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Comparative molecular dynamics assessment of gallic, ellagic and rosmarinic acids as green corrosion inhibitors on iron surfaces

Evaluación comparativa mediante dinámica molecular de los ácidos gálico, elágico y rosmarínico como inhibidores verdes de corrosión en superficies de hierro

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Abstract

Corrosion of metallic materials is an industrial and economic challenge that drives the search for environmentally friendly alternatives to conventional chemical inhibitors. In this work, molecular dynamics simulations were employed to study the adsorption and corrosion inhibition mechanisms of natural inhibitors on an iron surface. Gallic acid, ellagic acid, and rosmarinic acid were evaluated in aqueous media, together with a combined system containing gallic and ellagic acids, in order to analyze possible synergistic effects. System stability was assessed through potential energy analysis, while adsorption and interfacial organization were characterized using density profiles and radial distribution functions. Inhibitor mobility was analyzed through mean square displacement.

The results show that all inhibitors adsorb strongly onto the iron surface, forming stable layers that partially displace interfacial water. Ellagic acid exhibits predominantly flat adsorption and low mobility, gallic acid shows higher interfacial mobility, and rosmarinic acid presents an extended interfacial accumulation. In the combined system, an increase in surface coverage is observed, providing evidence of synergistic adsorption behavior.

Keywords: Corrosion inhibition, Molecular dynamics, Natural inhibitors, Interfacial adsorption, Metal surface.

Resumen

La corrosión de los materiales metálicos es un desafío industrial y económico que impulsa la búsqueda de alternativas ambientalmente amigables a los inhibidores químicos convencionales. En este trabajo se emplearon simulaciones de dinámica molecular para estudiar los mecanismos de adsorción e inhibición de la corrosión de inhibidores naturales sobre una superficie de hierro. Se evaluaron los ácidos gálico, elágico y rosmarínico en medio acuoso, así como un sistema combinado que contiene ácidos gálico y elágico, con el fin de analizar posibles efectos sinérgicos. La estabilidad del sistema se evaluó mediante la energía potencial, mientras que la adsorción y la organización interfacial se caracterizaron a partir de perfiles de densidad y funciones de distribución radial. La movilidad de los inhibidores se analizó mediante el desplazamiento cuadrático medio.

Los resultados muestran que todos los inhibidores se adsorben fuertemente sobre el hierro, formando capas estables que desplazan parcialmente el agua interfacial. El ácido elágico presenta una adsorción predominantemente plana y baja movilidad, el ácido gálico mayor movilidad interfacial y el ácido rosmarínico una acumulación interfacial extensa. En el sistema combinado se observa un incremento en la cobertura superficial, lo que evidencia un comportamiento de adsorción sinérgica.

Palabras clave: Inhibición de la corrosión, Dinámica Molecular, Inhibidores naturales, Adsorción interfacial, Superficie metálica.

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1 Introduction

The corrosion of metallic materials represents one of the main technological and economic challenges for modern industry, due to its direct impact on safety, operational reliability, and maintenance costs of equipment and infrastructure. Globally, the annual cost of corrosion has been reported to reach approximately USD 2.5 trillion, equivalent to ≈ 3.4% of the global Gross Domestic (GDP), underscoring the need to develop more efficient and sustainable control and mitigation strategies (Verma *et al*., 2018; Association for Materials Protection and Performance [AMPP], 2025).

One of the most widely used strategies for mitigating corrosion in metals is the application of inhibitors, whose performance is mainly associated with their ability to adsorb onto the metal surface and form a protective barrier against the corrosive environment. These inhibitors can be synthetic molecules (e.g., chemical inhibitors), biological, or derived from natural sources. However, many synthetic chemical inhibitors present disadvantages related to toxicity and environmental impact, which has driven the development and evaluation of inhibitors with lower ecological risk and improved sustainability (Verma *et al*., 2018; Marzorati *et al*., 2019; Alrefaee *et al*., 2021).

In this context, corrosion inhibitors of natural origin have gained increasing interest because they are often biodegradable and, in many cases, are obtained by extraction as mixtures of active compounds (Esquivel-Rojas *et al*., 2020; Moustafa *et al*., 2022; Shwetha *et al*. 2024; Thacker and Ram, 2025). In particular, the molecular-level study of green inhibitors is relevant because experimental approaches do not always allow a clear distinction between the contributions of individual molecules, and simulation studies frequently focus on a single inhibitor molecule, ignoring possible interactions in combined systems (El-Haddad *et al*., 2019; Sulaiman *et al*., 2019).

Among natural compounds with inhibitory potential, phenolic compounds stand out, particularly gallic acid, ellagic acid, and rosmarinic acid, which have been proposed as promising alternatives due to their affinity for metal surfaces and their favorable sustainability profile (Velázquez-González *et al*., 2014; Asadi *et al*., 2019; Belakhdar *et al*., 2020; Al-Jahdaly, 2023). In this sense, the present work aims to evaluate these biological inhibitors through molecular dynamics simulations, analyzing both their individual behavior and the potential synergistic effects between molecules.

Computational tools, particularly molecular dynamics (MD) and molecular simulation in general, have established themselves as useful methods for analyzing the corrosion inhibition mechanisms at the atomic level, as they enable the study of molecular orientation, adsorption, and interactions at the metal–electrolyte interface, reducing the dependence on extensive and costly experimental tests (Verma *et al*., 2018; Haris *et al*., 2021; Castillo-Robles *et al*., 2024; Arachchige *et al*., 2025).

In studies of inhibitor adsorption on iron, it is common to represent the metal surface as crystalline iron and to employ ideal crystallographic planes. The Fe(110) surface is widely used as an adsorption site in inhibition simulations, as it is one of the most representative and thermodynamically stable facets among the densely packed iron surfaces (Haris *et al*., 2021).

Regarding the analysis of molecular dynamics results, parameters such as the radial distribution function (RDF) are commonly used to describe the probability of finding pairs of atoms at a given distance and to extract relevant structural information from simulations (Chen *et al*., 2021). Despite the growth of theoretical studies on corrosion inhibition, limitations related to the simulation environment and the evaluation of combined systems have been reported, highlighting the need for studies that explicitly consider conditions closer to real scenarios and the effects of inhibitor combinations.

This paper presents a comparative evaluation based on molecular dynamics simulations of the behavior of gallic, ellagic, and rosmarinic acids as green inhibitors on iron surfaces in aqueous media, through the analysis of structural, energetic, and dynamic properties, RDF, density profiles, system energies, and mean square displacement (MSD). The aim is to contribute to the understanding of inhibitor–metal–electrolyte interactions at the molecular level and to compare the relative performance of these compounds under equivalent simulation conditions.

2 Materials and methods

The molecular dynamics simulations performed in this study were carried out with the aim of analyzing the behavior of green inhibitors on iron surfaces in aqueous media at the atomic and molecular levels. For this purpose, the GROMACS (Hess *et al*., 2008; Abraham *et al*., 2015) computational package was employed for system construction, simulation execution, and generation of molecular dynamics trajectories. The construction, editing, and visualization of the inhibitor molecules, as well as the structural inspection of the simulated systems, were performed using the VMD program (Humphrey *et al*., 1996), which facilitated the verification of molecular geometries and the correct initial arrangement of the system components.

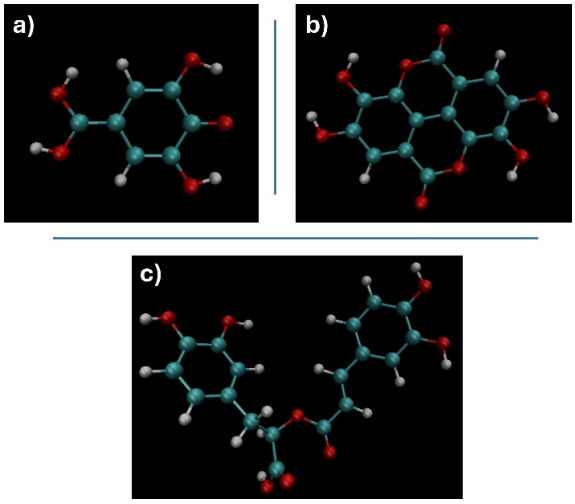

Figure 1. Optimized three-dimensional molecular structures of (a) gallic acid, (b) ellagic acid, and (c) rosmarinic acid.

The methodology employed included the selection of the inhibitor molecules, the construction of the metal surface model, the assembly of the simulation systems, and the definition of a common simulation protocol for all cases, to ensure comparable conditions among the different systems studied.

2.1 *Description of the inhibitor molecules*

This study considered three naturally occurring phenolic compounds with inhibitory potential: gallic acid, ellagic acid, and rosmarinic acid, whose molecular structures are shown in Figure 1. These compounds were selected due to their widespread presence in natural sources, their sustainability profile, and the presence of multiple oxygenated functional groups that give them potential affinity for metal surfaces, making them relevant candidates for corrosion inhibition studies using molecular dynamics simulations.

Gallic acid (Figure 1a) is a phenolic acid with a simple aromatic structure containing three hydroxyl groups and one carboxyl group. This structural configuration provides a high density of functional sites capable of participating in intermolecular interactions with the surrounding environment. The distribution of these functional groups favors its potential affinity for metal surfaces and its interaction with the aqueous medium, without assuming the explicit formation of chemical bonds during the simulation.

Ellagic acid (Figure 1b) exhibits a more rigid polycyclic structure, characterized by a condensed aromatic system incorporating multiple hydroxyl and carbonyl groups. This structural arrangement limits its conformational flexibility but provides an extended aromatic surface and several functional sites that may influence its orientation and relative proximity to the metal surface, as well as its behavior in solution.

Rosmarinic acid (Figure 1c), in contrast, exhibits a more complex and flexible molecular structure, consisting of two aromatic rings linked by an aliphatic chain that incorporates oxygenated functional groups. This greater structural flexibility, together with the presence of multiple hydroxyl and carboxyl groups, allows for a wider range of conformations and relative orientations, which may influence its dynamic behavior at the metal–solution interface.

The molecular structures of the inhibitors were constructed, edited, and visualized using molecular modeling and visualization tools, which allowed for verification of the initial geometry and correct assignment of atoms prior to their incorporation into the simulation systems. For all the systems studied, the inhibitor molecules were considered in their neutral form in order to comparatively analyze their behavior and interactions with the metal surface under equivalent simulation conditions.

2.2 *Construction of the iron surface model*

The iron surface was modeled as a crystalline slab built from a cubic arrangement consisting of 3920 iron atoms. This slab was designed to represent an ideal metallic surface suitable for adsorption studies, providing a sufficiently large surface area to minimize finite-size effects and to ensure a representative metal–solution interface during the simulations.

The interactions between iron atoms were described using a classical non-bonded Lennard–Jones (12–6) potential, as implemented within the molecular dynamics framework. In this representation, the metallic substrate is treated as a solid surface without explicitly accounting for metallic bonding, which offers a stable and computationally efficient description of the iron surface and is commonly adopted in molecular dynamics studies of metal–organic interfaces.

To focus the analysis on the behavior of the inhibitor molecules at the metal–solution interface, the iron slab was treated as a rigid substrate by applying positional restraints to all iron atoms throughout the simulations. This approach ensures a well-defined and stable surface while preventing structural distortions of the metallic lattice over the simulation time.

The resulting iron surface model was subsequently employed as the solid substrate for assembling the inhibitor–metal–solution systems described in the following sections.

2.3 *Construction of the simulation systems*

The simulation systems were constructed to evaluate the behavior of different phenolic inhibitors on an iron surface in aqueous media under comparable

conditions. Four systems were considered: (i) Fe + water + gallic acid, (ii) Fe + water + ellagic acid, (iii) Fe +water + rosmarinic acid, and (iv) a combined system containing Fe + water + gallic acid + ellagic acid. All individual systems contained the same number of inhibitor molecules (10 molecules), while the combined system contained 10 molecules of gallic acid and 10 molecules of ellagic acid.

For all cases, the simulation setup was initialized with the iron slab placed at the center of a cubic simulation box under vacuum conditions. Subsequently, the inhibitor molecules were introduced into the simulation box and randomly distributed in the region surrounding the metal surface. After positioning the inhibitors, the systems were solvated by adding explicit water molecules to represent the aqueous medium.

The aqueous environment was modelled using the TIP3P water model (Jorgensen *et al*., 1983), which is widely employed in simulations of biomolecules and interfacial systems. The inhibitor molecules were described using the CHARMM36 force field (Huang and MacKerell, 2013), which provides a consistent and well-established framework for modelling organic molecules. Interactions between the inhibitor molecules and the iron surface were treated through non-bonded Lennard–Jones and electrostatic interactions within the classical molecular dynamics framework, as commonly employed in simulation studies of corrosion inhibitors adsorbed on metallic surfaces (Sharma *et al*., 2019; Verma *et al*., 2018). This approach allows the analysis of interfacial adsorption, molecular organization, and dynamic behavior at the metal–solution interface under comparable simulation conditions, where adsorption is predominantly governed by non-bonded interactions. Charge transfer and chemisorption effects were not explicitly considered in the present model.

In all simulations, periodic boundary conditions were applied in the three spatial directions to avoid artificial surface effects associated with finite simulation boxes. This construction protocol ensured that all systems shared the same geometric and environmental conditions, allowing a direct comparison of the behavior of the different inhibitors at the iron–solution interface.

2.4 *Simulations details*

All molecular dynamics simulations were performed using GROMACS version 2021.2 (Hess *et al*., 2008; Abraham *et al*., 2015). The simulation protocol consisted of three sequential stages: energy minimization, equilibration, and production runs. Energy minimization was carried out for $5X10^5$ steps to eliminate unfavorable contacts and stabilize the initial configurations. Subsequently, an equilibration stage of $1X10^6$ steps was performed to allow the systems to reach thermal stability prior to data collection.

Production simulations were then conducted for $5X10^6$ steps under the NVT ensemble. All simulations were performed at a temperature of 298 K, which was maintained using the Nosé–Hoover thermostat. The equations of motion were integrated using the leap-frog algorithm, with a time step of 0.002ps.

The simulations were carried out in a cubic simulation box with dimensions of $l_x = l_y = l_z = 9.88$ nm. Periodic boundary conditions were applied in the three spatial directions to represent an extended system and avoid finite-size effects. Non-bonded interactions were treated using the Verlet cutoff scheme with a cutoff distance of 1.2 nm for both Lennard–Jones and short-range electrostatic contributions. Long-range electrostatic interactions were calculated using the Particle Mesh Ewald (PME) method. Bond constraints involving hydrogen atoms were handled using the LINCS algorithm, allowing the use of a 0.002 ps integration time step while maintaining simulation stability.

To preserve the structural integrity of the metallic substrate, positional restraints were applied to all iron atoms, ensuring that the iron slab remained rigid throughout the simulations. Trajectories and energy data were recorded during the production stage for subsequent structural, energetic, and dynamic analyses.

Adsorption-related parameters were estimated from the molecular dynamics simulations. The Fe–inhibitor interaction energy was obtained from the non-bonded contributions, considering Lennard–Jones and short-range Coulombic interactions. Surface coverage (Γ) was calculated from the number of inhibitor molecules and the surface area, while the equivalent concentration was estimated from the number of molecules and the simulation box volume.

The dynamic behavior of the inhibitors at the iron–solution interface was analyzed from the mean square displacement (MSD) obtained from the production trajectories. Apparent diffusion coefficients were estimated from the linear region of the MSD curves using the Einstein relation, $D = \frac{1}{6}\frac{d\langle r^2(t)\rangle}{dt}$, where D is the apparent diffusion coefficient and $\langle r^2(t)\rangle$ is the mean square displacement. Residence times were estimated by monitoring the permanence of inhibitor molecules within the interfacial region during the simulation time. These properties were obtained as time-averaged values over equilibrated trajectories, and the associated variability is reflected in the fluctuations of the MSD profiles and in the fitting procedure used to determine diffusion coefficients.

3 Results and discussion

In this section, the molecular-level behavior of phenolic inhibitors at the iron–solution interface is analyzed using molecular dynamics simulations. The results are organized into two complementary approaches.

First, the interfacial structure is examined through density profiles and radial distribution functions (RDF), supported by interaction energy and surface coverage (Γ) analyses to describe adsorption behavior and molecular arrangement at the interface. Second, the dynamic behavior of the inhibitors is evaluated using mean square displacement (MSD), from which apparent diffusion coefficients and residence times near the surface are determined, providing insight into molecular mobility and stability of adsorption.

The stability of the simulated systems was verified through the time evolution of the potential energy, confirming that stable equilibrium conditions were achieved in all cases. In addition, the convergence of structural (density profiles and RDF) and dynamic (MSD) descriptors indicates that the selected simulation time (10 ns) is sufficient to capture the relevant adsorption and interfacial behavior within the scope of this study.

3.1 Interfacial structure and adsorption behavior

The structural organization at the iron–solution interface was analyzed using density profiles along the surface-normal direction for all systems, as shown in Figure 2. In all cases, the water density profile exhibits a bulk-like region in the center of the simulation box, followed by a pronounced depletion near the iron surface. This behavior reflects the exclusion of water molecules from the immediate vicinity of the metal due to the presence of adsorbed inhibitor molecules.

For the individual systems, all inhibitors show a non-uniform density distribution with preferential accumulation near the surface, confirming their affinity for the iron interface. In the case of ellagic acid, a well-defined interfacial peak is observed (see the inset (a) in Figure 2), indicating strong localization and the formation of a compact adsorbed layer that partially displaces interfacial water molecules. Gallic acid also exhibits accumulation near the surface, as shown in inset (b) in Figure 2, although with a less pronounced and more localized density profile, consistent with its smaller molecular size. In contrast, rosmarinic acid displays a broader density distribution along the surface-normal direction (see the inset (c) in Figure 2), suggesting that the molecule occupies a wider interfacial region, likely due to its larger structure and greater conformational flexibility.

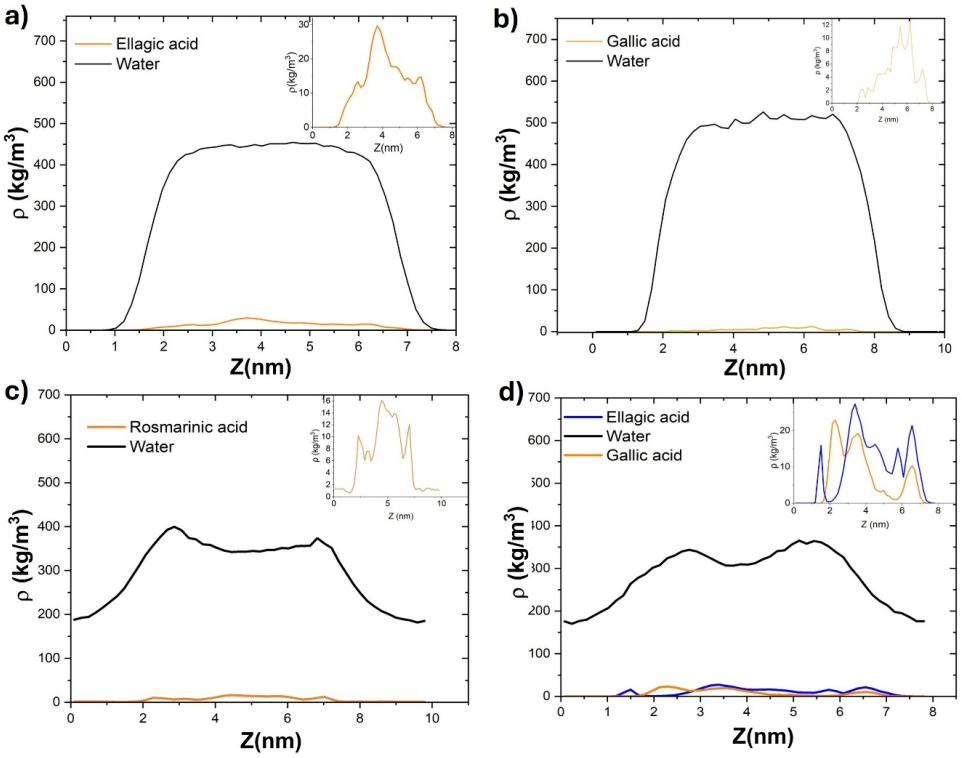

Figure 2. Density profiles along the surface-normal (z) direction for (a) ellagic acid, (b) gallic acid, (c) rosmarinic acid, and (d) the combined system. Insets show a zoom of the inhibitor density near the interface.

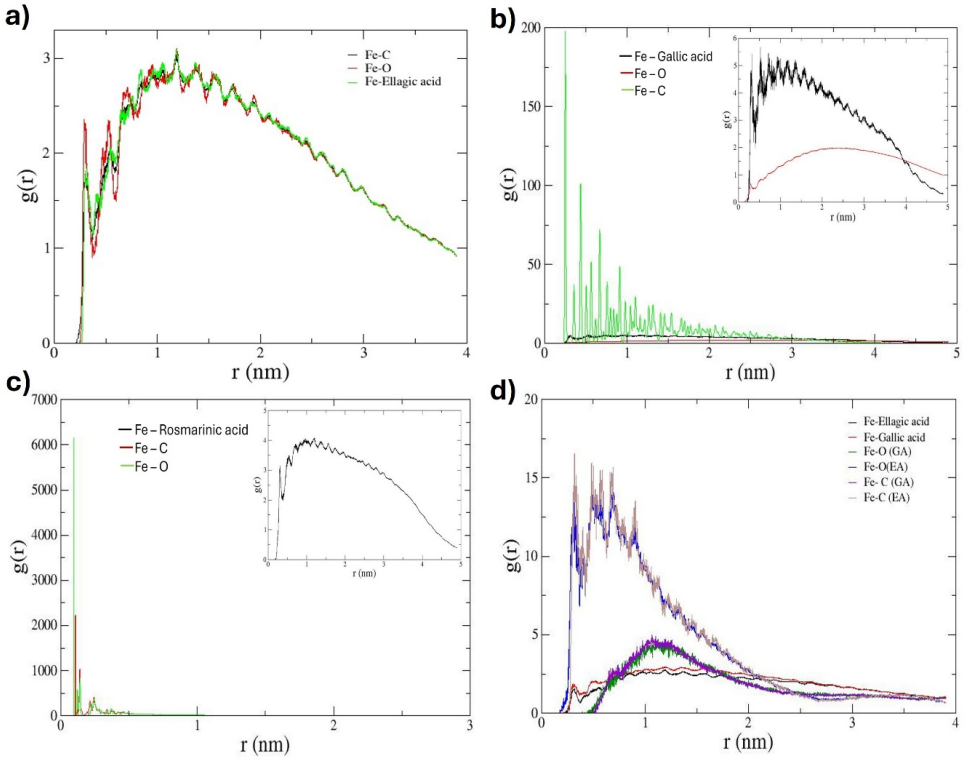

Figure 3. Radial distribution functions (RDF) between iron atoms and inhibitor atoms for (a) ellagic acid, (b) gallic acid, (c) rosmarinic acid, and (d) the combined system. Insets highlight the main features of the distributions.

In the combined system, the simultaneous presence of ellagic and gallic acids leads to a more pronounced displacement of water from the vicinity of the iron surface compared to the individual cases (see inset (d) in Figure 2). Both inhibitors accumulate within the interfacial region, with partially overlapping density maxima, indicating that they coexist near the surface rather than competing for adsorption sites. This enhanced and more continuous surface coverage constitutes a clear structural signature of synergistic adsorption.

The adsorption mechanism inferred from the density profiles is further supported by the radial distribution functions between iron atoms and selected atomic species of the inhibitors, as shown in Figure 3. For all systems, the RDFs reveal short-range correlations between the iron surface and the inhibitor atoms, confirming their preferential location in the interfacial region.

For the individual systems, distinct adsorption behaviors are observed. In the case of ellagic acid, the Fe–C and Fe–O RDFs exhibit similar profiles, indicating that carbon and oxygen atoms are located at comparable distances from the surface. This suggests a predominantly flat or quasi-parallel adsorption geometry, where the aromatic framework interacts collectively with the metal surface.

Gallic acid shows sharper RDF features at short distances, particularly for Fe–C interactions, indicating more localized interactions with the surface, likely due to its smaller size and greater flexibility. In contrast, rosmarinic acid exhibits strong short-range correlations, especially for Fe–O interactions, suggesting that oxygen-containing groups play a key role in surface anchoring, leading to a more complex adsorption configuration.

In the combined system, the RDF profiles indicate that both inhibitors interact simultaneously with the iron surface through carbon and oxygen atoms. This supports their coexistence at the interface and suggests a cooperative adsorption mechanism arising from complementary interactions.

Differences in RDF magnitude are attributed to the interfacial nature of the systems and the limited number of inhibitor molecules; therefore, the analysis focuses on the position and shape of the distributions.

The adsorption behavior described above is supported by the quantitative parameters summarized in Table 1, including Fe–inhibitor interaction energy, surface coverage (Γ), and equivalent concentration. As shown in Table 1, all individual systems were constructed under identical conditions, resulting in the same surface coverage and equivalent concentration. Therefore, the observed differences in adsorption behavior can be attributed primarily to the molecular structure of the inhibitors.

Table 1. Adsorption-related parameters obtained from molecular dynamics simulations for the individual inhibitor systems.

System	E (Fe-Inhibitor) (kJ/mol)	Γ (molecules/nm^2)	Equivalent Concentration (mM)
Ellagic acid	-2193.01	0.102	17.2
Gallic acid	-1712.18	0.102	17.2
Rosmarinic acid	-2533.09	0.102	17.2
Gallic + Ellagic acid	See text	0.205	34.4

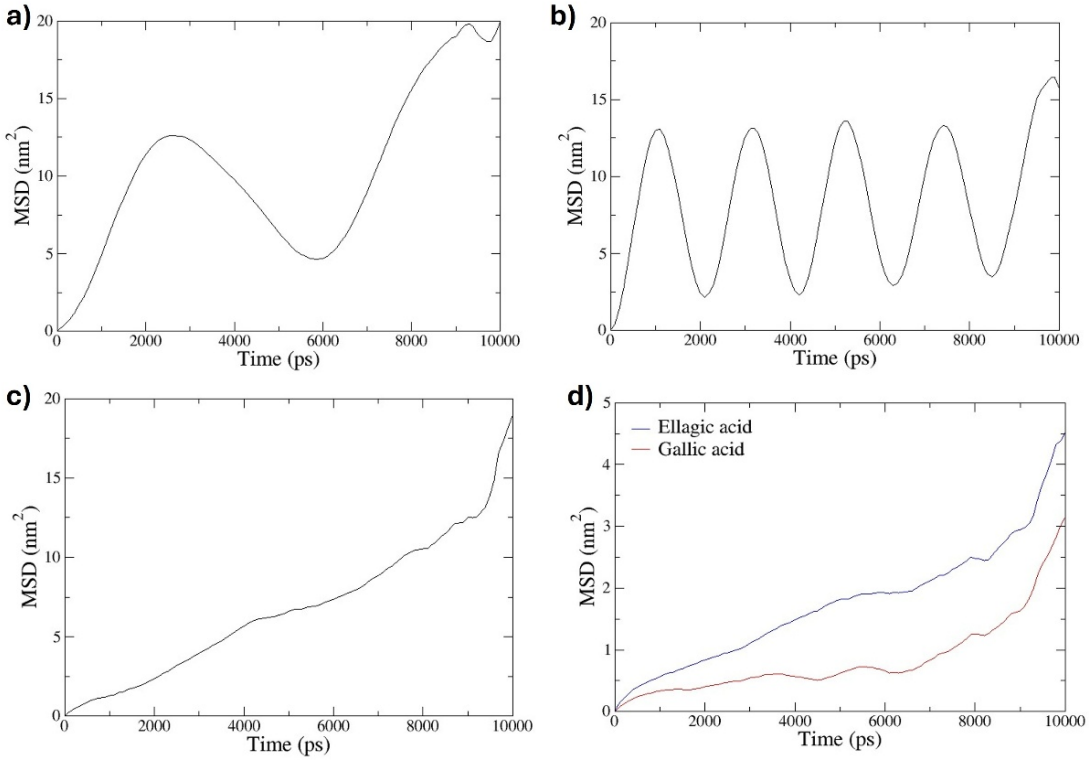

Figure 4. Mean square displacement (MSD) as a function of time for (a) ellagic acid, (b) gallic acid, (c) rosmarinic acid, and (d) the synergistic system containing gallic and ellagic acids at the Fe–solution interface.

Among the individual systems, rosmarinic acid exhibits the most negative interaction energy, indicating the strongest affinity for the iron surface, followed by ellagic and gallic acids. This trend is consistent with the structural observations, where rosmarinic acid shows both extended interfacial distribution and strong localized interactions.

For the combined system, the increased surface coverage reflects the simultaneous presence of both inhibitors. The interaction energies show that each molecule interacts favorably with the iron surface, with Fe–gallic (-1921.50 kJ/mol) and Fe–ellagic (-1196.39 kJ/mol) contributions dominated by Lennard–Jones interactions. In addition, the interaction between ellagic and gallic acids (-176.31 kJ/mol) indicates a moderate but favorable intermolecular attraction, supporting their coexistence at the interface. This behavior is consistent with the density profiles, which show the presence of both inhibitors in the interfacial region, while the RDF analysis confirms that both molecules interact with the surface through carbon and oxygen atoms. Together, these results support a cooperative adsorption mechanism and the formation of a more stable and continuous interfacial layer.

3.2 Dynamic behavior of inhibitors at the interface

The dynamic behavior of the inhibitors at the iron–solution interface was evaluated through the mean square displacement (MSD), as shown in Figure 4. In general, the MSD profiles reveal that the motion of the molecules is strongly influenced by the interfacial environment, where adsorption onto the metal surface restricts their mobility compared to bulk diffusion. The higher mobility observed during the equilibration stage supports this interpretation, suggesting that the inhibitors initially explore the aqueous region before reaching a more confined interfacial state during production.

Table 2. Apparent diffusion coefficients and residence times obtained from the MSD analysis for the individual and synergistic inhibitor systems at the Fe-solution interface.

System	Inhibitor	Apparent diffusion coefficient ($1X10^{-5}$ cm^2/s)	Residence time (ns)
Ellagic acid	Ellagic acid	Not reliably determined	10
Gallic acid	Gallic acid	Not reliably determined	10
Rosmarinic acid	Rosmarinic acid	0.2231	10
Synergistic system	Gallic acid	0.0107	10
Synergistic system	Ellagic acid	0.0448	10

For the individual systems, clear differences are observed depending on the molecular structure of each inhibitor. Ellagic acid exhibits an initial increase in MSD followed by regions with reduced slope, indicating that once adsorbed onto the surface, its mobility becomes significantly restricted (Figure 4a). This behavior is consistent with the formation of a compact and stable interfacial layer, as previously suggested by the density profiles and RDF analysis.

In contrast, gallic acid shows a more gradual and fluctuating increase in MSD over time (Figure 4b). Although the molecule remains associated with the surface, its behavior suggests a greater degree of lateral motion and local rearrangements within the adsorbed layer. This can be attributed to its smaller size and higher conformational flexibility, which allow it to explore the surface more dynamically while maintaining interfacial interactions.

Rosmarinic acid, on the other hand, presents the highest MSD values among the individual systems (Figure 4c), indicating a greater mobility within the interfacial region. The continuous increase in its MSD suggests that the molecule can access a wider region near the surface, which is consistent with its larger structure and multiple functional groups that enable both adsorption and surface diffusion. This behavior is quantitatively supported by the apparent diffusion coefficient reported in Table 2 (0.2231 $\times 10^{-5}$ cm^2/s), which reflects a comparatively higher interfacial mobility.

For the combined system, the MSD curves reveal a differentiated behavior between the two inhibitors (Figure 4d). Ellagic acid exhibits a higher displacement compared to gallic acid, indicating an increase in lateral mobility in the presence of the second molecule. In contrast, gallic acid shows more restricted motion, suggesting that it remains more localized at specific interfacial sites. This complementary behavior reflects a redistribution of roles at the interface, where one molecule contributes to dynamic surface coverage while the other favors local stabilization. This difference is reflected in the apparent diffusion coefficients, where ellagic acid (0.0448 $\times 10^{-5}$ cm^2/s) shows higher mobility than gallic acid (0.0107 $\times 10^{-5}$ cm^2/s) within the mixed system.

The apparent diffusion coefficients obtained from the MSD analysis are summarized in Table 2. In some cases, particularly for the individual ellagic and gallic acid systems, the MSD curves did not exhibit sufficiently extended linear regions during production to obtain reliable diffusion coefficients. Rather than indicating a limitation of the simulation, this behavior is associated with the confined nature of the interfacial region and the persistent adsorption of the inhibitors.

The relatively low apparent diffusion coefficients observed for all systems are therefore consistent with restricted surface mobility and should be interpreted as descriptors of interfacial dynamics rather than bulk diffusion. In addition, the residence time analysis shows that all molecules remain within the interfacial region throughout the simulation time (10 ns), with no evidence of complete desorption. This result further supports the stability of the adsorbed layers.

Overall, the dynamic analysis complements the structural observations, showing that although all inhibitors remain adsorbed on the surface, their mobility differs depending on their molecular characteristics. In the combined system, this balance between localized adsorption and lateral mobility leads to a cooperative behavior that favors the formation of a stable and adaptable protective layer at the metal–solution interface.

3.3 Comparison with experimental and theoretical studies

To place the present results in context, a comparison with experimental, theoretical (DFT), and previous molecular simulation studies for phenolic inhibitors was carried out. Experimental investigations have consistently reported high corrosion inhibition efficiencies for phenolic-rich systems, often exceeding 90% in acidic media (Radi *et al*., 2025; Abuelela *et al*., 2023). This behavior is commonly attributed to the adsorption of oxygen-containing functional groups and aromatic systems onto the metal surface, which promote the formation of protective layers (Abuelela *et al*., 2023; Li *et al*., 2023). For example, plant extracts containing gallic and ellagic acids have shown inhibition efficiencies around 91.8%, supported by electrochemical, DFT, and Monte Carlo analyses (Abuelela *et al*., 2023). Similarly, high inhibition efficiencies close to 97% have been reported for

rosmarinic-based systems, confirming their strong adsorption capability and protective behavior (Radi *et al*., 2025).

The behavior observed in the present simulations is consistent with these experimental findings. The density profiles, RDF analysis, and interaction energies indicate that the inhibitor molecules remain preferentially adsorbed at the Fe–solution interface. In particular, the Fe–inhibitor interaction energies and the residence time of 10 ns confirm the stability of the adsorbed layer, while the low apparent diffusion coefficients indicate restricted interfacial mobility rather than bulk diffusion. These features are consistent with the widely accepted mechanism for phenolic inhibitors, where hydroxyl, carbonyl, and π-electron systems govern adsorption and surface protection (Abuelela *et al*., 2023).

From a theoretical perspective, DFT and molecular-level studies have shown that inhibition efficiency is strongly correlated with the presence of electron-rich regions, particularly oxygen-containing functional groups and aromatic systems, which act as preferential adsorption sites on metallic surfaces (Mostafatabar *et al*., 2022; Abuelela *et al*., 2023; Bahlakeh *et al*., 2019). In addition, electrochemical and experimental analyses have confirmed that these compounds inhibit corrosion through adsorption and electron donation mechanisms at the metal interface (Fang *et al*., 2019). This interpretation is consistent with the present results, where structural analysis reveals preferential localization of these functional groups near the Fe–surface, supporting a favourable adsorption mechanism.

In the case of gallic acid, previous studies have shown that its inhibiting behavior strongly depends on the system and experimental conditions. For example, it has been reported that gallic acid may not exhibit inhibition in certain acidic environments due to limited adsorption on the metal surface (Kwolek *et al*., 2022). At the same time, recent analyses highlight its relevance as a green inhibitor while emphasizing that synergistic interactions with other compounds remain insufficiently explored (Li *et al*., 2023). In the present work, the gallic–ellagic system was evaluated under controlled molecular dynamics conditions, showing an increase in surface coverage from 0.102 to 0.205 molecules/nm^2, together with a favorable intermolecular interaction energy (-176.31 kJ/mol), providing quantitative evidence of cooperative adsorption at the Fe–solution interface.

Rosmarinic acid also shows strong agreement with previous experimental and computational studies. Radi *et al*. (2025) reported an inhibition efficiency of approximately 97% for rosmarinic-based systems, supported by electrochemical and surface analyses. In the present simulations, rosmarinic acid exhibits the most negative Fe–inhibitor interaction energy among the individual systems and the highest apparent interfacial mobility, suggesting a balance between strong adsorption and lateral surface diffusion, which is consistent with its reported behavior.

Previous computational studies have mainly focused on simplified representations, often evaluating adsorption at the level of individual molecules or limited surface coverage conditions. While these approaches have provided valuable insights into adsorption mechanisms, they do not always capture the behavior of inhibitor systems at concentrations commonly used in experimental studies. In this work, the simulations were performed using multiple inhibitor molecules corresponding to concentrations in the parts-per-million (ppm) range, allowing a more realistic representation of surface coverage and intermolecular interactions at the Fe–solution interface. This makes it possible to capture not only molecule–surface interactions, but also interactions between inhibitor molecules, which contribute to the formation and stabilization of the protective layer.

Within this framework, the combined analysis of structural (density profiles, RDF), energetic (interaction energies), and dynamic (MSD) descriptors provides a consistent description of the interfacial behavior, enabling the identification of cooperative effects between inhibitors under conditions that are closer to practical systems.

Conclusions

This work provides a molecular-level assessment of the adsorption behavior of gallic, ellagic, and rosmarinic acids on an iron surface in aqueous media using molecular dynamics simulations under comparable conditions. The combined analysis of density profiles, RDF, interaction energies, MSD, and residence times confirms that the three inhibitors exhibit a strong tendency to remain adsorbed at the Fe–solution interface, forming stable interfacial layers that partially displace water molecules from the metal surface.

The individual inhibitors showed distinct adsorption patterns associated with their molecular structure. Ellagic acid favored a compact and persistent adsorbed layer, consistent with its rigid aromatic framework and restricted mobility. Gallic acid exhibited stronger local rearrangement and lateral mobility, while rosmarinic acid showed the most favorable Fe–inhibitor interaction energy among the individual systems, together with extended interfacial distribution and higher apparent mobility. These differences indicate that adsorption strength and surface mobility are both important descriptors for evaluating inhibitor performance at the molecular scale.

The combined gallic–ellagic system revealed a cooperative adsorption behavior. The increase in surface coverage from 0.102 to 0.205 molecules/nm^2, together with the favorable ellagic–gallic interaction energy, supports the coexistence of both molecules at the interface rather than competitive adsorption. This synergistic arrangement promotes a more continuous and stable protective layer, in which localized anchoring and lateral mobility act in a complementary manner.

Overall, the results demonstrate that molecular dynamics can provide useful quantitative descriptors to compare green corrosion inhibitors beyond qualitative adsorption observations. The findings highlight the relevance of molecular structure, interfacial mobility, interaction energy, and cooperative effects in the design of natural inhibitor systems. In this sense, phenolic compounds, either individually or in combination, represent promising environmentally friendly alternatives for corrosion inhibition strategies.

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