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The investigation of protection efficiency of some environmentally friendly inhibitors - A DFT study

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Abstract

The quantum characteristics and protection efficiency against corrosion of some environmentally friendly inhibitor molecules were determined theoretically. For this purpose, Gossypo, Gallocatechin, Glabridin, Vitamin C, Alanine, Glycine, Glutamic acid, Camphor, Alpha pinene and 1,8-cineole were investigated. The Density Functional Theory (DFT) was operated with the level of B3LYP/6-31G basis set by using Gaussian 03 program package. Results were presented for optimized molecules. According to obtained data, electronegative atoms in molecule backbone (such as N, O) and multiple bonds retard corrosion reactions via active adsorption centers. As a result of molecular adsorption which is occurred most likely physically, the inhibitor molecules are displaced with water molecules. The charged species may accumulate on the first inhibitor layer with the help of positively charged locations and may form bridges, most likely as a result of the protonated substituent of the molecule attracting other inhibitor molecules through the interaction between the negative atoms, resulting in multilayer accumulation on the surface.

Keywords: Corrosion, DFT, Green inhibitor

Bazı çevre dostu inhibitörlerin koruma etkinliğinin araştırılması - DFT çalışması

Özet

Bazı çevre dostu inhibitör moleküllerin kuantum özellikleri ve korozyona karşı koruma etkinliği teorik olarak belirlenmiştir. Bu amaçla Gosipol, Gallokateşin, Glabridin, C Vitamini, Alanin, Glisin, Glutamik asit, Kafur, a-Pinen, ve 1,8-Sineol incelenmiştir. Yoğunluk Fonksiyonel Teorisi (DFT), Gaussian 03 program paketi kullanılarak B3LYP/6-31G temel baz seti düzeyinde çalıştırılmıştır. Optimize edilmiş moleküller için sonuçlar sunulmuştur. Elde edilen verilere göre molekül yapısındaki elektronegatif atomlar (N, O gibi) ve çoklu bağlar aktif adsorpsiyon merkezleri aracılığıyla korozyon reaksiyonlarını geciktirir. Büyük olasılıkla fiziksel olarak meydana gelen moleküler adsorpsiyon sonucunda inhibitör molekülleri su molekülleri ile yer değiştirir. Yüklü türler, pozitif yüklü konumların yardımıyla birinci inhibitör tabakası üzerinde birikebilir ve büyük olasılıkla molekülün protonlanmış sübstitüentinin negatif atomlar arasındaki etkileşim yoluyla diğer inhibitör molekülleri çekmesinin bir sonucu olarak köprüler oluşturabilir, bu durum yüzeyde çok katmanlı birikime neden olur.

Anahtar kelimeler: Korozyon, DFT, Yeşil inhibitör

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1. Introduction

Corrosion is defined as the chemical or electrochemical reaction between a material, usually a metal or alloy, and its environment that produces a deterioration of the material and its properties. Corrosion has harmful consequences that affect industrial metals (especially mild steel: MS; stainless steel: SS; aluminum: Al; copper: Cu; etc.), the environment, and human health. Furthermore, corrosion costs have a significant impact on the economies of developed countries [1, 2]. For corrosion protection, especially in closed-circuit system and metal pickling, the use of organic inhibitor compounds is the most practically and effective method [3, 4]. The risk of organic inhibitors is their waste products may have environmental hazards [5, 6]. Therefore attention has been focused on green inhibitors which are plant and seeds extracts, etc [7-16]. Because they provide a variety of naturally created chemical compounds that are environmental - friendly, inexpensive, widely available, and renewable, and can be produced through simple extraction techniques [17]. Mourya et al. investigated the corrosion inhibition performance of Marigold flower extract [2]. This green inhibitor adhered to the mild steel surface according to the Langmuir adsorption isotherm, indicating monolayer adsorption. The adsorption activation characteristics showed that the inhibitor was physically adsorbed. The corrosion performance of mild steel (MS) increased with increasing inhibitor concentration. The highest values were obtained in the presence of 1g L^{-1} inhibitor solution. The inhibition efficiency values were 96.10, 96.30 and 98.19% by using linear polarization measurements, gravimetric analysis and polarization measurements respectively. The quantum chemical calculation provides foresight for adsorption behavior of molecules. Therefore most of scientist examines quantum programs before experimental studies [1, 19-26].

Bahlakeh et al. [19] emphasized that Mustard seed extract have various complex mixture of chemical compounds; such as allyl isothiocyanate, diallyl trisulfide, arabinose, galactose, rhamnose, and xylose. Therefore we need experimental considerations due to solve such complexity. They stated that recent efforts to correlate the inhibitive impact of extract and the electronic characteristics of its key ingredients have focused on quantum chemical computations within the framework of the density functional theory (DFT), with often positive findings. The calculated values of corrosion rate and inhibition efficiency during 72 hours for mild steel in the presence of 100 mg/L Mustard seed extract were 0.041 ± 0.003 mg cm^{-2} h^{-1} and 84%, respectively. The inhibition efficiency increased with increasing concentration, after 72 hours, in the 150 and 200 mg/L Mustard seed extract containing 1 M HCl solution the values were 85 and 88%, respectively.

This paper covers manuscripts related to the application of a number of green inhibitors against corrosion for industrial metals in many simulated and real aqueous media. The mechanisms of adsorption and quantum parameters for each inhibitor have also been highlighted via theoretical based approaches. Electrochemical experiments and modeling studies may help to build a bridge between molecule geometry and inhibitory efficiency. Future research could look into the use of a new family of inhibitors to protect against corrosion.

2. Materials and methods

Quantum chemical calculations of the molecules were performed with the Gaussian 03W. The geometric optimizations were done by using the B3LYP 6-31G basis set. We operated the program for single inhibitor molecules, the solvent effects were not considered. Energy calculations were also carried out at DFT/ B3LYP/6-31G. The energy of highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE) between LUMO and HOMO,

dipole moment and related functions were determined. The obtained results were compared with the literature data. The optimized molecular structures and HOMO, LUMO surfaces were visualized using Gauss View.

The absolute electronegativity (χ), absolute hardness (η) and absolute softness (δ) values were calculated [27-29];

$$A = -E_{LUMO} \quad (1)$$

$$I = -E_{HOMO} \quad (2)$$

$$\chi = \frac{I+A}{2} \quad (3)$$

$$\eta = \frac{I-A}{2} \quad (4)$$

$$\delta = \frac{1}{\eta} \quad (5)$$

3. Results and discussion

Molecules were selected according to main compound in green inhibitors which are plant and seeds extracts, etc. and presented in Table 1. Some of them were calculated by us and marked as * in tables.

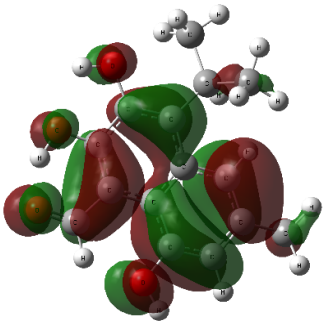
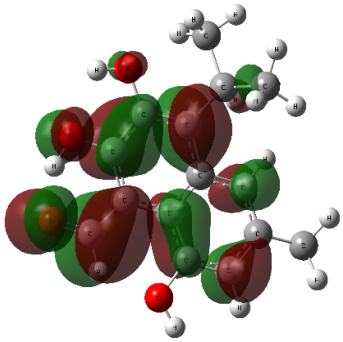
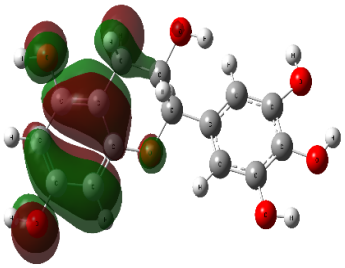
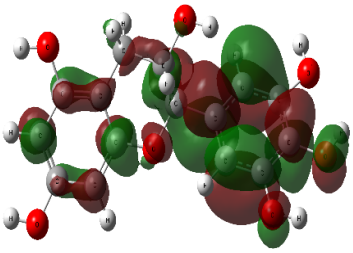
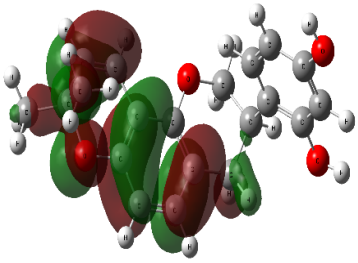
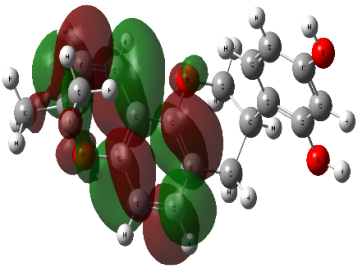
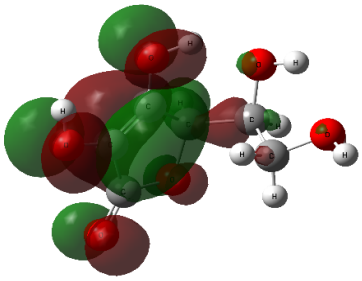
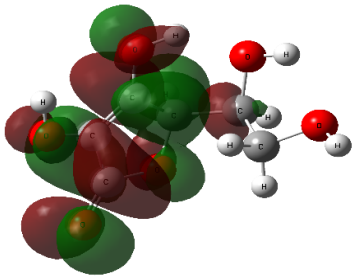
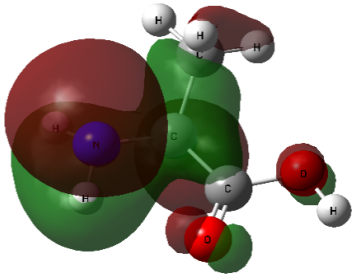
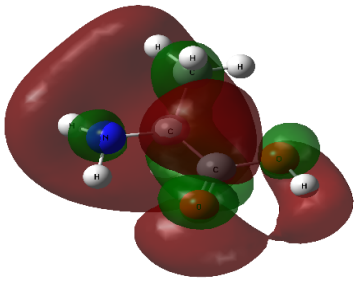
Table 1. The molecules, methods, source of green inhibitors and references

	Molecules	Method	Source of Green Inhibitors	REF
1	Gossypo*	DFT/B3LYP/6-31G	Gossipium hirsutum L.	[17]
2	Gallocatechin*	DFT/B3LYP/6-31G	Musa paradisica peel	[26]
3	Glabridin*	DFT/B3LYP/6-31G	Egyptian licorice	[30]
4	Vitamin C*	DFT/B3LYP/6-31G	Seaweed	[31]
5	Alanine*	DFT/B3LYP/ 6-31G	Animal glue	[32]
6	Glycine*			
7	Glutamic acid*			
8	Camphor*	DFT/B3LYP/6-31G	Thymus algeriensis	[33]
9	Alpha pinene*			
10	1,8-cineole*			
11	4-methoxy-2 nitro aniline	DFT/B3LYP/6-31G	Anisole derivatives	[18]
12	4-methoxy-N-methylaniline			
13	3-bromo-4methoxy-benzaldehyde			
14	Allyl isothiocyanate	DFT/B3LYP/6-31G**	Mustard seed	[19]
15	Diallyl trisulfide			
16	Arabinose			
17	Galactose			
18	Rhamnose			
19	Xylose			
20	Phyllanthin	DFT/B3LYP/6-31G	Phyllanthus amarus	[20]

The frontier orbitals images of molecules between 1-10th calculated by us were given in Figure 1. N,O, and electronegative terminals of molecules had HOMO orbitals, while the heterocyclic section of molecules had LUMO orbitals (Fig. 1). These effective corrosion inhibitors had higher E_{HOMO} and lower E_{LUMO} energies. According to frontier molecular orbital theory, the creation of a transition state is caused by an interaction between reacting species' HOMO and LUMO orbitals [15, 34, 35]. The E_{HOMO} energy is associated with electron donating ability of the molecule. The high E_{HOMO} proves that the molecule has a trend to donate electrons to acceptor molecule's LUMO orbital [29, 36, 37].

Table 2. Theoretical parameters of inhibitor molecules (*data calculated in this study).

	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	χ	η	δ	μ (Debye)
1*	-5.758	-2.077	3.681	3.918	1.841	0.543	4.834
2*	-5.834	-0.028	5.806	2.931	2.903	0.344	3.290
3*	-5.321	-0.580	4.741	2.950	2.371	0.422	2.191
4*	-6.300	-1.110	5.191	3.705	2.595	0.385	6.313
5*	-6.893	-0.691	6.202	3.792	3.101	0.322	2.142
6*	-6.342	-0.394	5.948	3.368	2.974	0.336	1.500
7*	-7.086	-0.897	6.188	3.992	3.094	0.323	2.543
8*	-5.930	-0.826	5.104	3.378	2.552	0.392	0.165
9*	-6.322	-0.495	5.826	3.408	2.913	0.343	3.301
10*	-6.216	-1.826	4.390	4.021	2.195	0.456	1.764
11	-5.533	-2.393	3.140	3.963	1.570	0.637	8.150
12	-4.986	-0.019	4.967	2.503	2.484	0.403	2.193
13	-6.901	-1.947	4.954	4.424	2.477	0.404	4.956
14	-7.003	-0.129	6.874	3.566	3.437	0.291	-
15	-6.862	-1.788	5.074	4.325	2.537	0.394	-
16	-7.191	-1.133	6.058	4.162	3.029	0.330	-
17	-7.184	0.757	7.941	3.214	3.971	0.252	-
18	-7.049	0.785	7.834	3.132	3.917	0.255	-
19	-7.151	0.935	8.086	3.108	4.043	0.247	-
20	-5.590	-0.170	5.420	2.880	2.710	0.369	2.020

Molecules	HOMO	LUMO
Gossypo		
Gallocatechin		
Glabridin		
Vitamin C		
Alanine		

Glycine

Glutamic acid

Camphor

Alpha pinene

1,8-cineole

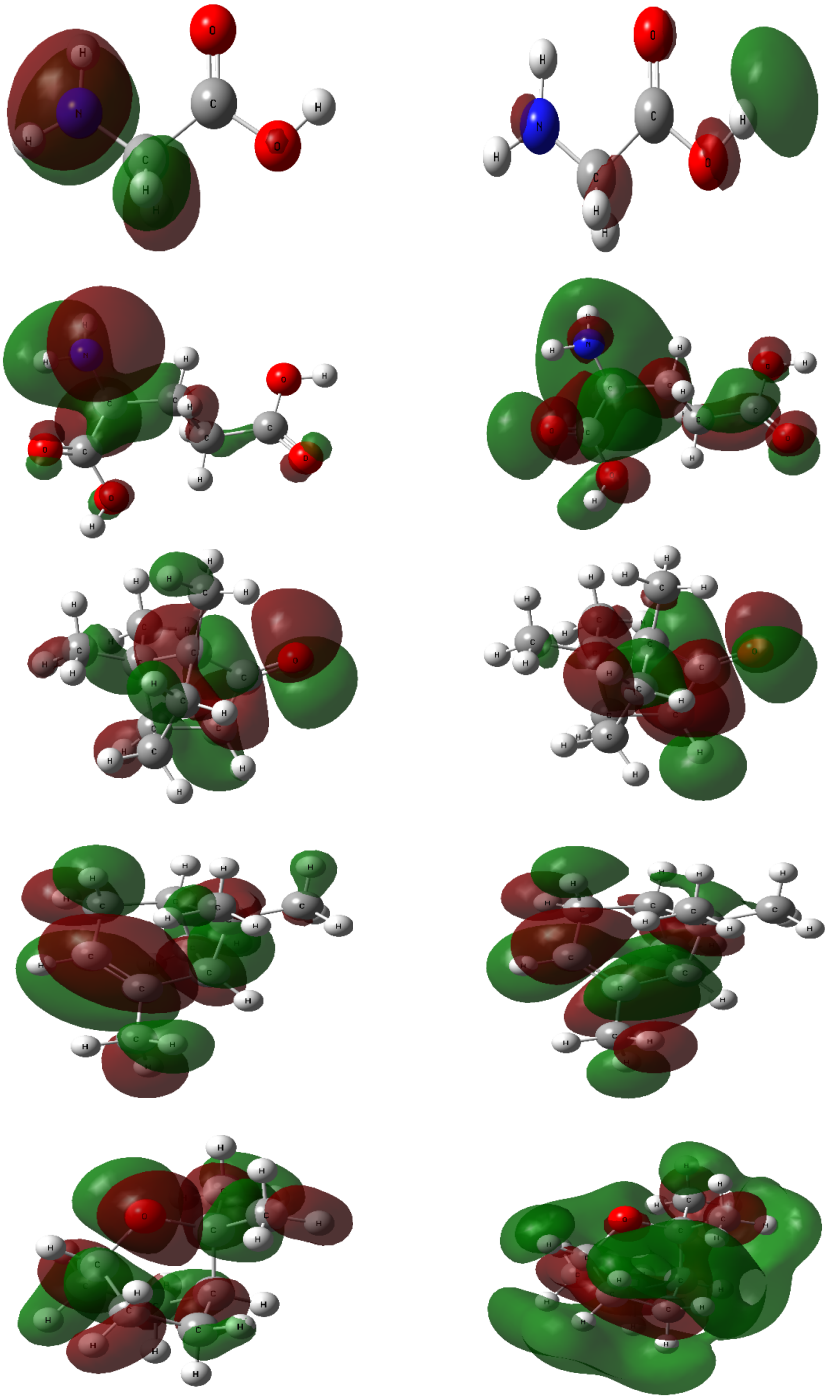


Figure 1. The HOMO and LUMO images of the calculated molecules.

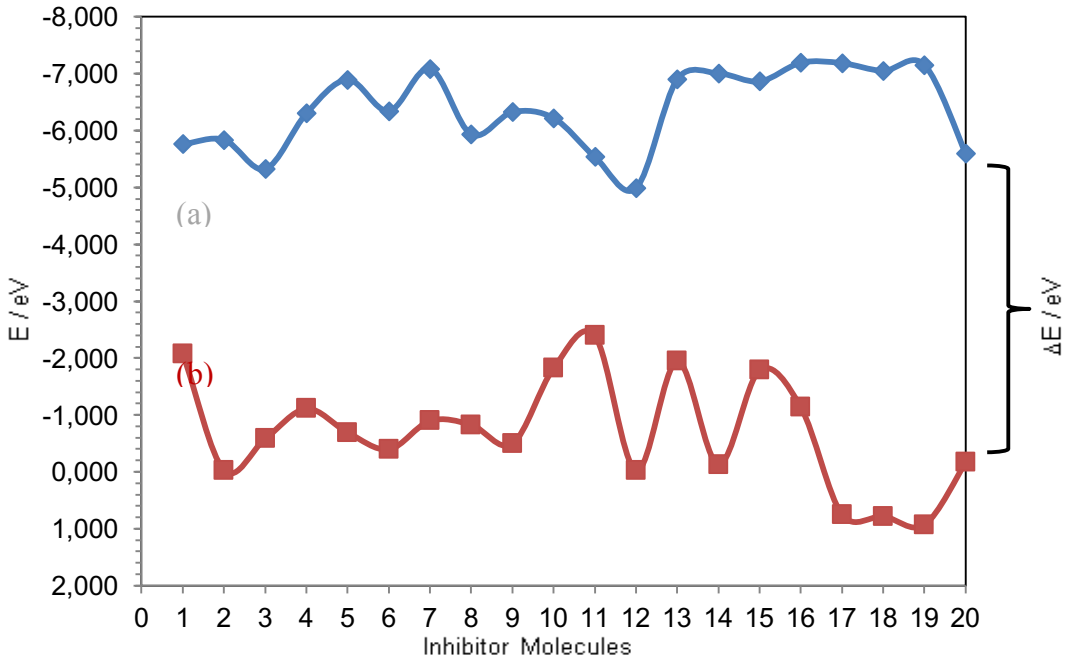


Figure 2. The E_{HOMO} (a) and E_{LUMO} (b) values of all molecules. (Some of the frontier orbitals of molecules were given inset)

In Fig. 2 and Table 2, almost all molecules had lower band gap energy, which causes the improvement on the reactivity of the molecule, and furthermore facilitates adsorption and provides higher inhibition efficiency [15, 38]. In Table 2, among the inhibitor molecule, the higher dipole moment values were determined for the Vitamin C and 4-methoxy-2 nitro aniline molecule as 6.313 and 8.150 Debye, respectively. According to experimental results that were presented in literature [31] the Vitamin C was studied as a component of Seaweed extract. The inhibition effect of it on the corrosion of mild carbon steel in studied by weight loss, polarization and electrochemical impedance spectroscopy (EIS) methods. Deyab [31] declared that the obtained inhibition efficiency values were 93.54%; 90.79% and 93.64% by using weight loss, polarization and EIS methods, respectively. In Table 2, the highest dipol moment was observed for 4-metoxy-2 nitro aniline that was Anisole derivative, was presented as sustainable-green inhibitor for mild steel corrosion in acidic medium [18]. Furthermore the 4-methoxy-2 nitro aniline had lowest band gap among the molecules in Table 2. It is well known in the theory of frontier molecular orbital that an increase in E_{HOMO} and a decrease in E_{LUMO} are usually linked to higher inhibitory efficiency. The difference between the two (energy gap) provides a measure of the stability of the complex formed on the metal surface [18]. 4-metoxy-2 nitro aniline has tendency to accept electrons due to the presence of an attractor group ($-NO_2$). This may provide backbounding, over LUMO orbitals [18]. The lowest absolute electronegativity was obtained for 4-metoxy-N-methylaniline in Table 2. In generally, the efficiency of inhibitor compounds rises when absolute electronegativity decreases. The inhibitor molecules function as a soft base, whereas the metal surface functions as a soft acid. As a result, soft molecules are more reactive than hard molecules, and the efficiency of inhibitior increases as absolute electronegativity decreases. As can be seen from Table 2, the higher dipole moment values were detected for efficient corrosion inhibitors. The dipol-dipol interactions enhance the adsorption ability of molecules. The highest negative charge is found surrounding the electronegative atoms.

Consequently, it's worth noting that inhibitor molecules adsorb mainly through electrostatic interactions between the negatively charged atoms and the positively charged metal surface.

4. Conclusion

The following conclusions were obtained based on theoretical calculations:

The corrosion tests confirmed that these green inhibitor molecules can effectively protect industrial metals. They are generally mixed type inhibitors, which adsorb the metal surface according to Langmuir adsorption isotherm model, the theoretically calculated HOMO orbitals are mainly located on the N,O and electronegative terminal of molecules, the LUMO orbitals are seen on hetero cyclic part of molecules. The adsorption of inhibitor molecules, which should interact electrostatically with the positively charged electrode surface, is encouraged by the negative charged atoms. Inhibitor compounds are characterized by their decreased ΔE values. The calculated ΔE values were varied from 3.681 eV to 6.202 eV. The comparison of ΔE values with literature showed that similar results were obtained. The larger dipole moment is determined for molecules which encourage the adsorption of molecule to metal surface. The higher dipole moment of the green inhibitor candidates, which were calculated in this study and belongs to Vitamin C and Gossypo were 6.313 and 4.834 Debye, respectively.

Consequently, the theoretical results confirmed the experimental findings which were presented for Gossypo, Gallocatechin, Glabridin, Vitamin C, Alanine, Glycine, Glutamic acid, Camphor, Alpha pinene and 1,8-cineole molecules. The obtained results were showed that the similar trends were detected in the literature values.

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Research and publication ethic statement: The study does not require Ethics Approval.

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