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By Universitas Muhammadiyah Sidoarjo

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A Theoretical Study of Phytochemicals as Green Corrosion Inhibitors

Sebuah Studi Teoritis Tentang Fitokimia sebagai Penghambat Korosi Hijau

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Abstract

In this research, the effectiveness role of phytochemicals as agents for inhibiting corrosion was studied, including eugenol, cinnamaldehyde, and cinnamic acid. All quantum chemical calculations related to the phytochemical molecules studied using Biovia software and DFT technique are presented. A comparison of the adsorption properties on the iron(110) surface and corrosion inhibition of the studied phytochemicals is discussed. Furthermore, computational methods involving Monte Carlo simulations and molecular dynamics were employed to evaluate adsorption energies and stable configurations of inhibitors at the iron (110) surface. The phytochemicals under investigation have the following adsorption energies: Eugenol Eads = -98.442869 kcal/mol > Cinnamic acid Eads = -93.00807248 kcal/mol > Cinnamon Eads = -87.671968 kcal/mol. All theoretical studies confirmed that the surface adsorption effectiveness and corrosion inhibition performance of the studied phytochemicals follow the sequence; Eugenol (HH3) > cinnamic acid (HH2) > cinnamaldehyde (HH1).

Highlights:

Phytochemicals (eugenol, cinnamaldehyde, cinnamic acid) studied for corrosion inhibition.

Quantum chemical calculations and DFT technique used for adsorption properties.

Adsorption energy sequence: Eugenol > Cinnamic acid > Cinnamaldehyde.

Keywords: phytochemicals , DFT , corrosion inhibitors

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Introduction

The electrochemical reactions that leads to the degradation of metallic structures is known as corrosion. It is frequently resulting from incredibly corrosive environments along with hydrochloric acid and nitric. Failure to control corrosion will bring about big financial losses 1. Thus, intensive studies are being carried out for finding environmentally friendly and cost effective corrosion inhibitors with high efficiency. Natural organic compounds have great potential to be used as anti-corrosion agents. These compounds were chosen as anticorrosion agents because they meet the requirements of being an effective and economical agent, environmentally friendly, non-toxic and free of harmful contaminants. 2.

Extensive experimental studies have been carried out to investigate the efficacy of compounds derived from natural products as inhibitors of corrosion. As highly efficient corrosion inhibitors, alkaloids extracted from natural products are one of them 1,2 In the alkali form, components such as aromatic rings and atoms with lone electron pairs (e.g., oxygen and nitrogen) function as electron donors. These elements interact with metallic surfaces through electrostatic forces or by acting as electron donor-acceptor pairs. These compounds allow the inhibitor to bond strongly with the metal's surface, forming a thin protective barrier that reduces the rate of corrosive reactions 3.

The primary strength of cinnamon compounds is that they provide a natural and sustainable way to inhibit corrosion on metallic surfaces. Thus, restraining inhibitors of corrosion have been dismissed due to their poor performance and environmental hazards when used conventionally⁴. The compounds in cinnamon show clearly that they are able to establish protective barriers as well as prevent detrimental reactions Several scholars in the recent research have established that cinnamon compounds can act as active corrosion inhibitors⁵.

Corrosion is an electrochemical reaction that takes place in metal materials rendering them weak and shortens their life expectancy. It begins with corroding agents, including oxygen and moisture together with environmental contaminants reacting on the metal surface to give rise to rust or oxide layers. Corrosive substances must be located and removed because they can travel through the metal surface, thus hastening corrosion.⁶

These industries have also made extensive use of conventional corrosion inhibitors as protective coatings and anti-corroding chemicals for metal surfaces. Coatings, cathodic protection, and corrosion-resistant metals are a few of the most widely used conventional inhibitors. However, these methods have their flaws which make them less effective and viable in the long run.⁷

For instance, coatings are very susceptible to scratching or rubbing away and left bare metal that is instantly ready for corrosion. Likewise, the cathodic protection is anchored on sacrificial anodes that need to be replaced and safely disposed of in accordance with environmental regulations. Lastly, these corrosion resistant alloys tend to be expensive and cannot work in every application.^{7,8}

Since industries strive to find more environmentally friendly and less costly methods regarding corrosion inhibition, alternative routes are taken into account such as natural compounds.⁹ Several compounds of cinnamon have shown the ability to prevent corrosion and protect metal surfaces from it. As opposed to conventional inhibition, natural based ingredients represent an environmentally friendly and permanent solution for preventing corrosion.⁵

With respect to cinnamon, the naturally occurring anticorrosion compounds are cinnamaldehyde and eugenol. These materials can effectively eliminate the corrosion because they form a coating on metallic surfaces that prevents penetration of these agents.¹⁰ Furthermore, cinnamon compounds present in corrosion preventives may provide a long-term effective control without affecting the favorable physical and chemical properties of surface metal. Its sustainability and cost effectiveness would make it an increasingly effective replacement to traditional corrosion inhibitors.¹¹

The cinnamon ingredients exhibit unique activities through distinctive natural properties that prevent metal surfaces from corrosion. In this case, the mechanisms through which they prevent corrosion have also been widely explored with facts supporting their effectiveness. Among the important mechanisms is surface formation layer that protects metal against further corrosion. This obstacle occurs as a result of the adsorption of cinnamon ingredients on the metallic surface. In addition, cinnamon ingredients can eliminate corrosion-related free radicals and other ionic species in order to lower the rate of such reactions. The intrinsic antimicrobial properties of cinnamon due to the bioactive constituents that are inherent in it can also prevent metal corrosion caused by microorganisms.⁹⁻¹¹

A metal surface can be coated, sprayed or infused with materials encompassing cinnamon compounds. They are affordable, eco-friendly and permanent applications that might become a substitute for existing corrosion inhibitors. The other studies will undoubtedly reveal more regarding ways of cinnamon compounds and use as new inhibitors.¹²

In recent times components of cinnamon have grabbed a lot attention due to their capability as corrosion inhibitors. Several works have been conducted to ascertain the activity of such compounds as inhibitors hindering corrosion and protecting surfaces from metal.¹¹

For instance, one of the such studies published in Journal Applied Electrochemistry investigated cinnamon extracts' usage as an alternative inhibitor to Q235 steel forming a substrate for hydrochloric acid solution. It was established that cinnamon extract can effectively suppress the rate of steel disintegration.^{13,14}

In a research reported in the Journal of Molecular Liquids, cinnamon oil was found to be an inhibitor for mild steel corrosion in acidic medium. The experimental results indicated that the oil effectively inhibited the corrosion of steel.¹⁵ Furthermore, an article on a research paper in Materials Chemistry and Physics discussed cinnamon bark extract as one of the new naturally available sources that are used to prevent copper corrosion. The findings showed that the extract exhibited a good inhibitory activity, which protected against copper surface corrosion. Lastly, the mixing of experimental data and the description of specifics regarding corrosion inhibition mechanisms are substantially aided via theoretical analysis.¹⁶

In the modern-day paintings, the results of cinnamon compounds on corrosion inhibition of an iron floor had been investigated using a hybrid method based totally on DFT calculations and molecular modeling. The study shed light on the mechanism by way of which those compounds coat by means of focusing on their inhibition of surface metallic. The experimental outcomes validated the theoretical fashions used in this take a look at, adding to the body of proof assisting their predictive power in predicting corrosion inhibition response.^{11,12,14}

Methods

DFT-based quantum parametric calculations

To forecast the configuration, electron allocation, and electron movement to the iron surface of phenol, cinnamic acid, and cinnamon, quantum chemical simulations are employed. A widely adopted method for evaluating molecular reactivity is density functional theory (DFT)¹⁷. The ab initio approach is frequently utilized due to its high accuracy ¹⁸. During the quantum chemical calculation phase, the density functional theory (DFT) approach utilizing the 6-311++G(d,p) basis set is applied foundation unit is used for all calculations as well as the optimization of eugenol, Cinnamaldehyde, and cinamic acid. carried out, and the optimized geometries that result are determined to be minimal strength capacity surfaces by the use of harmonic vibration frequency calculations. The Gaussian 09 software is utilized to conduct calculations related to quantum chemistry. ¹⁹

Various quantum chemical parameters were computed, including absolute Electronegativity value (χ), global electrophilicity index (ω), global stiffness (η), softness (σ), First ionization energy (I), Electron attachment energy (A), fraction of electron transferred (ΔN), as well as the energy levels of the uppermost filled molecular orbital (EHOMO) and lowermost empty molecular orbital (ELUMO). According to the Koopman Theorem²⁰, EHOMO and ELUMO can be utilized to determine the First ionization energy (I), Electron attachment energy (A), Electronegativity value (χ), and global hardness (η). The First ionization energy (I) signifies the amount of energy needed to remove an electron from a molecule ²¹, and is connected to the EHOMO energy through the equation [1]

$$I = -E(\text{HOMO}) \quad [1]$$

The energy released when a proton is added to a system is referred to as electron attachment energy (A) ²¹ This energy is related to ELUMO through the equation [2]

$$A = -E(\text{LUMO}) \quad [2]$$

Electronegativity refers to an atom's or atomic group's ability to attract electrons²². This characteristic can be calculated using the equation [3]

$$X = (A + I) / 2 \quad [3]$$

Chemical hardness (η) measures an atom's ability to resist charge transfer ²³. An estimate of η can be obtained via equation [4]

$$\eta = (I - A) / 2 \quad [4]$$

As per Pearson's theory ²⁴, we can determine the percentage of electrons transferred (ΔN) from Cinnamaldehyde, Cinnamic acid, and Eugenol molecules to an iron atoms using equation [5]

$$\Delta N = (\chi(\text{Fe} - \text{Inh})) / (2(\eta\text{Fe} + \eta\text{Inh})) \quad [5]$$

Proportion of electrons transferred (ΔN) is determined using Equation (5), which incorporates the absolute electronegativity (χ_{inh}) and hardness (η_{inh}) of the inhibitor molecule, as well as the hardness of copper (η_{Fe}). These calculations utilize the theoretically derived electronegativity of bulk iron ($\chi_{\text{Fe}} = 7.0\text{eV}$),²⁵ and assume a global hardness of $\eta_{\text{Fe}} = 0\text{eV}$ for metallic bulk, where $I = A$.

The global electrophilicity index (ω) is expressed through Equation (6), which employs the global hardness and

electronegativity parameters.

$$\omega = \mu^2 / 2\eta \quad (6)$$

Based on Koopmans's theorem²⁰, EHOMO and ELUMO can be utilized to determine the First ionization energy (I), Electron attachment energy (A), Electronegativity value (χ), and global hardness (η). First ionization energy [I] is characterized as the energy important to eliminate an electron from a molecule²¹. It is associated with E(HOMO) through Condition [1].

Molecular modeling

Researchers utilized the Monte Carlo (MC) simulation technique to identify the most stable arrangement of inhibitor adsorption on a pristine iron surface^{26,27}. This simulation was executed using the Materials Studio 2020 software from BIOVIA. The process began by cleaving the iron crystal along the (110) plane, which previous studies have identified as the most stable surface. The Fe (110) plane was then expanded into an (8x8) supercell, creating a substantial surface area for inhibitor interaction^{27,28}. The simulation modeled the interaction between inhibitors and the Fe (110) surface within a 19.85 x 19.85 x 38.11 Å simulation box, employing periodic boundary conditions. This method aimed to simulate a representative portion of the interface while reducing the impact of artificial boundary effects. A 30 Å thick vacuum slab was also introduced above the Fe (110) plane. Throughout all simulations, the architectures of every system component under study were optimized using the compass force field.²⁹⁻³²

Result and Discussion

Improved structures

Cinnamon derivatives (phytochemicals), eugenol (HH3), cinnamaldehyde (HH2), and cinnamic acid (HH1) have several functional groups including allyl, groups that are carboxyl, hydroxyl, and hydroxyl (Table 1). Using hybrid DFT, figure 1 shows optimal structure of inhibitory phytochemicals B3LYP/6-31G++(2d,p)

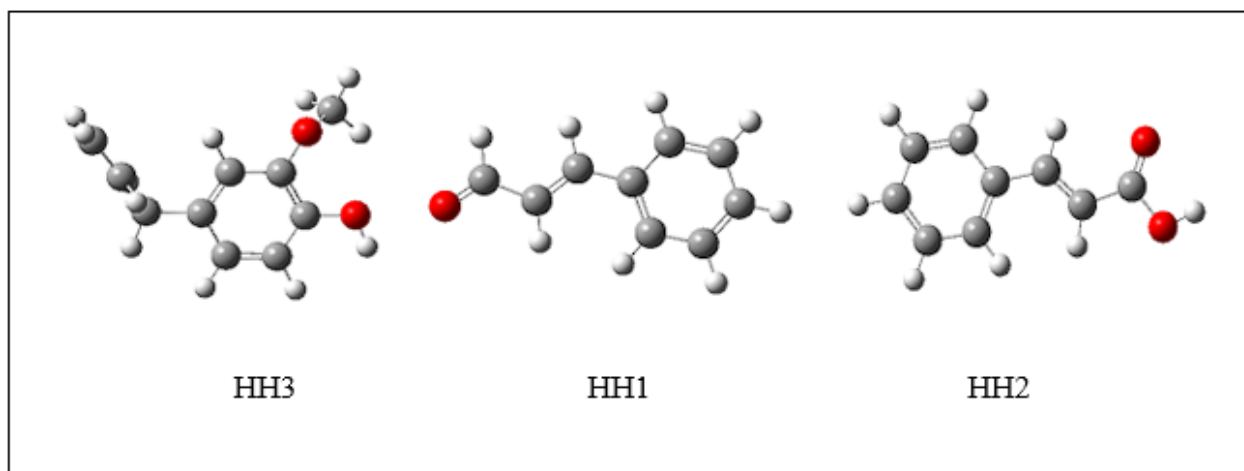


Figure 1. Optimal structures of phytochemical compounds

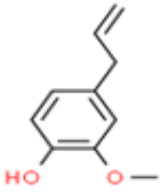
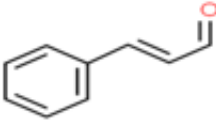
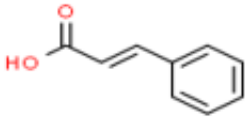
Symbols	Structure/Name	Functional group
HH3	 <p>Eugenol</p>	allyl
HH1	 <p>cinnamaldehyde</p>	Aldehyde
HH2	 <p>cinnamic acid</p>	Carboxylic acid

Figure 2. Chemical info of HH1, HH2 and HH3 cinnamon derivatives.

Before beginning another theoretical calculations, a structure improvement step was established for the studied molecules to determine the geometry with minimum energy. Specifically, the determination of the appropriate geometries of the inhibitors HH1, HH2 and HH3 at the potential energy minimum²¹. was studied. Hence, it is crucial to achieve improved systems of the studied inhibitors to ultimately determine their quantum parameters, which includes an electrostatic potential (ESP) map.

Electrostatic Potential (ESP) 2D Maps

ESP maps can be considered ideal tools to show the movement of electrons in a compound. This method generates maps of the regions where electrons are located in a given compound, according to Study³³. Outline diagrams of electronic density show that the oxygen atoms in the dimers that coordinate the molecule in question occupy their advantageous sites for bonding. We should take into account the distinction between oxygen atoms characterized by a functional group (oxygen atoms) and other atoms. In essence, what this means is that the hydroxyl and methoxy groups in HH3, the formyl groups in HH1, and the carboxyl groups in HH2 contain these oxygen atoms. The interfacial sites marked with dark red lines in the studies³⁴. The dusky crimson color in the contour map with negative potentials specifically inclose the oxygen molecules and their locales in HH1, HH2, and H3 molecules, while the green color is scattered in a location with high positive potentials, consistent with the electrostatic contour representation in DVT /B3LYP/6-31. The calculation phase of G++(2nd,p) (Figure 2).

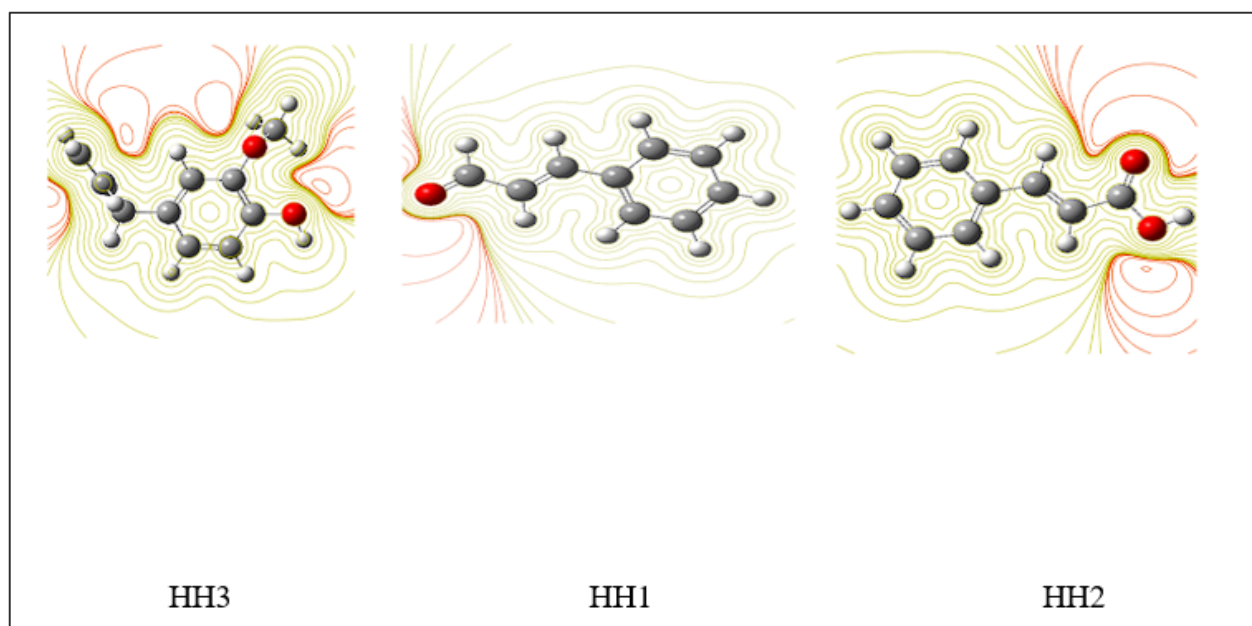


Figure 3.

The energies and parameters associated with (HOMO) and (LUMO).

The reactivity of chemical compound is mainly dependent on their HOMO and LUMO. Figure 3 displays the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for the molecules under investigation^{35,36}. In the cases of the compounds HH1, HH2, and HH3 there is a clear visual presence of π -orbitals at the ring level, especially in the benzene ring which is somewhat removed from the molecular plane and thus has an aryl character.

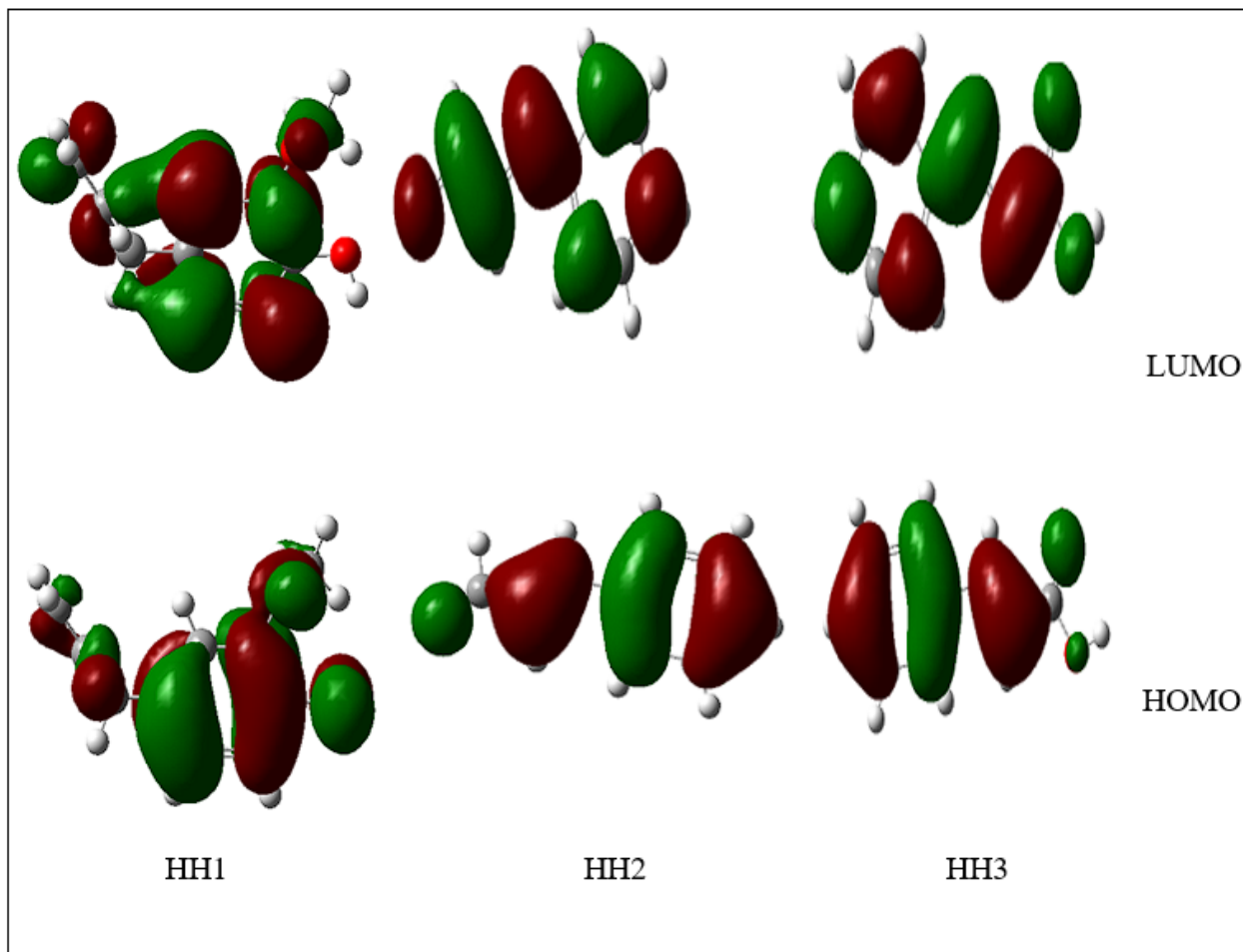


Figure 4. *Electronic density of inhibitor molecules*

The aim of the quantum molecular study indexed in Table 2 is to provide an in depth description of the active and structural homes of the molecules beneath look at. For the inhibitors, the B3LYP/6-31G++(2nd,p) strategies yielded the subsequent quantum chemical parameters: LUMO, HOMO, Gap energy (ΔE), Global stiffness (η), Electron attachment energy (A), Global stiffness (η), Electronegativity value (χ), Global electrophilicity index (ω), and Proportion of electrons transferred (ΔN). These are consultant outcomes, as seen by the small but significant variations in the ELUMO and EHOMO values for each method. ELUMO and EHOMO function the foundation for the calculation of all different parameters which might be approximated in accordance with Koopman's theorem³⁷ so that you can verify the inhibitors reactivity and selectivity. Let's start with the energy gap. Because ΔE , is a crucial indicator of the inhibitor compound's reactivity, an effective inhibitor has a narrow energy gap. ³⁸. The results indicate that HH3 has strong inhibitory potency in comparison to HH2 and HH1, respectively, with every value for ΔE found for the inhibitors tested by the different methods having the following order $HH1 > HH2 > HH3$. (Table 2). Furthermore, inhibitors' reactivity can also be predicted using Different parameters, such as the electronegativity derived from E(LUMO and HOMO) using Equation 2, are considered based on observations indicating that HH3 exhibits lower electronegativity compared to HH2 and HH1. Consequently, in terms of the reactivity of these compounds, HH3 has an additional tendency to react as an electron donor ³⁹.

Inhibitors DFT calculation	HH 1 (Cinnamaldehyde)	HH2 (Cinnamic acid)	HH3 (Eugenol)
HOMO	- 0.25352	- 0.24924	- 0.22320
LUMO	- 0.09061	- 0.08285	- 0.01881
Gap energy (ΔE)	-0.16291	-0.16639	-0.20439
Dipole moment (D)	4.903116	2.702386	2.067160
Global <u>stiffness</u> (η)	0.081455	0.083195	0.09279
Softness (σ)	12.2767	12.01995	10.7770
First ionization energy (I)	0.25352	0.24924	0.22320
Electron attachment energy (A)	0.09061	0.08285	0.01881
Electronegativity value (χ)	0.172065	0.166045	0.121005
Proportion of electrons transferred (ΔN)	0.278084723	0.284275443	0.319150973
Global electrophilicity index (ω)	0.18117344	0.1658901	0.0788997
Total energy	- 423.019715	- 498.281141	- 538.750537

Figure 5. Calculation of quantum chemical parameters of inhibitors (HH1, HH2, HH3)

The global stiffness (η) values were determined by utilizing the equation 4, and then, the global electronegativity (ω) were represented in relation to the electronegativity value (χ) and Global stiffness (η) parameters in line with equation 6. Each those parameters play a decisive role in fully understanding the reaction of the inhibitory, including ΔN that was defined in the equation 4, since it is the result of collecting the previous parameters, it plays a major role in describing the inhibitor, as it gives a comprehensive description of the inhibitor's effectiveness. Therefore, the order of increasing global hardness is as follows: HH3, HH2, and HH1, i.e., the inhibitor HH3 is more effective than the other inhibitors (HH2 and HH1) as mentioned in Table 2. The chemical stiffness of molecules is directly related to the strength of electron interactions in molecular orbitals (HOMO and LUMO), which indicates the atom's resistance to charge transfer. This relationship has been established. 40 Regarding electronegativity, which characterizes a strong electrophile, while its simple value effectively describes large electrophiles for cores with significant charges, it typically represents metal surface costs. Based on the obtained values, the interaction with a charged metal surface follows the order HH3 > HH2 > HH1. Furthermore, the quantitative fraction of transferred electrons, ΔN , for HH3, HH2, and HH1 aligns with accepted principles, as shown in Table 2. This data confirms that HH3 has the highest electron transfer capacity, This indicates that it demonstrates superior inhibitory capabilities in comparison to the alternative inhibitors HH2 and HH1. The quantity of electrons transferred (ΔN) offers insight into the number of electrons moved to the receiving surface⁴¹.

Distribution of Charges

Atoms or sites in compounds with highly negative electron charge values exhibit an increased propensity to donate electrons when interacting with metallic surfaces. The interaction sites of HH1, HH2, and HH3 molecules are oxygen atoms, which possess similar molecular capabilities to aldehyde (HC=O) and alcohol (-OH alcohol) or (-OH acid) groups. To establish these correlations, the Mulliken evaluation is frequently employed as a common strategy⁴². Figure 4 illustrates the partial Mulliken charges at specific atoms of the optimized molecules under investigation, with the data collected in Table 4. These distributions of Mulliken charges were determined to the molecules using B3LYP/6-31G++(2nd,p) method. These charges are distributed among some atoms, which include oxygen (O) and carbon (C). These electronic charges can play a crucial role in determining the bonding capacity of the molecule, as all hydrogen atoms show positive charges, and the atom closest to oxygen has the highest positive charge. This is due to nature. The electronegativity of oxygen is represented by the presence of positive charges on the two carbon atoms adjacent to the oxygen atoms, while the remaining carbon atoms have negative charges.

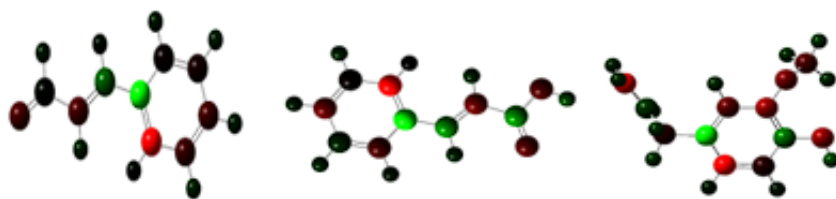


Figure 6. Mulliken charge analysis of inhibitors

Atom	O ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	O ₂
Inhibitors												
HH1	-0.235	0.932	-0.949	-0.029	-0.185	-0.283	-0.231	0.015				
HH2	-0.25	0.93	-1.12	-0.27	0.45	-0.021	0.11	-0.39	-0.39	-0.40		-0.33
HH3	-0.28	0.85	-0.11	-0.23	-0.37	-0.71	0.35	-0.09	0.16	-0.16	-0.18	-0.37

Figure 7. Mulliken charges distribution for the molecules

Simulation analysis

Monte Carlo (MC) simulations were employed to examine the adsorption characteristics of HH1, HH2, and HH3 inhibitors on the Fe (110) surface. Figures (5, 6, and 7) demonstrate the adsorption sites of these molecules on the metal surface from two distinct perspectives. The inhibitor molecules are positioned parallel to the iron (110) surface. When viewed from above, all molecules appear to be lying flat on the metallic surface.

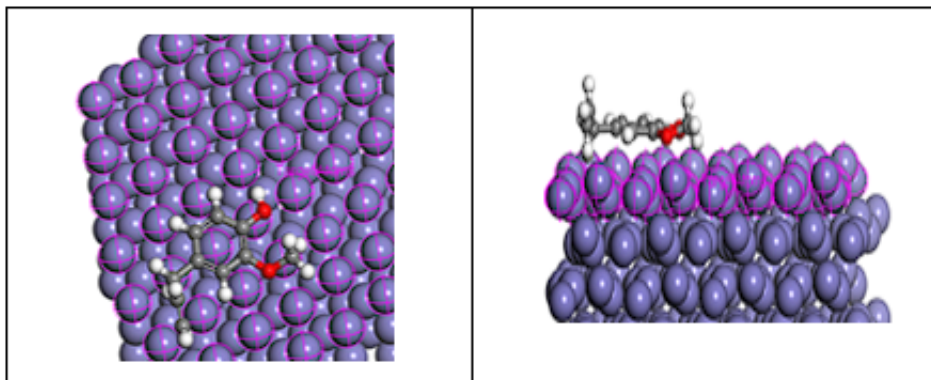


Figure 8. Arrangement of HH3 inhibitor on the Fe(110) surface in terms of adsorption configuration. The top view is shown on the left, while the side view is shown on the right.

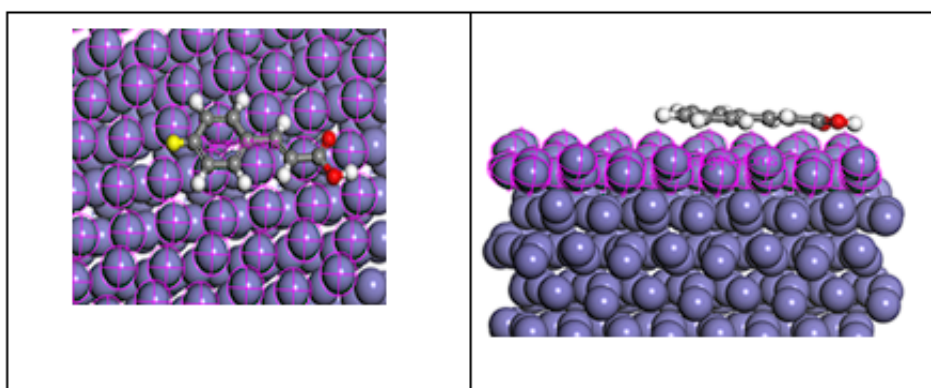


Figure 9. Arrangement of HH2 inhibitor on the Fe(110) surface in terms of adsorption configuration. The top view is shown on the left, while the side view is shown on the right.

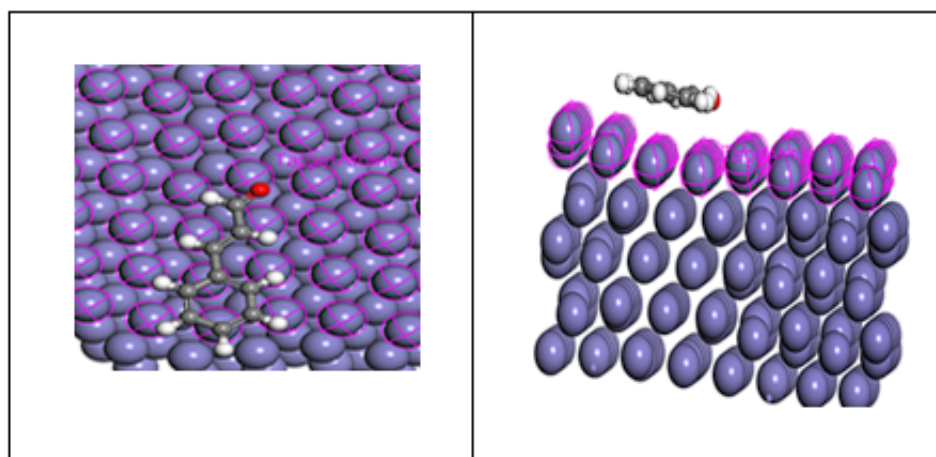


Figure 10. Arrangement of HH1 inhibitor on the Fe(110) surface in terms of adsorption configuration. The top view is shown on the left, while the side view is shown on the right

Inhibitors	HH1	HH2	HH3
Adsorption energy	-87.67196837	-93.00807248	98.44286972

Table 1. Measurement of the adsorption energy of cinnamon derivatives (HH1, HH2, and HH3) on the Fe(110) surface measured in Kcal/mol.

The adsorption energy for each molecule is shown in Table 4. It turns out that the adsorption energies are negative values for the molecules because the interaction between them and the metal surfaces is inherently heat-emitting. On the other hand, the adsorption binding force to the metal surface is negative to the interaction force. The more negative the adsorption energy value is, the stronger the binding obviously, and the easier it is to adsorb the molecule on the steel surface. From Table 4, all corrosion inhibitors show similar values in the adsorption energy required to bind to the iron(110) surface. Significantly stronger binding energies were obtained for HH1, HH2, and HH3. However, HH3 shows the greatest binding strength compared to the other identified molecules, indicating that it is more easily adsorbed on the metal surface and provides satisfactory surface protection against corrosion. This reason can be attributed to the good structural planarity, effective back-donating tendency, excessive electronic affinity, chemical softness of the eugenol inhibitor, and close alignment on the iron surface (Figure 5).

Conclusion

This research examines the anti-corrosion skills of three phytochemicals: eugenol, cinnamaldehyde, and cinnamic acid. Quantum chemical calculations are performed using DFT to determine the molecular properties and interactions of those compounds. Calculations reveal that eugenol has the strongest adsorption force on the iron(110) surface, which is observed by cinnamic acid and cinnamaldehyde. Monte Carlo simulation and molecular dynamics simulation were also performed to look at the strong formations of dimers adsorbed on the iron surface over time. Both theoretical adsorption energies from DFT and molecular simulation results confirm that the sequence from best to worst in corrosion inhibition performance is eugenol, followed by cinnamic acid, then cinnamaldehyde. Eugenol shows the strongest binding to iron and the best ability to prevent corrosion due to the presence of very strong electron absorption centers (O and pi bonds) that block the active sites of iron. Therefore, eugenol shows the greatest promise as a natural iron corrosion inhibitor based on the theoretical quantum chemical calculations performed in this study.

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