110) 24.82 Å × 24.82 Å × 35.69 Å 491 H ₂ O, 9 Cl ⁻ , 9 H ₃ O ⁺ 1.0 fs, 2000 ps Forcite, COMPASS, NVT,	Planar orientation E _{binding} = 829.17	[54]
Isoniazid derivative $(\mathbf{x}_{n}, \mathbf{y}_{n}, \mathbf{y}_{n}, \mathbf{y}_{n}, \mathbf{y}_{n}) = (\mathbf{x}_{n}, \mathbf{y}_{n})$	Mild steel 1 M HCl	Fe (110) 24.82 Å × 24.82 Å × 25.14 Å 491 H ₂ O, 9 Cl [−] , 9 H ₃ O ⁺ 1.0 fs, 5000 ps COMPASS, NVT	Close to Fe surface E _{binding} = 804.20	[104]
Substituted acridines	Mild steel 15% HCl	Fe (110) 24.82 Å × 24.82 Å × 43.21 Å 500 H₂O, 5 Cl [−] , 5 H₃O ⁺ 1.0 fs, 500 ps COMPASSII, NVT	Parallel to Fe surface E _{binding} = 791.40	[105]
Bisbenzothiazole derivative $S \sim S \sim S$	Mild steel 1 M HCl	Fe (110) 39.85 Å \times 39.85 Å \times 76.79 Å 150 H ₂ O, 15 Cl ⁻ , 15 H ₃ O ⁺ 1.0 fs, 200 ps COMPASS, NVT	Distributed over Fe surface E _{binding} = 789.20	[106]
Thiadiazole-Derived Bis-Schiff Base	Mild steel 1 M HCl	$\begin{array}{l} \mbox{Fe}\ (110) \\ 24.82\ \mbox{\AA}\ \times\ 24.82\ \mbox{\AA}\ \times\ 35.69\ \mbox{\AA} \\ 491\ \mbox{H}_2O, 9\ \mbox{Cl}^-, 9\ \mbox{H}_3O^+ \\ 1.0\ \mbox{fs}, 2000\ \mbox{ps} \\ \mbox{COMPASS}, NVT \end{array}$	Parallel to Fe surface E _{binding} = 758.79	[107]
Thiazole carboxylates $C \rightarrow C \rightarrow S \rightarrow N \rightarrow C \rightarrow C$	Mild steel 1 M HCl	Fe (110) 25.02 Å × 25.02 Å × 38.32 Å 491 H ₂ O, 9 Cl ⁻ , 9 H ₃ O ⁺ 0.1 fs, 5000 ps Forcite, COMPASS, NVT	Planar arrangement E _{binding} = 753.20	[43]
Phosphonic acid	Mild steel 1 M HCl	Fe (110) 9.78 Å × 29.78 Å × 60.13 Å 500 H ₂ O, 10 Cl ⁻ , 10 H ₃ O ⁺ 1 fs, 100,000 steps Forcite, NVT	Parallel to Fe surface E _{binding} = 722.00	[108]
Pyridinium-derived ionic liquid \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow	Mild steel 1 M HCl	Fe (110) 32.27 Å × 32.27 Å × 34.13 Å 500 H ₂ O, 5 Cl ⁻ , 5 H ₃ O ⁺ 1.0 fs, 400 ps Forcite, COMPASS, NVT	Parallel to Fe surface E _{binding} = 689.27	[109]
Benzimidazole derivative	Mild steel 1 M HCl	Fe (110) 32.27 Å × 32.27 Å × 31.13 Å 500 H ₂ O, 5 Cl ⁻ , 5 H ₃ O ⁺ 1 fs, 400 ps Forcite, COMPASS, NVT	Parallel to Fe surface E _{binding} = 641.94	[45]

		Table 3. Cont.		
Name and Chemical Structure of Corrosion Inhibitor	Metal and Acid Solution	 MD Parameters Fe Surface Simulation Box Size Aqueous Phase Time Step and Simulation Time or Total Step Module, Force Field and Ensemble 	MD Result Orientation and Binding Energy (kJ/moL)	Ref.
Aloe polysaccharide	Mild steel 15% HCl	Fe (110) 24.82 Å × 24.82 Å × 43.21 Å 500 H ₂ O, 5 Cl ⁻ , 5 H ₃ O ⁺ 1.0 fs, 500 ps COMPASSII, NVT	Parallel to Fe surface E _{binding} = 598.75	[110]
Quinoxaline derivative	Mild steel 1 M HCl	Fe (110) 500 H ₂ O, 5 Cl ⁻ , 5 H ₃ O ⁺ NVT Forcite	Parallel to Fe surface E _{binding} = 583.12	[111]
Amine derivative	Mild steel 1 M HCl	Fe (110) 24.82 Å × 24.82 Å × 38.10 Å 100 H ₂ O, 1 Cl ⁻ , 1 H ₃ O ⁺ 1.0 fs, 500 fs COMPASS	Parallel to Fe surface E _{binding} = 541.55	[112]
Mixture of cellulose derivative and Gemini surfactant $H_{3}C$, $H_{3}C$,	Mild steel 1 M HCl	$\begin{array}{l} \mbox{Fe}\ (110) \\ 24.82\ \mbox{\AA}\ \times\ 24.82\ \mbox{\AA}\ \times\ 35.69\ \mbox{\AA} \\ 491\ \mbox{H}_2O, 9\ \mbox{Cl}^-, 9\ \mbox{H}_3O^+ \\ 0.1\ \mbox{fs}, 2000\ \mbox{ps} \\ \mbox{COMPASS}, NVT \end{array}$	Parallel to Fe surface E _{binding} = 507.48	[113]
Pyrazole derivatives	Mild steel 1 M HCl	Fe (110) 14.89 Å × 14.89 Å × 6.45 Å 230 H ₂ O, 15 Cl ⁻ , 15 H ₃ O ⁺ 1 fs, 500 ps COMPASSII, NVT	CI molecule oriented towards Fe atoms E _{binding} = 456.81	[41]
Pyran derivatives OH O O CH ₃	Mild steel 1 M H ₂ SO ₄	Fe (110) 27.45 Å × 27.45 Å × 29.14 Å 500 H ₂ O, 5 10 SO4 ^{2–} , 20 H ₃ O ⁺ Forcite, COMPASS, NVT	Flat configuration E _{binding} = 438.47	[51]
Lemon seeds extract	Mild steel 1 M HCl	Fe (110) 25.22 Å × 25.22 Å × 39.62 Å 1.0 fs, 2000 ps Forcite, COMPASS, NVT	Parallel to Fe surface E _{binding} = 375.65	[64]
Chondroitin sulfate $H_{O}, Q_{O}, $	Mild steel 1 M HCl	Fe (110) 24.82 Å × 24.82 Å × 25.14 Å 491 H ₂ O, 9 Cl [−] , 9 H ₃ O ⁺ 1.0 fs, 5000 ps COMPASS, NVT	Parallel to Fe surface E _{binding} = 334.24	[114]
Pistachio nut extract \downarrow_{OH}^{H} \downarrow_{H}^{OII} $\downarrow_{H}^$	Mild steel 1 M HCl	Fe (110) H ₂ O, Cl ⁻ , H ₃ O ⁺ (and vacuum) 1.0 fs, 50,000 steps COMPASS, Forcite	Distributed over Fe surface E _{binding} = 317.25	[115]

Table 3. Cont.				
Name and Chemical Structure of Corrosion Inhibitor	Metal and Acid Solution	 MD Parameters Fe Surface Simulation Box Size Aqueous Phase Time Step and Simulation Time or Total Step Module, Force Field and Ensemble 	MD Result Orientation and Binding Energy (kJ/moL)	Ref.
Penicillamine drug	Mild steel 1 M HCl	Fe (110) H ₂ O, Cl ⁻ , H ₃ O ⁺ 1.0 fs, 1000 fs COMPASS, NVT	Close to Fe surface E _{binding} = 268.00	[88]
Artemisia herba alba Extract	Mild steel 1 M HCl	Fe (110) 27.30 Å × 27.30 Å × 37.13 Å 500 H ₂ O, 5 Cl ⁻ , 5 H ₃ O ⁺ 1 ns, 200 ps Forcite, COMPASS, NVT	Parallel to Fe surface E _{binding} = 256.00	[116]
Rosa damascena flower extract $\downarrow HO, \downarrow HO, I H$	Mild steel 1 M HCl	Fe (110) 491 H ₂ O, 9 Cl ⁻ , 9 H ₃ O ⁺ 1.0 fs, 20,000 steps COMPASS, NVT	Planar orientation E _{binding} = 237.69	[117]
Ziziphora leaves extract $\downarrow \downarrow $	Steel 1 M HCl	Fe (110) 24.82 Å × 24.82 Å × 38.10 Å 491 H₂O, 9 Cl [−] , 9 H₃O ⁺ 1.0 fs, 1000 ps COMPASS, NVT	Parallel to Fe surface E _{binding} = 216.68	[118]
Phosphonium compound	Mild steel 0.5 M H ₂ SO ₄	Fe (110) 37.22 Å × 37.22 Å × 38.69 Å 5 Cl ⁻ , 5 H ₃ O ⁺ 1.0 ns, 600 ps Forcite, COMPASS, NVT	CI molecule located on Fe atoms E _{binding} = 212.75	[119]
Lavandula mairei extract	Mild steel 1 M HCl	Fe (001) 27.30 Å × 27.30 Å × 33.13 Å 500 H ₂ O, 5 Cl ⁻ , 5 H ₃ O ⁺ 1.0 fs, 400 ps Forcite, COMPASS, NVT	Distributed over Fe surface E _{binding} = 197.75	[98]
Phosphorus polymer	Carbon Steel 1 M HCl	Fe (110) 39.72 Å × 39.72 Å × 56.08 Å 500 H ₂ O, 50 Cl ⁻ , 50 H ₃ O ⁺ 1.0 ps, 300 ps COMPASSII, NVT	CI molecule positioned above Fe atoms	[36]

4. Future Prospects

MD simulations have been used to obtain molecular-level information in order to understand the mechanism of corrosion inhibition. The expected results of MD simulation in corrosion studies can be categorized into two: (1) the configuration of the inhibitor molecule upon adsorption on the metal surface and (2) the strength of adsorption based on the computed energy values (adsorption and binding energy). The main challenges for upcoming circumstances are to further explore the ability of MD simulation to provide value-added results that is able to describe the corrosion inhibition mechanism in more detail. For instance, the simulation of more than one inhibitor molecule can be performed with the aid of high performance computers, which is possible to simulate the adsorption isotherm (such as Langmuir, Freundlich and Temkin) theoretically. Possibly, the electrochemical potential of the corrosion system can be modelled with the integration of MD simulation with other computational methods.

With respect to the current technology of MD simulation, the scope of reported corrosion inhibition studies which concentrated on the effect of the inhibitor molecular structure and different metal substrate towards inhibition performance is only the tip of the iceberg. Other feasibly conducted studies such as the effect of different types of aqueous phase and flow condition (stagnant or agitated) towards the adsorption strength have yet to be reported elsewhere. In addition, the presence of impurities in the actual metal (such as carbon in mild steel) could also affect the performance of corrosion inhibitor to an extent. More broadly, future research should consider the alloying elements of the metal instead of only using pure metal atoms in the simulation model. Apparently, the use of mixtures of atoms in MD simulation model; such as iron and carbon that resembles steel, is well established in other field especially in material science. Hence, it is possible to construct similar system for corrosion application as well. It is also worth to mention that the metal surface roughness is another parameter that can be taken into account in an MD simulation model of inhibitor adsorption. Quite a number of studies related to this parameter in other fields are available in the literature, yet none was found in the field of corrosion. Since the surface roughness is a significant parameter in the experimental approach, adding this parameter into consideration will produce results that are applicable to real cases.

It is encouraging to mention that the use of radial distribution function (RDF) in MD in the field of corrosion science has been emerging over the past years. RDF provides the information that can be used to determine the type of adsorption of the inhibitor on the metal atoms; either physically or chemically. It is anticipated that more corrosion inhibitor adsorption simulation that utilizes RDF are to be published in the future.

5. Conclusions

In this review, MD simulation is described in terms of its basic principles, computational flow and expected outcome on the inhibition mechanism of ferrous metal in acidic solution. Steps in performing MD simulation such as the construction of a corrosion system, and selection of the boundary condition, simulation tool, ensembles, time step and force field are emphasized in the hope to provide readers better understanding in the theoretical approach of corrosion studies.

Aside from that, some recent works on interactions between a corrosion inhibitor and ferrous metal surface in acid solution studied using MD simulation have been collected and summarized in this review. It can be concluded that most inhibitors are adsorbed on the metal surface in a planar or parallel orientation, which larger surface coverage of the metal, and hence better performance. The vital parameters quantified from the MD simulation such as binding energy and adsorption energy are useful to determine the degree of adsorption between the inhibitor and metal atoms. The insights gained from this review may be of assistance to researchers in developing new and improved corrosion inhibitors. Finally, the challenges and future trends of MD simulation in corrosion science are also obviously highlighted in the final section. Considerably more work will need to be done to overcome the challenges and to boost the potential of MD simulation in the field of corrosion science.

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