OKU Fen Bilimleri Enstitüsü Dergisi
8(1): 472-489, 2025

OKU Journal of The Institute of Science and Technology, 8(1): 472-489, 2025

Osmaniye Korkut Ata Üniversitesi
Fen Bilimleri Enstitüsü
Dergisi

Osmaniye Korkut Ata University
Journal of The Institute of Science
and Technology

Korozyon Araştırmalarında DFT Yaklaşımı

Goncagül AKSARAY[1*], **Mehmet Erman MERT**[2], **Başak DOĞRU MERT**[3]

[1]Cukurova University, Faculty of Art and Sciences, Department of Chemistry, 01330, Adana, Türkiye
[2]Adana Alparslan Türkeş Science and Technology University, Advanced Technology Research and Application Center, 01250, Adana, Türkiye
[3]Adana Alparslan Türkeş Science and Technology University, Engineering Faculty, Energy Systems Engineering Department, 01250, Adana, Türkiye

[1]https://orcid.org/0000-0003-4338-6049
[2]https://orcid.org/0000-0002-0114-8707
[3]https://orcid.org/0000-0002-2270-9032
*Corresponding author: goncagulaksaray@gmail.com

Derleme

Makale Tarihçesi:
Geliş tarihi: 05.06.2024
Kabul tarihi:11.11.2024
Online Yayınlanma: 15.01.2025

Anahtar Kelimeler:
Korozyon
İnhibisyon
DFT

ÖZ

Korozyon, çevresel kimyasal reaksiyonlarla malzemelerin bozulması nedeniyle çeşitli endüstrilerde önemli zorluklar doğurmaktadır. Bu çalışma, korozyon mekanizmalarının anlaşılmasında ve etkili korozyon inhibitörlerinin geliştirilmesinde Yoğunluk Fonksiyonel Teorisinin (DFT) önemini vurgulamıştır. Rol molekülleri, korozyon önleme performanslarını belirlemek amacıyla DFT analizi yoluyla araştırılan 1,2-dihidroksibenzen, m-guaiakol, kateşin, guaifenesin, çemen otu ve üzümdeki gallik asittir. Enerji aralığı (ΔE), mutlak elektronegatiflik (χ), sertlik (η), yumuşaklık (δ) ve dipol momenti dahil olmak üzere temel parametreler, verimliliklerini araştırmak için analiz edildi. Kateşin, en düşük ΔE'si ile, yüksek inhibisyon performansına işaret eden gelişmiş elektron bağışlama yetenekleri sergiledi. Kateşin, en düşük ΔE'si ile, yüksek inhibisyon performansına işaret eden gelişmiş elektron verme yetenekleri sergiledi. Ek olarak, Elektrokimyasal Impedans Spektroskopisi bu bileşiklerin korozyona karşı koruma verimliliğini doğruladı. DFT'nin hesaplama talepleri ve doğru değişim-korelasyon fonksiyonlarına duyulan ihtiyaç gibi sınırlamalarına rağmen, hesaplama metodolojilerindeki ilerlemeler ve deneysel verilerle entegrasyon, tahmin gücünü arttırabilir. Bu çalışma, korozyona dayanıklı malzemelerin tasarımına rehberlik etmede DFT'nin önemini vurgulamakta ve teorik modelleri geliştirmek ve tahminleri doğrulamak için disiplinler arası iş birliğine duyulan ihtiyacı vurgulamaktadır.

DFT Approach in Corrosion Research

Reviews

Article History:
Received: 05.06.2024
Accepted: 11.11.2024
Published online: 15.01.2025

Keywords:
Corrosion
Inhibition
DFT

ABSTRACT

Corrosion, degradation of materials due to environmental chemical reactions, poses significant challenges across various industries. This study emphasized the importance of Density Functional Theory (DFT) in understanding corrosion mechanisms and developing effective corrosion inhibitors. The role molecules were 1,2-dihydroxybenzene, m-guaiacol, catechin, guaifenesin, fenugreek and gallic acid in grape which were investigated via DFT analysis in order to determine their corrosion inhibition performance. Key parameters, including the energy gap (ΔE), absolute electronegativity (χ), hardness (η), softness (δ), and dipole moment, were analyzed to investigate their efficiency. Catechin, with its lowest ΔE, demonstrated enhanced electron-donating capabilities, indicating high inhibition performance. Additionally, electrochemical impedance spectroscopy confirmed corrosion protection efficiency for these compounds. Despite the limitations of DFT, such as computational demands and the need for accurate exchange-correlation functionals, advancements in computational methodologies and integration with experimental data can enhance its predictive power. This study highlights the importance of DFT in guiding the design of corrosion-resistant materials and emphasizes the need for interdisciplinary collaboration to refine theoretical models and validate predictions.

To Cite: Aksaray G., Mert ME., Mert BD. Korozyon Araştırmalarında DFT Yaklaşımı. Osmaniye Korkut Ata Üniversitesi Fen Bilimleri Enstitüsü Dergisi 2025; 8(1): 472-489.

1. Introduction

Corrosion refers to the deterioration of materials, particularly metals, through chemical interactions with their surrounding environment (Rahal et al., 2024). This process generally occurs when metal surfaces react with corrosive agents like oxygen, moisture, acids, or salts, resulting in the formation of unwanted compounds such as oxides, hydroxides, or salts (Yüce et al., 2016; Palaniappan et al., 2019). Corrosion can occur through a variety of mechanisms, including chemical reactions, electrochemical processes, and physical degradation. Corrosion represents a common problem in numerous industries (Holla et al., 2024). In the aviation sector, for instance, aircraft components are routinely exposed to harsh environmental conditions, including humidity, salt, and elevated temperatures, which induce corrosion in structural materials like aluminum alloys. Similarly, in the automotive industry, road salt, moisture, and chemical pollutants accelerate the corrosion of vehicle parts. In the oil and gas industry, pipelines, storage tanks, and offshore platforms are particularly vulnerable to corrosion due to the corrosive nature of the transported fluids; if not adequately managed, this can result in expensive maintenance, repairs, and even catastrophic failures (Ma et al., 2020; Bobby et al., 2022; Edraki et al., 2024). In infrastructure, corrosion of steel reinforcement in concrete structures can compromise the integrity of bridges, buildings and highways, posing significant safety risks to building occupants and the public. In critical industries such as nuclear energy production and healthcare, corrosion-related failures can lead to serious consequences such as environmental pollution, loss of life and economic repercussions (Mert et al., 2014; Altunay and Kaya, 2017; Alfalah et al., 2023). Combating corrosion is essential not only to extend the lifespan and maintain the performance of materials, but also to ensure the safety and reliability of infrastructure and industrial operations. Understanding the mechanisms and factors that influence corrosion is crucial for developing effective prevention and mitigation strategies to combat the harmful effects of corrosion and ensure the longevity and durability of materials in various applications (Anadabe et al., 2020). Corrosion processes represent a complex chain of events mediated by chemical reactions and electrochemical events. Chemical reactions involve the interaction of surface metal atoms with surrounding environmental molecules, leading to chemical transformations (Emmanuel, 2024). When a metal surface comes into contact with water and oxygen, it can trigger chemical reactions that result in the formation of metal oxides and hydroxides. These reactions contribute to the formation of a passive oxide layer on the metal surface and can initiate further corrosion processes. Electrochemical events occur at the metal-surface-electrolyte interface. These events are redox reactions that occur on the metal surface, involving the transfer of electrons between electrodes (Mert et al., 2014; Sundaram et al., 2021). Oxygen molecules present on the metal surface can react with electrons from metal ions in the electrolyte to form oxygen ions, thereby accelerating corrosion on the metal surface. The mechanisms of material degradation involve a range of chemical and physical changes occurring on the metal surface, influencing the progression of corrosion. For example, local corrosion mechanisms such as pitting corrosion can lead to the formation and deepening of micro-pits on the metal surface, significantly reducing the durability of the material. Local differences in corrosion rates between anodic and cathodic zones further add to the complexity of corrosion processes and further complicate material degradation mechanisms (Farahati et al., 2020).

2. Material and Method

2.1. Applications of DFT in Corrosion Studies

Density Functional Theory (DFT) is widely used to understand corrosion mechanisms because it provides atomic-level information about the complex nature of chemical reactions and surface interactions that govern corrosion processes. DFT effectively predicts the energetics and kinetics of corrosion-related events, allowing researchers to uncover the fundamental principles that drive corrosion processes, such as metal dissolution, adsorption of corrosive species, and formation of corrosion products (Ansari et al., 2013; Döşlü et al., 2018; Bouhouche et al., 2024). DFT calculations allow us to identify the basic reaction pathways, intermediate species, and surface structures involved in corrosion processes, as well as draw conclusions about the mechanisms that cause material degradation. These data on corrosion mechanisms can be used to build targeted corrosion prevention and mitigation techniques (Adil Mahraz et al., 2024).

DFT enables the prediction of various physical and chemical properties through quantum mechanical approaches to accurately describe the electronic structure of materials. This approach, based on the Hohenberg-Kohn theorem (1964) and Kohn-Sham equations (1965), allows efficient calculation of electronic energies and forces and provides the basis for the study of a variety of phenomena, from molecular bonding and chemical reactions to material properties such as electronic band structures, magnetic behavior and physical properties (Rindt et al., 2015). Additionally, DFT calculations can provide valuable information for the design of next-generation corrosion-resistant materials by elucidating the mechanisms by which specific alloying elements, surface treatments, or protective coatings reduce corrosion. The integration of DFT with experimental techniques enables a comprehensive approach to materials design, where theoretical predictions can be verified and improved through experimental validation.

The first step to grasping DFT is to have a solid understanding of the basic ideas of quantum mechanics which form the basis of its calculations. Quantum mechanics elucidates the behavior of particles at atomic and subatomic scales, furnishing a theoretical framework for comprehending the electronic structures of atoms and molecules. At the core of quantum mechanics lies the principle of wave-particle duality, asserting that particles like electrons exhibit both wave-like and particle-like characteristics. This duality finds expression in Schrödinger's wave equation, delineating the wavefunction of a particle and providing probabilistic insights into its position, momentum, and energy. In the context of DFT, the electronic configuration of atoms and molecules is delineated by the electronic density-a foundational measure representing the likelihood of finding an electron at a specific point in space. According to Hohenberg-Kohn theorem, a system's ground-state energy is uniquely determined by its electronic density, forming the basis for DFT's development. The Kohn-Sham equations, derived from this theorem, serve as the cornerstone of DFT computations, facilitating the determination of a system's electronic energy through the resolution of a set of self-consistent equations (Li et al., 2021; Wang et al., 2024).

DFT computations entail approximating the exchange-correlation energy, which accommodates electron-electron interactions beyond the mean-field approximation of Hartree-Fock theory. Various exchange-correlation functionals have been formulated to approximate this energy term, each with its own merits and demerits. Commonly employed functionals encompass the local density approximation (LDA), generalized gradient approximation (GGA), and hybrid functionals amalgamating a fraction of Hartree-Fock exchange. These functionals enable DFT computations to accurately depict the electronic structures of atoms and molecules across diverse systems, from simple diatomic molecules to intricate materials (Gholamhosseinzadeh et al., 2019). Overall, quantum mechanics concepts provide a theoretical basis for DFT computations, allowing researchers to investigate the electronic structures and characteristics of materials with high precision and efficiency.

The Kohn-Sham equations constitute the central mathematical framework of DFT, providing a methodology to ascertain a system's electronic density. Essentially, the Kohn-Sham formalism represents a reformulation of the many-body Schrödinger equation elucidating the behavior of a system of interacting electrons. These equations disassemble the system's total electronic energy into distinct contributions from non-interacting electrons traversing an effective potential. This effective potential encompasses both the external potential attributable to the nuclei and any supplementary potentials stemming from electron-electron interactions. The self-consistent field (SCF) technique used in DFT computations systematically solves the Kohn-Sham equations to determine the system's electronic density (Wang et al., 2024). The process commences with an initial estimation of the electronic density, typically derived from a rudimentary model or prior computation. Subsequently, the Kohn-Sham equations are self-consistently solved to procure a new electronic density, which in turn updates the effective potential. This iterative procedure persists until the electronic density converges to a stable solution, signifying that the calculated electronic structure accurately mirrors the system's ground state. Through this iterative self-consistent field approach, DFT computations can efficiently and precisely determine the electronic density and associated properties of an extensive array of materials and molecular systems. DFT computations rely on a suite of approximations and methodologies to render them computationally tractable for practical applications. The exchange-correlation functional is a key approximation that extends Hartree-Fock theory's mean-field approximation to electron-electron interactions (Mohammed et al., 2024). Various exchange-correlation functionals, such as the local density approximation (LDA) and generalized gradient approximation (GGA), have been devised to approximate this energy term. These functionals simplify the exact exchange-correlation energy, facilitating efficient DFT computations while still furnishing accurate depictions of electronic structure and properties. Another critical approximation in DFT computations is spatial discretization, entailing the division of the system into a finite grid or set of basis functions. This discretization enables the efficient numerical solution of the Kohn-Sham equations, as it converts the continuous problem of solving differential equations into a discrete set of algebraic equations. Diverse numerical techniques, including plane-wave basis sets, Gaussian basis sets, and grid-based methods, can be employed for this purpose, each harboring its own advantages and limitations. Additionally, the selection of basis set and grid parameters can significantly influence the accuracy and efficiency of DFT computations, necessitating meticulous deliberation and optimization. Parallelization and algorithmic optimizations play a important role in rendering DFT computations computationally viable for large-scale systems. Parallel computing techniques, such as parallelization across multiple processors or nodes, enable DFT computations to be executed concurrently, substantially reducing computation times for intricate systems. Furthermore, algorithmic optimizations, encompassing efficient matrix diagonalization algorithms and iterative solution methods, aid in enhancing the scalability and efficiency of DFT computations. These optimizations take advantage of advances in computer hardware and software to enable the modeling of increasingly large and complex systems using DFT (Čertík et al., 2024; Feng et al., 2024; Martínez et al., 2024).

The B3LYP 6-311G(d,p) methodology, a widely employed DFT approach, is highly esteemed for its precision in characterizing the electronic structure and attributes of molecules and materials (Ugi, 2024). This method amalgamates a hybrid exchange-correlation functional with a basis set renowned for its adaptability and dependability, rendering it apt for an extensive array of applications across chemistry, physics, and materials science. Within computational chemistry, B3LYP 6-311G (d,p) finds frequent utilization in scrutinizing molecular systems, encompassing inquiries into molecular geometries, vibrational frequencies, electronic spectra, and reaction mechanisms. Its convenient treatment of exchange and correlation phenomena renders it adept at projecting precise electronic energies and geometries of molecules, thus furnishing invaluable insights into their chemical conduct. Furthermore, B3LYP 6-311G (d,p) holds significant utility in the domain of corrosion inhibition research, which endeavors to alleviate the deleterious consequences of corrosion on metal surfaces. Corrosion inhibitors, chemical compounds introduced into corrosive environments, exhibit efficacy in curtailing corrosion rates by fostering the formation of a protective layer atop metal surfaces. A thorough understanding of the molecular interactions between corrosion inhibitors and metal surfaces is critical for the development and improvement of effective inhibitor compounds (Thakur et al., 2024). DFT, especially techniques like B3LYP 6-311G(d,p), furnishes a potent tool for delving into the adsorption behavior of corrosion inhibitors on metal surfaces at a molecular level (Al-Nami, 2020). By simulating the electronic structure and energetics of inhibitor-metal interactions, researchers can elucidate the mechanisms underpinning corrosion inhibition and refine their efficacy. This computational paradigm complements experimental methodologies by furnishing intricate insights into the fundamental processes governing corrosion inhibition. For example, researchers leverage B3LYP 6-311G(d,p) computations to prognosticate the adsorption energies, geometries, and electronic characteristics of inhibitor molecules on metal surfaces (Narang et al., 2023). Through comparisons between computational outcomes and experimental findings, they can authenticate theoretical constructs and gain deeper insights into the structure-activity relationships dictating inhibitor efficacy. Furthermore, DFT computations serve in identifying key chemical features that contribute to inhibitor efficiency, hence directing the scientific design of new corrosion inhibitors with increased properties. In essence, B3LYP 6-311G (d,p) appears as an important computational tool for understanding corrosion inhibition mechanisms and developing effective inhibitor chemicals (Kumar et al., 2021). By harnessing the predictive capabilities of DFT, researchers can expedite the exploration and refinement of corrosion inhibitors possessing superior performance and resilience, thereby catalyzing advancements in materials science and engineering.

3. Results and Discussion

3.1. Restrictions of DFT

While DFT offers important insights into corrosion processes, several restrictions temper its application in this field. Computational demands limit the size of systems that can be effectively studied, constraining its utility for large-scale corrosion scenarios. Additionally, the accuracy of DFT calculations hinges on the selection of exchange-correlation functionals, which may struggle to capture certain aspects of corrosion, such as metal dissolution, with precision. Addressing solvation effects, inherent in electrolyte environments where corrosion occurs, poses another challenge, often necessitating computationally intensive methods (Mert et al., 2011). Moreover, the static nature of DFT calculations may overlook dynamic processes inherent in corrosion, such as ion diffusion and surface fluctuations. Describing surface reconstruction and defects accurately within the DFT framework requires sophisticated methodologies and careful consideration of surface structures. Furthermore, while DFT insights are invaluable, experimental validation remains essential, albeit challenging, particularly for complex corrosion processes. Despite these limitations, DFT remains a vital tool for understanding corrosion mechanisms and guiding the design of corrosion-resistant materials, especially when integrated with experimental and complementary computational approaches.

3.2. Enhancing DFT Methodologies for Corrosion Studies

To overcome the limitations of DFT in corrosion studies, several strategies can be employed. One approach involves advancing computational methodologies to enhance the efficiency and accuracy of DFT calculations for larger systems. This may entail the development of more sophisticated exchange-correlation functionals tailored specifically for corrosion processes, potentially incorporating empirical data or machine learning techniques to improve predictive capabilities (Sirivastava et al., 2017).

Additionally, efforts to incorporate solvent effects into DFT simulations through continuum solvent models or explicit solvation treatments could better mimic realistic electrolyte environments and their impact on corrosion behavior. Furthermore, advancements in computational hardware and parallelization techniques can help alleviate the computational burden associated with large-scale corrosion simulations, enabling the study of more complex systems over longer timescales. Dynamic aspects of corrosion phenomena, such as ion diffusion and surface kinetics, could be addressed through the integration of DFT with molecular dynamics or kinetic Monte Carlo methods, allowing for a more comprehensive understanding of corrosion processes. Additionally, the development of multiscale modeling approaches that seamlessly integrate atomistic DFT simulations with mesoscale or continuum-level models could bridge the gap between molecular-scale insights and macroscopic corrosion behavior. Experimentally validated computational models and databases specifically tailored for corrosion studies could serve as valuable resources for benchmarking and refining DFT methodologies. Collaborative efforts between experimentalists and computational scientists are essential for validating DFT predictions against experimental data, identifying discrepancies, and refining theoretical models to better capture the intricacies of corrosion processes (Manssouri et al., 2021). By addressing these challenges and adopting a multidisciplinary approach, researchers can enhance the predictive power of DFT in corrosion studies and accelerate the development of corrosion-resistant materials and coatings.

3.3. Integrating Experimental Data with DFT for Corrosion Studies

According to obtained previous studies, the quantum theoretical data and experimental findings were combined and summarized for some aromatic compounds (Aksaray et al., 2023).

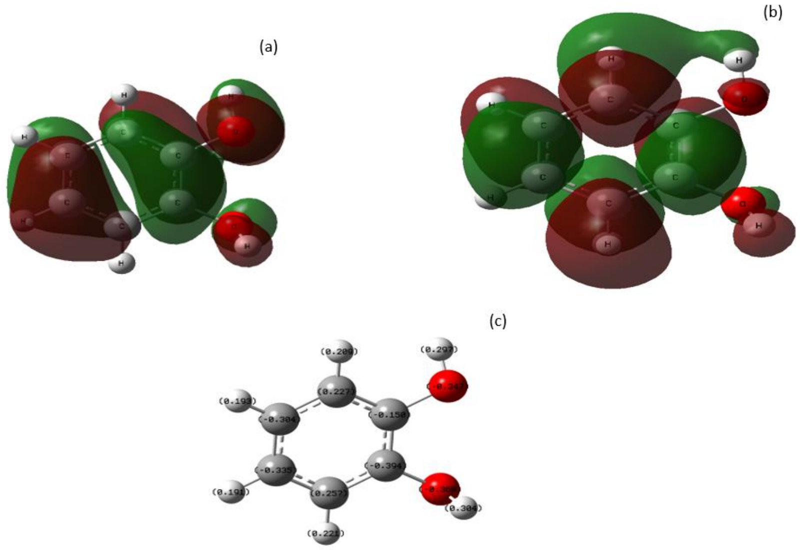

Figure 1. The HOMO (Highest Occupied Molecular Orbital) (a), LUMO (Lowest Unoccupied Molecular Orbital) (b) and Mulliken charges (c) of 1,2-Dihydroxybenzene

In the theoretical investigation outlined in this study, a quantum theoretical approach was employed to conduct structural analyses of all molecules, yielding critical insights into their electronic properties. Figures 1-3 depict essential parameters, including the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE) between LUMO and HOMO, and Mulliken charges on the backbone atoms. These analyses are fundamental in understanding the inhibition performance of inhibitor molecules, with particular emphasis on the gap between HOMO and LUMO energy (ΔE), which plays a significant role in stability. Additionally, absolute electronegativity (χ), absolute hardness (η), and absolute softness (δ) values were calculated, providing insights into the molecules' electronic structures and reactivity. The comparison of these parameters among the molecules reveals valuable information regarding their potential as corrosion inhibitors.

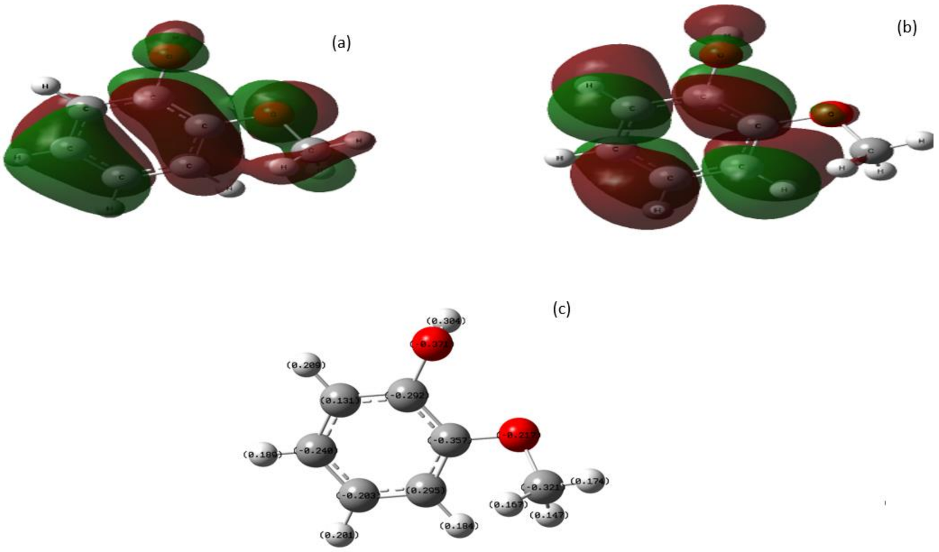

Figure 2. The HOMO (a), LUMO (b) and Mulliken charges (c) of m-Guaiacol

For instance, molecules with lower ΔE values, such as catechin, exhibit enhanced electron-donating capabilities, suggesting their potential as effective corrosion inhibitors. Moreover, the minimum χ and η values observed for catechin further support its potential efficacy as a corrosion inhibitor. The analysis also highlights the importance of dipole moment, with catechin exhibiting the highest dipole moment among the molecules studied, indicative of its potential for enhanced adsorption onto metal surfaces. Overall, the integration of experimental data with DFT calculations provides valuable insights into the electronic properties and corrosion inhibition potential of molecules, contributing to the development of effective corrosion mitigation strategies in materials science and engineering.

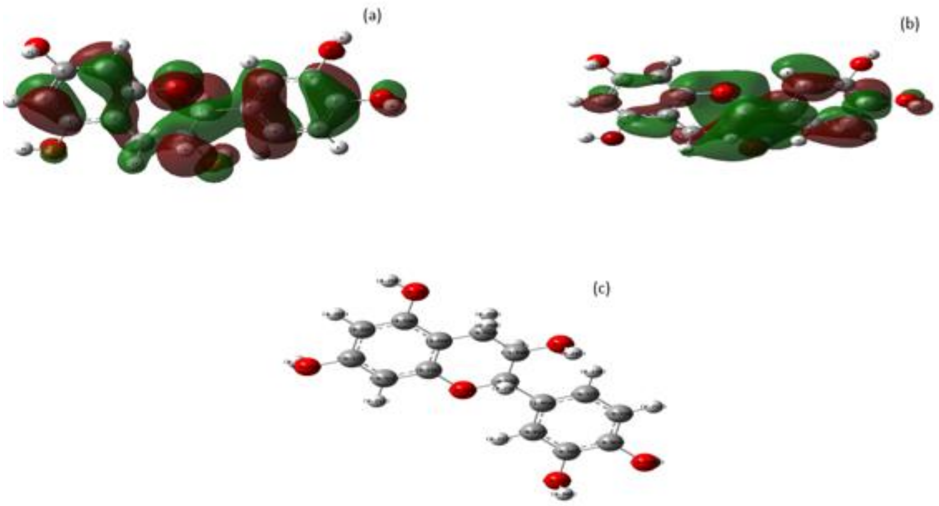

Figure 3. The HOMO (a), LUMO (b) and Mulliken charges (c) of Catechin

Table 1. The DFT parameters of all molecules and inhibition efficiency (IE) for 168h

Molecules	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	χ (eV)	η (eV)	δ (eV)	Dipole moment (Debye)	IE (%)
1,2-Dihydroxybenzene	-6.781	-0.777	6.003	3.779	3.002	0.333	2.926	
m-Guaiacol	-6.679	-0.739	5.941	3.709	2.970	0.337	2.814	99.1
Catechin	-5.843	-0.750	5.093	3.296	2.546	0.393	3.944	
Guaifenesin	-6.035	-0.525	5.510	3.280	2.755	0.363	4.228	94.7

In Table 1, the parameters were calculated according to Equations (1)-(5).

$$A= - E_{LUMO} \tag{1}$$

$$I= - E_{HOMO} \tag{2}$$

$$\chi = I+A/2 \tag{3}$$

$$\eta = I-A/2 \tag{4}$$

$$\delta = 1/ \eta \tag{5}$$

According to the findings presented in Table 1, the molecule catechin exhibits the lowest energy gap (ΔE) among the studied compounds, suggesting a higher propensity to donate electrons. This characteristic indicates its potential as an electron donor to the metal surface, thus acting as a corrosion inhibitor. Such molecules, often referred to as “n-donor” or “electron-rich” inhibitors, can form protective coatings on metal surfaces by donating electrons, thereby slowing down oxidation and corrosion processes. Additionally, in DFT analysis, parameters such as absolute electronegativity (χ), absolute hardness (η), and absolute softness (δ) offer valuable insights into a molecule's corrosion inhibition properties. Lower values of χ and η, as observed for catechin, are indicative of increased inhibition effectiveness, as these molecules tend to behave as soft bases interacting with the soft acid metal surface. Furthermore, the dipole moment, another significant parameter, correlates with corrosion inhibition efficiency. Molecules with larger dipole moments, such as catechin, possess greater polarity and can interact more effectively with metal surface charges, thereby enhancing their adsorption onto the metal surface. Thus, the maximum dipole moment observed for catechin underscores its potential as an effective corrosion inhibitor.

The electrochemical impedance spectroscopy data were investigated over a 168-hour immersion period in 0.5 M HCl, both with and without the presence of the studied molecules (as listed in Table 1). To conduct a thorough analysis and establish correlations between molecular structure and electrochemical performance, the experimental findings were juxtaposed with quantum theoretical properties. The results indicated a corrosion protection efficiency of approximately 95-99% after 48 and 168 hours, respectively.

In another study (Aksaray et al., 2023), for Guaifenesin, the inhibition efficiency was observed to be 76.61% after 1 hour, 81.9% after 24 hours, 88.26% after 48 hours, 88.57% after 96 hours, and 94.66% after 168 hours of exposure.

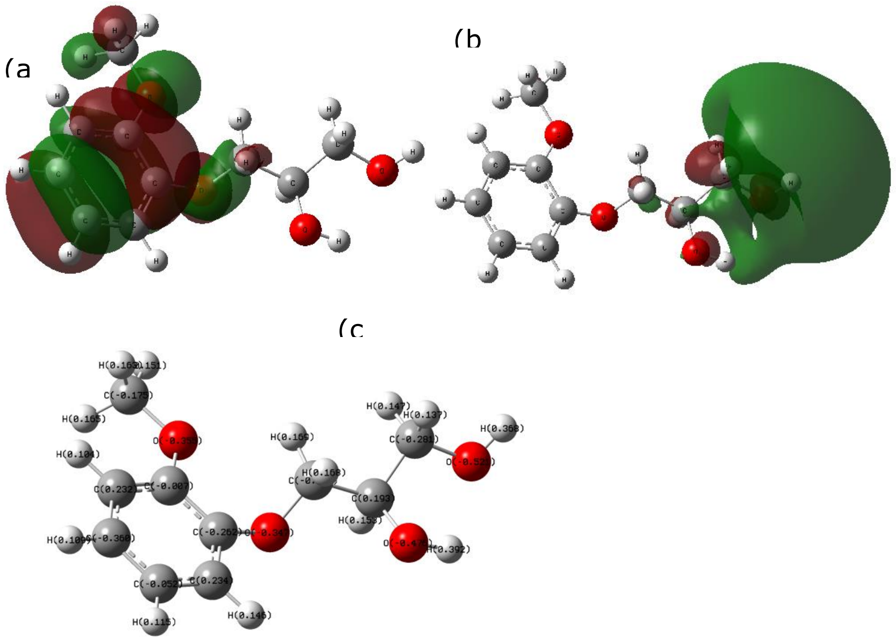

Figure 4. The HOMO (a), LUMO (b) and Mulliken charges (c) of Guaifenesin

Figure 4 depicted that a significant HOMO is present on the phenyl group and a substantial LUMO is observed on the alcohol group, enhancing the molecules' adsorption capacity. The calculated HOMO and LUMO values were -6.035 eV and -0.525 eV, respectively, aligning with literature findings. Notably, the determined energy gap (ΔE) was approximately 5.51 eV, consistent with reported values for Tiazofurin drug, Linagliptin, and chemically modified expired Dapsone drug, which were approximately 4 eV, 2.774 eV, and 3.39-3.36 eV, respectively (Singh et al., 2019; Pour-Ali and Hejazi, 2022; Iroha et al., 2023) The calculated dipole moment was 4.228 Debye, suggesting potential enhancement in inhibition due to dipole-dipole interactions between molecules and metal surfaces. Mulliken charges on oxygen atoms were found to be -0.521, -0.476, -0.355, and -0.347 atomic units, indicating that molecule adsorption likely occurs predominantly from these regions onto the positively charged mild steel surface in acidic media.

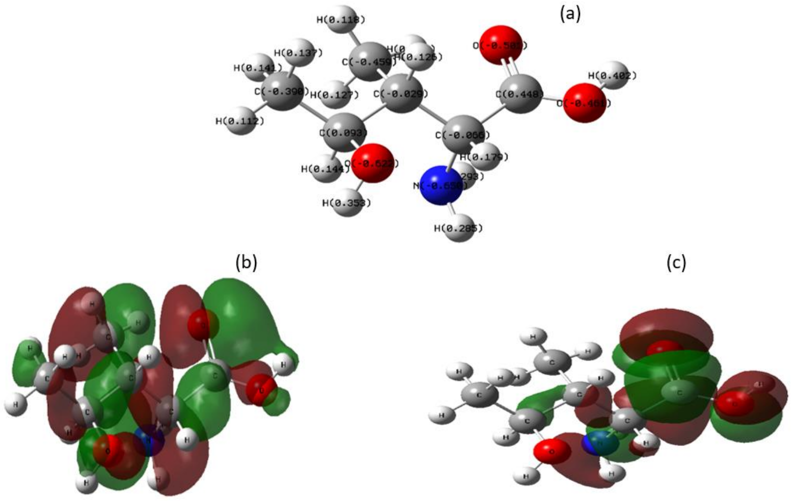

Figure 5. The Mulliken charges (a); HOMO (b) and LUMO (c) of active ingredient of Fenugreek

Figure 5 illustrated that large HOMO on the whole molecule and large LUMO on the carboxylic acid which improved molecules' capacity for adsorption. The obtained HOMO and LUMO values were -6.34 and -1.22 eV, respectively. The dipole moment was 3.3096 Debye. Due to dipole-dipole interactions between molecules and metal surfaces, the increased dipole moment may result in an increase in inhibition (Aksaray et al., 2023).

Figure 6 illustrated that large HOMO on the phenyl group and large LUMO on the alcohol group improved molecules’ capacity for adsorption. The obtained HOMO and LUMO values were -6.71 and -1.70 eV, respectively. The dipole moment was 2.3579 Debye. Due to dipole-dipole interactions between molecules and metal surfaces, the increased dipole moment may result in an increase in inhibition (Aksaray et al., 2023).

Table 2 gives the DFT parameters of some molecules in the literature.

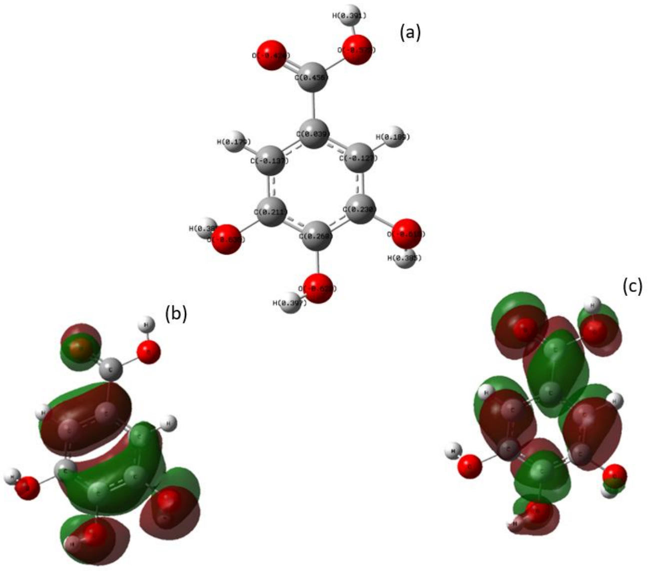

Figure 6. The Mulliken charges (a); HOMO (b) and LUMO (c) of gallic acid in grape

Table 2. The DFT parameters of some molecules in literature

Molecules	E HOMO (eV)	E LUMO (eV)	ΔE (eV)	χ (eV)	η (eV)	δ (eV)	Dipole moment (Debye)	References
Imidazole	-6.560	-0.510	6.050	-	-	-	-	Saraswat et al. (2020)
Purine	-7.250	-1.700	5.500	-	-	-	-	
Adenine	-6.340	-0.990	5.350	-	-	-	-	
BAP	-6.360	-1.190	5.170	-	-	-	-	
PASP	-5.467	-1.756	3.891	3.702	1.946	0.514	3.521	Chen et al. (2021)
THA-OCH3	-5.990	-1.470	4.520	3.730	2.260	0.442	3.651	Verma et al. (2021)
THA-H	-6.160	-1.660	4.500	3.910	2.250	0.444	3.651	
THA-Br	-6.320	-1.920	4.400	4.120	2.220	0.454	3.651	
TTA	-5.211	-0.807	4.404	3.009	2.220	0.451	3.680	Damej et al. (2022)
Epi-gallocatechin-3-gallate	-5.864	-1.393	4.471	3.628	2.235	0.447	4.590	Berrissoul et al. (2022)
QMHC	-5.986	-1.986	4.000	3.986	2.000	0.209	-	El Faydy et al. (2022)
BQMT	-5.469	-1.659	3.810	3.564	1.905	0.330	-	
$QMHCH_2^{2+}$	-10.996	-8.408	2.588	9.702	1.294	-1.886	-	
$BQMTH_2^{2+}$	-10.408	-7.929	2.479	9.168	1.239	-1.754	-	
AMP1	- 5.370	- 0.007	5.362	2.688	2.681	0.187	3.575	Moumeni et al. (2023)
AMP2	- 5.393	−0.082	5.310	2.737	2.655	0.188	3.470	
EDMP	-6.580	-1.090	5.490	3.840	2.740	-	-	Wang et al. (2024)
DTBP	-5.920	-0.040	5.880	2.980	1.470	-	-	

A comparative analysis of the DFT parameters from Table 1 and the literature values from Table 2 highlights the relationship between molecular electronic properties and their corrosion inhibition efficiency. The molecules in Table 1, such as 1,2-dihydroxybenzene and guaifenesin, show inhibition efficiencies strongly influenced by the HOMO-LUMO energy gap (ΔE) and dipole moments. For example, 1,2-dihydroxybenzene, with a ΔE of 6.003 eV and a dipole moment of 2.926 Debye, demonstrates a higher inhibition efficiency (99.1%) compared to molecules like catechin, which has a ΔE of 5.093 eV and a higher dipole moment (3.944 Debye).

In contrast, the literature values from Table 2 suggest that molecules such as imidazole and its derivatives also exhibit relatively high ΔE values (6.050 eV for imidazole), indicating stability and moderate inhibition potential. However, PASP, with a significantly lower ΔE (3.891 eV) and a dipole moment of 3.521 Debye, correlates with a more effective adsorption onto the metal surface, as supported by the literature (Chen et al., 2021). Similarly, molecules like TTA and epi-gallocatechin-3-gallate show intermediate ΔE values of 4.404 eV and 4.471 eV, respectively, which also suggest moderate inhibition performance, reflecting their ability to stabilize interactions on metal surfaces.

Molecules from the literature with lower ΔE values, such as QMHC derivatives (ΔE ~4.000 eV), show variations in dipole moments, with larger values correlating with better molecular polarity and hence better surface adsorption properties. This trend is consistent with the dipole moment of guaifenesin from Table 1, which, despite its moderate ΔE (5.510 eV), exhibits a relatively high dipole moment (4.228 Debye), contributing to an inhibition efficiency of 94.7%. Therefore, the comparative analysis reveals that both the ΔE and dipole moment play crucial roles in determining corrosion inhibition efficiency, with a clear trend toward higher dipole moments enhancing surface interaction and thus improving inhibitor performance.

4. Conclusion

This study underscored the critical role of DFT in elucidating corrosion mechanisms and guiding the development of corrosion inhibition strategies. Through a comprehensive analysis of molecular structures and electronic properties, informed by both theoretical DFT calculations and experimental data, valuable insights into the corrosion inhibition potential of aromatic compounds have been gained. The investigation revealed that molecules with lower energy gaps (ΔE), such as catechin, exhibit enhanced electron-donating capabilities, suggesting their efficacy as corrosion inhibitors. Additionally, parameters such as absolute electronegativity (χ), absolute hardness (η), and absolute softness (δ) offer valuable insights into the corrosion inhibition properties of molecules, with lower χ and η values indicating increased inhibition effectiveness. The dipole moment, another significant parameter, correlates with corrosion inhibition efficiency, with molecules possessing larger dipole moments showing enhanced adsorption onto metal surfaces. Furthermore, electrochemical impedance spectroscopy data demonstrated substantial corrosion protection efficiency for the studied molecules, further validating their potential as corrosion inhibitors.

Despite the significant contributions of DFT to corrosion studies, several limitations must be addressed to enhance its utility in this field. Computational demands and the selection of exchange-correlation functionals remain challenges, particularly for large-scale corrosion scenarios. Additionally, accurately describing dynamic processes such as ion diffusion and surface fluctuations within the DFT framework requires further refinement. Collaborative efforts between experimentalists and computational scientists are essential for validating DFT predictions and refining theoretical models to better capture the intricacies of corrosion processes.

Moving forward, advancements in computational methodologies, including the development of tailored exchange-correlation functionals and the incorporation of solvent effects, hold promise for overcoming these limitations and enhancing the predictive power of DFT in corrosion studies. Integration with experimental data and complementary computational approaches will further facilitate the development of corrosion-resistant materials and coatings, contributing to advancements in materials science and engineering.

5. Conflict of Interest

The authors declare no conflict of interest.

6.Acknowledgement

We are greatly thankful to Prof. Dr. Birgül YAZICI and Prof. Dr. Gülfeza KARDAŞ.

7. Researchers' Contribution Rate Declaration Summary

The authors declare that they have contributed equally to the article.

8.References

Adil Mahraz M., Salim R., Loukili EH., Assouguem A., Kara M., Ullah R., Bari A., Fidan H., Laftouhi A., Mounadi Idrissi A., Hammouti B., Rais Z., Taleb M. Exploratory evaluation supported by experimental and modeling approaches of Inula viscosa root extract as a potent corrosion inhibitor for mild steel in a 1 M HCl solution. Open Life Sciences 2024; 19(1): 20220879.

Alfalah MGK., Elid A., Ali AAA., Kamberli E., Nazlı B., Koyun S., Kandemirli F. Improvement of corrosion resistance for brass in 3.5% NaCl media by using 4-fluorophenyl-2, 5-dithiohydrazodicarbonamide. Journal of the Turkish Chemical Society Section A: Chemistry 2023; 10(4): 869-876.

Al-Nami SY. Investigation of adsorption and inhibitive effect of expired helicure drug on mild steel corrosion in hydrochloric acid solution. International Journal of Electrochemical Science 2020; 15: 2685-2699.

Altunay N., Kaya S. Theoretical investigation of corrosion inhibition of iron metal by some benzothiazole derivatives: A Monte Carlo study. Journal of the Turkish Chemical Society Section A: Chemistry 2017; 4(2): 573-578.

Aksaray G., Mert ME., Mert BD. Çeşitli doğal tohumların korozyondan koruma performansını göstermek için yoğunluk fonksiyonel teorisi yaklaşımı. The 17th International Scientific Research Congress - Science and Engineering 2023; 147-153.

Aksaray G., Mert ME., Mert BD. Experimental and theoretical investigation: The effect of cherry stems on corrosion behavior of mild steel. 5th International Artemis Congress on Life, Engineering, and Applied Sciences 2023; 192-201.

Aksaray G., Mert ME., Mert BD. Experimental and theoretical study on bricanly syrup: A potential corrosion inhibitor for mild steel in HCl Aegean 9th International Applied Sciences Congress 2023; 139-147.

Anadebe VC., Onukwuli OD., Abeng FE., Okafor NA., Ezeugo JO., Okoye CC. Electrochemical-kinetics, md-simulation and multi-input single-output (MISO) modeling using adaptive neuro-fuzzy inference system (ANFIS) prediction for dexamethasone drug as eco-friendly corrosion inhibitor for mild steel in 2 M HCl electrolyte. Journal of the Taiwan Institute of Chemical Engineers 2020; 15: 251-265.

Ansari KR., Quraishi MA., Ebenso EE., Prashant. Electrochemical and thermodynamic investigation of diclofenac sodium drug as a potential corrosion inhibitor for mild steel in hydrochloric acid. International Journal of Electrochemical Science 2013; 8(12): 12860-12873.

Bello A., Uzairu A., Shallangwa GA. Understanding inhibition of steel corrosion by some potent triazole derivatives of pyrimidine through density functional theory and molecular dynamics simulation studies. Journal of the Turkish Chemical Society Section A: Chemistry 2019; 6(3): 451-462.

Berrissoul A., Ouarhach A., Benhiba F., Romane A., Guenbour A., Outada H., Dafali A., Zarrouk A. Exploitation of a new green inhibitor against mild steel corrosion in HCl: Experimental, DFT and MD simulation approach. Journal of Molecular Liquids 2022; 349: 118102.

Bobby KM., Rahuma M., Khakbaz H., Melchers R. Antipsychotic drug waste: A potential corrosion inhibitor for mild steel in the oil and gas industry. Waste Managment 2022; 145: 38-47.

Bouhouche I., Bouiti K., Chraka A., El Hamil A., Labjar N., Damour H., Dahrouch A., Nasrellah H., Benmessaoud M., El Hajjaji S. Eco-conscious corrosion inhibitor synthesis via Soxhlet extraction: Experimental study in HCl 1M and theoretical analysis using DFT and MC simulations. Canadian Metallurgical Quarterly 2024: 1-19.

Čertík O., Pask JE., Fernando I., Goswami R., Sukumar N., Collins LA., Manzini G., Vackář J. High-order finite element method for atomic structure calculations. Computer Physics Communications 2024; 297: 109051.

Chen X., Chen Y., Cui J., Li Y., Liang Y., Cao G. Molecular dynamics simulation and DFT calculation of “green” scale and corrosion inhibitor. Computational Materials Science 2021; 188: 110229.

Damej M., Hsissou R., Berisha A., Azgaou K., Sadiku M., Benmessaoud M., Labjar N. New epoxy resin as a corrosion inhibitor for the protection of carbon steel C38 in 1M HCl. experimental and theoretical studies (DFT, MC, and MD). Journal of Molecular Structure 2022; 1254: 132425.

Döşlü ST., Mert BD., Yazıcı B. The electrochemical synthesis and corrosion behaviour of TiO_2/poly (indole-co-aniline) multilayer coating: Experimental and theoretical approach. Arabian Journal of Chemistry 2018; 11(1): 1-13.

Edraki M., Sheydaei M. Investigation of date seed powder as green corrosion inhibitor for mild steel: A study of solution and coating phases. Hybrid Advances 2024; 6: 100238.

El Faydy M., Benhiba F., Warad I., Saoiabi S., Alharbi A., Alluhaybi AA., Lakhrissi B., Abdallah M., Zarrouk A. Bisquinoline analogs as corrosion inhibitors for carbon steel in acidic electrolyte: Experimental, DFT, and molecular dynamics simulation approaches. Journal of Molecular Structure 2022; 1265: 133389.

Emmanuel JK. Corrosion protection of mild steel in corrosive media, a shift from synthetic to natural corrosion inhibitors: A review. Bulletin of the National Research Centre 2024; 48(1): 26.

Farahati R., Mousavi-Khoshdel SM., Ghaffarinejad A., Behzadi H. Experimental and computational study of penicillamine drug and cysteine as water-soluble green corrosion ınhibitors of mild steel. Progress in Organic Coatings 2020; 142: 105567.

Feng J., Wan L., Li J., Jiao S., Cui X., Hu W., Yang J. Massively parallel implementation of iterative eigensolvers in large-scale plane-wave density functional theory. Computer Physics Communications 2024; 299: 109135.

Gholamhosseinzadeh MR., Aghaie H., Zandi MS., Giahi M. Rosuvastatin drug as a green and effective inhibitor for corrosion of mild steel in HCl and H_2SO_4 solutions. Journal of Materials Research and Technology 2019; 8(6): 5314-5324.

Holla B., Mahesh R., Manjunath HR., Anjanapura VR. Plant extracts as green corrosion inhibitors for different kinds of steel: A review. Heliyon 2024; 10(14): e33748.

Iroha NB., Anadebe VC., Maduelosi NJ., Nnanna LA., Isaiah LC., Dagdag O., Berisha A., Ebenso EE. Linagliptin drug molecule as corrosion inhibitor for mild steel in 1 M HCl solution: Electrochemical, SEM/XPS, DFT and MC/MD simulation approach. Colloids and Surfaces A: Physicochemical and Engineering Aspect 2023; 660: 130885.

Kumar SH., Karthikeyan S., Vivekanand PA., Rajakumari S. Pioglitazone (PGZ) drug as potential inhibitor for the corrosion of mild steel in hydrochloric acid medium. materials today: Proceedings 2021; 36(4): 803-808.

Li L., Hoyer S., Pederson R., Sun R., Cubuk ED., Riley P., Burke K. Kohn-Sham equations as regularizer: Building prior knowledge into machine-learned physics. Phsical Review Letters 2021; 126(3): 036401.

Ma X., Dang R., Kang Y., Gong Y., Luo J., Zhang Y., Fu J., Li C., Ma Y. Electrochemical studies of expired drug (formoterol) as oilfield corrosion inhibitor for mild steel in H_2SO_4 media. International Journal of Electrochemical Science 2020; 15(3): 1964-1981.

Manssouri M., El Ouad Y., Chraka A., Khaddor M., Znin M., Majidi L. Aqueous extracts of Aaronsohnia pubescens subsp. pubescens aerial parts as Green Corrosion Inhibitor for Mild Steel in hydrochloric acid solution. Journal of the Turkish Chemical Society Section A: Chemistry 2021; 8(3): 953-968.

Martínez PA., Vock T., Kharchi LR., Pedroza-Montero JN., Wu X., Hasnaoui K., de la Lande A. A multi-GPU implementation of real-time time-dependent auxiliary Density Functional Theory for the investigation of nanosystems irradiations. Computer Physics Communications 2024; 295: 108946.

Mohammed BA., Kareem RO., Hamad OA. The electronic structure and physicochemical characteristics of chlorohydroquinone compounds using density functional theory and Hartree-Fock techniques. South African Chemical Institute 2024; 78: 85-94.

Moumeni O., Mehri M., Kerkour R., Boublia A., Mihoub F., Rebai K., Khan AA., Erto A., Darwish AS., Lemaoui T., Chafai N., Benguerba Y. Experimental and detailed DFT/MD simulation of α-aminophosphonates as promising corrosion inhibitor for XC48 carbon steel in HCl environment. Journal of the Taiwan Institute of Chemical Engineers 2023; 147: 104918.

Mert BD., Mert ME., Kardaş G., Yazıcı B. Experimental and theoretical investigation of 3-amino-1, 2, 4-triazole-5-thiol as a corrosion inhibitor for carbon steel in HCl medium. Corrosion Science 2011; 53(12): 4265-4272.

Mert BD., Yüce AO., Kardaş G., Yazıcı B. Inhibition effect of 2-amino-4-methylpyridine on mild steel corrosion: Experimental and theoretical investigation. Corrosion Science 2014; 85: 287-295.

Mert BD., Mert ME., Kardaş G., Yazici B. The experimental and quantum chemical investigation for two isomeric compounds as aminopyrazine and 2-amino-pyrimidine against mild steel corrosion. Anti-Corrosion Methods and Materials 2016; 63(5): 369-376.

Narang R., Vashishth P., Bairagi H., Shukla SK., Mangla B. Electrochemical and surface study of an antibiotic drug as sustainable corrosion inhibitor on mild steel in 0.5 M H_2SO_4. Journal of Molecular Liquids 2023; 384: 122277.

Palaniappan N., Alphonsa J., Cole IS., Balasubramanian K., Bosco IG. Rapid investigation expiry drug green corrosion inhibitor on mild steel in NaCl medium. Materials Science and Engineering: B 2019; 249: 114423.

Pour-Ali S., Hejazi S. Tiazofurin drug as a new and non-toxic corrosion ınhibitor for mild steel in HCl solution: Experimental and Quantum Chemical Investigations. Journal of Molecular Liquids 2022; 354: 118886.

Rahal HT., Abdel-Gaber AM., El-Rifai MS., El-Housseiny S. The potential of natural leaf extracts as green inhibitors for mild steel corrosion in hydrochloric acid solutions. Moroccan Journal of Chemistry 2024; 12(8): 1554-74.

Rindt CCM., Gaastra-Nedea SV. 15-Modeling thermochemical reactions in thermal energy storage systems. Advances in Thermal Energy storage systems. Woodhead Publishing 2015: 75-415.

Saraswat V., Yadav M., Obot IB. Investigations on eco-friendly corrosion inhibitors for mild steel in acid environment: Electrochemical, DFT and Monte Carlo Simulation approach. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2020; 599: 124881.

Singh P., Chauhan DS., Chauhan SS., Singh G., Quraishi MA. Chemically modified expired dapsone drug as environmentally benign corrosion ınhibitor for mild steel in sulphuric acid useful for industrial pickling process. Journal of Molecular Liquids 2019; 286: 110903.

Srivastava M., Tiwari P., Srivastava SK., Prakash R., Ji G. Electrochemical investigation of irbesartan drug molecules as an inhibitor of mild steel corrosion in 1 M HCl and 0.5 M H_2SO_4 solutions. Journal of Molecular Liquids 2017; 236: 184-197.

Sundaram RG., Vengatesh G., Sundaravadivelu M. Surface morphological and quantum chemical studies of some expired drug molecules as potential corrosion ınhibitors for mild steel in chloride medium. Surfaces and Interfaces 2021; 22: 100841.

Thakur A., Dagdag O., Berisha A., Ebenso EE., Kumar A., Sharma S., Ganjoo R., Assad H. Mechanistic insights into the corrosion inhibition of mild steel by eco-benign Asphodelus Tenuifolius aerial extract in acidic environment: Electrochemical and computational analysis. Surface and Coatings Technology 2024; 480.

Ugi B. DFT and electrochemical study of novel green corrosion ınhibitor (pyrantrin) for 1100-H14 aluminum corrosion remediation in 1 M H_2SO_4 acidic environment. Journal of the Turkish Chemical Society Section A: Chemistry 2024; 11(1): 253-260.

Verma DK., Kazi M., Alqahtani MS., Syed R., Berdimurodov E., Kaya S., Salim R., Asatkar A., Haldhar R. N–hydroxybenzothioamide derivatives as green and efficient corrosion inhibitors for mild steel: Experimental, DFT and MC simulation approach. Journal of Molecular Structure 2021; 1241: 130648.

Wang X., Liu J., Zhang Z., Xiang Q., Zhang J., Chen L., Xie H. Mechanism for corrosion inhibition of pure iron in 1 M HCl by Rauiella Fujisana: Experimental, GCMS, DFT, VASP and solidliquid modeling studies. Industrial Crops and Products 2024; 207: 117692.

Wang X., Chen H., Kou J., Sun S. An unconditionally energy-stable and orthonormality-preserving iterative scheme for the Kohn-Sham gradient flow based model. Journal of Computational Physics 2024; 498: 112670.

Yüce AO., Telli E., Mert BD., Kardaş G., Yazıcı B. Experimental and quantum chemical studies on corrosion inhibition effect of 5, 5 diphenyl 2-thiohydantoin on mild steel in HCl solution. Journal of Molecular Liquids 2016; 218: 384-392.