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DFT study for some components of olea europae

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Abstract

The hazardous effects of corrosion influence not only metals but also environment and human health. Furthermore, cost of corrosion deeply strokes the economics of industrialized nations. In order to combat corrosion, especially in closed-circuit system and metal pickling, the use of organic inhibitor compounds is the most practically and effective method. The risk of organic inhibitors is their waste products may have environmental hazards. Therefore, attention has been focused on "green inhibitors" which are plant and seeds extracts, etc. Because they serve as various sources of naturally synthesized chemical compounds which are eco-friendly, cheap, readily available and renewable sources of materials and can be produced by simple extraction procedures. In this study, adsorption and corrosion inhibition properties of olea europae components which are green inhibitors were investigated theoretically. The molecular optimizations were performed using the Density Functional Theory (DFT) with the Beck's three parameter exchange functional and the Lee–Yang–Parr non-local correlation functional (B3LYP) with 6-311++G (d, p) basis set of atomic orbitals as implemented in Gaussian 03 program package. The energy of highest occupied molecular orbital (EHOMO), energy of the lowest unoccupied molecular orbital (ELUMO), energy gap (ΔE) between LUMO and HOMO, dipole moment, Mulliken charges on the backbone atoms were determined. The optimized molecular structures and HOMO, LUMO surfaces were visualized using Gauss View program package.

Keywords: Corrosion, DFT, Olea europae

Olea europae bitkisinin bazı bileşenleri için yük yoğunluğu teorisi çalışması

Özet

Korozyonun zararlı etkileri sadece metalleri değil aynı zamanda çevre ve insan sağlığını da etkilemektedir. Ayrıca, korozyon maliyeti, sanayileşmiş ulusların ekonomisini derinden etkiler. Özellikle kapalı devre sistemleri ve dekapajda, korozyonla mücadele etmek için organik inhibitör bileşiklerin kullanımı en pratik ve etkili yöntemdir. Organik inhibitörlerin kullanımlarının riski, atıklarının çevreye olumsuz etkileri olabilir. Bu nedenle, bitki ve tohum özütleri gibi "yeşil inhibitor" maddeler üzerinde durulmuştur. Çünkü bunlar, çevre dostu, ucuz, kolay ulaşılabilir ve yenilenebilir malzeme kaynakları olan ve basit ekstraksiyon yöntemleriyle elde edilen kimyasal bileşiklerdir. Bu çalışmada yeşil inhibitör maddeler olan olea europae bileşenlerinin adsorpsiyon ve korozyon inhibisyon özellikleri teorik olarak incelenmiştir. Moleküler optimizasyonlar, Beck'in üç parametre değişkeni fonksiyonu ile Yoğunluk Fonksiyonel Teorisi (DFT) ve 6-311 ++ G (d, p) baz seti ile Lee-Yang-Parr (B3LYP) kullanılarak yapıldı. En yüksek enerjili dolu orbital enerjisi (EHOMO), en düşük enerjili boş orbital enerjisi (ELUMO), LUMO ve HOMO arasındaki enerji farkı (ΔE), dipol moment, Mulliken atomik yükler Gaussian 03 program yazılımı ile belirlenmiştir. Optimize moleküler yapılar ve HOMO, LUMO yüzeyler Gauss View program paketi kullanılarak görüntülenmiştir.

Anahtar Kelimeler: Korozyon, DFT, Olea europaea

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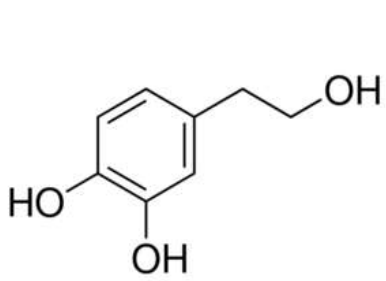
1. Introduction

Corrosion is inevitable phenomenon for metal industry, in order to solve corrosion problems there are many alternative methods have been applied. Especially for acid pickling and closed-circuit systems, organic inhibitors are suitable protection ways [1-5]. The main affair about these inhibitors, they are generally synthetic organic molecules and unfortunately, most of them have harmful affect to environment. In order to decrease toxic and harmful results of using corrosion inhibitors, green alternatives should be suitable. For this purpose, many researches have been achieved and herbal extracts, seeds and etc, have been used. Rose et al. [1] used Tabernaemontana Divaricate (TD) extract as corrosion inhibitor for protection of steel in 1 M HCl. The corrosion rate decreased almost 21 times in presence of 500 ppm TD extract. According to EIS results efficiency was 89.4% n 1.0 M HCl at 298 K. Ecorr values were -0.563 and -0.575 V (vs SCE) in 1.0 M HCl and presence of 500 ppm TD extract, respectively. Results showed that TD extract should be suitable inhibitor which can be called green and environmentally friendly. Soltani et al. used the extract of Salvia officinalis leaves [2] Some chemical molecules of its components are Sagecomarin, Rosmarinic acid, Luteolin 7-glucoside, Luteolin 7-glucoronide, Salvianolic acid and Carnosol. The results of steel corrosion in 1 M HCl with addition of various concentrations of Salvia officinalis extract showed that it has almost 96% inhibition efficiency for 2 g/L concentration. Mourya et al. investigate the corrosion inhibition performance of Marigold flower extract [3]. The adsorption of this green inhibitor on the mild steel surface obeys Langmuir adsorption isotherm, indicating monolayer adsorption. The activation parameters governing adsorption show that the inhibitor is physically adsorbed. The results of quantum chemical calculation indicate high feasibility of adsorption of molecular and protonated Lutein, major component of Marigold flower. In the field of corrosion studies, the quantum chemical calculation provides foresight for adsorption behavior of molecules. Therefore, most of scientist examines quantum programs before experimental studies [4-13]. Soltani et al. [2] emphasized that plant extracts have various complex mixture of chemical compounds so, we need experimental considerations due to solve such complexity. They indicated that, efforts in recent times have relied on quantum chemical computations within the framework of the density functional theory (DFT) to correlate the inhibitive effect of extract and the electronic properties of its main constituents, often with positive results [14]

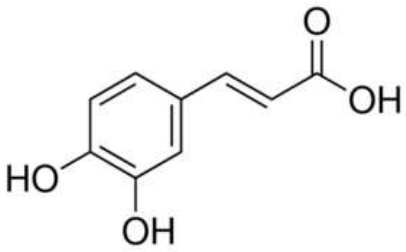
This paper emphasizes adsorption mechanism and some quantum parameters for olea europae components. It may provides lay a bridge on the molecular geometry and inhibition efficiency by electrochemical tests [15] and modelling study.

2. Experimental

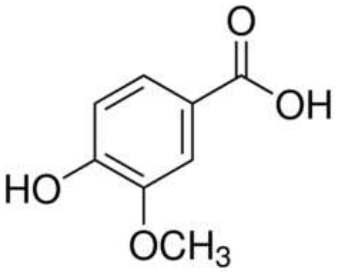
The calculations were carried out using density functional theory (DFT) with 6-311++G (d,p) basis set with the Gaussian 03W program. The optimized molecular structures and HOMO, LUMO surfaces were visualized using Gauss View. Molecules were given in Fig. 1.



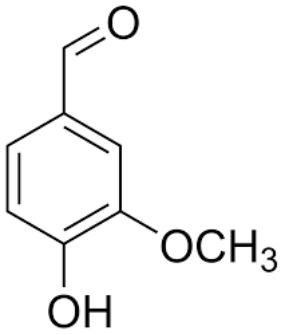
3-Hydroxytyrosol



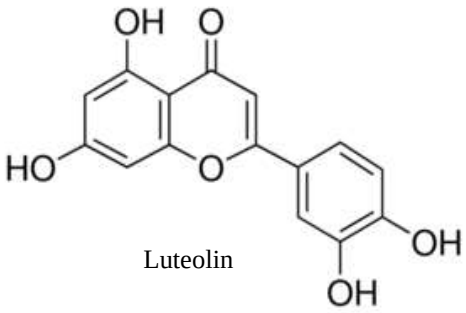
Caffeic acid



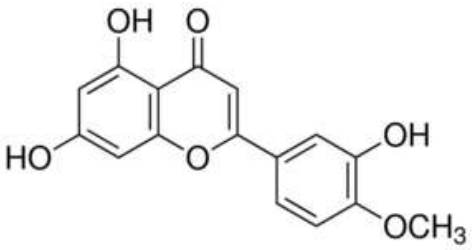
Vanillic acid



Vanillin



Luteolin



Diosmetin

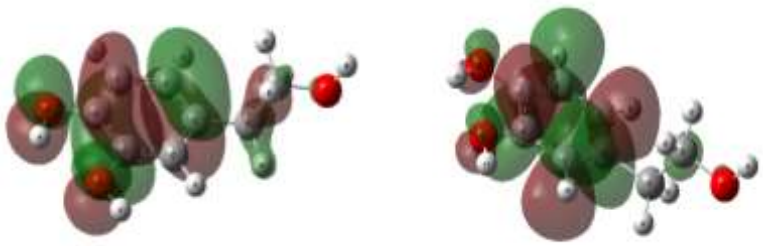
Figure 1. The studied components of olea europae

3. Results and discussion

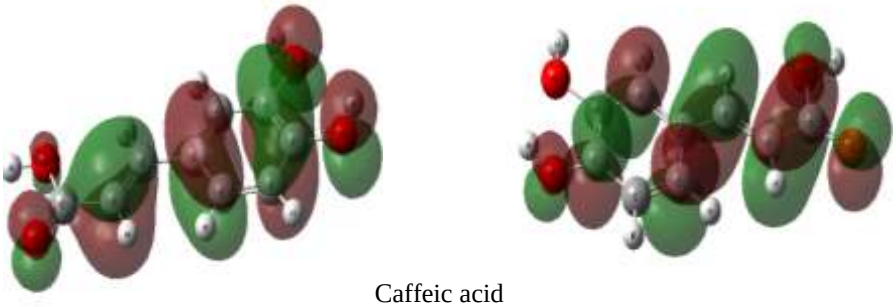
The quantum chemical calculations were employed to give further insight into the adsorption characteristics and inhibition efficiency of molecules which were given in Fig. 1. For this purpose, the energy of highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE) between LUMO and HOMO and Mulliken charges on the backbone atoms were determined by optimization. Some parameters were given in Table 1. In Table 1, E_{HOMO} deal with electron donating ability of the molecule and the inhibition efficiency increases with increasing its values. High E_{HOMO} values prove that the molecule has tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbitals. Higher E_{HOMO} value facilitates adsorption (and therefore inhibition) by influencing on the transport process through the adsorbed layer. The energy gap between LUMO and HOMO (ΔE) is a parameter with the smaller value causes higher inhibition efficiencies of the molecule. [11-14].

The HOMO and LUMO locations were given in Fig. 2. The location of orbitals was seen on cyclic structures. Most probably adsorption is occurred on these regions of molecules.

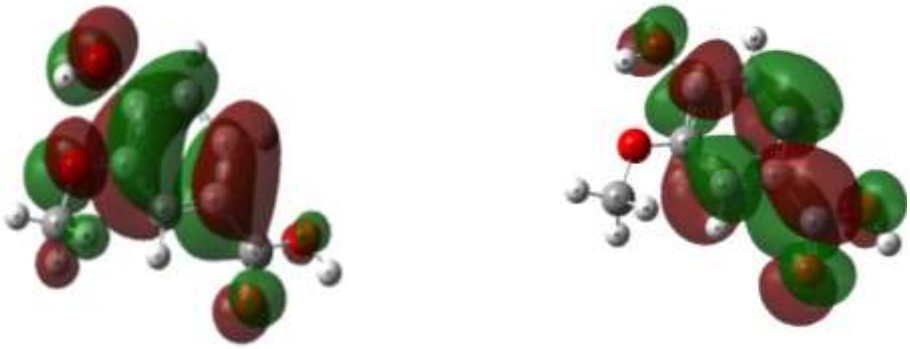
HOMO LUMO



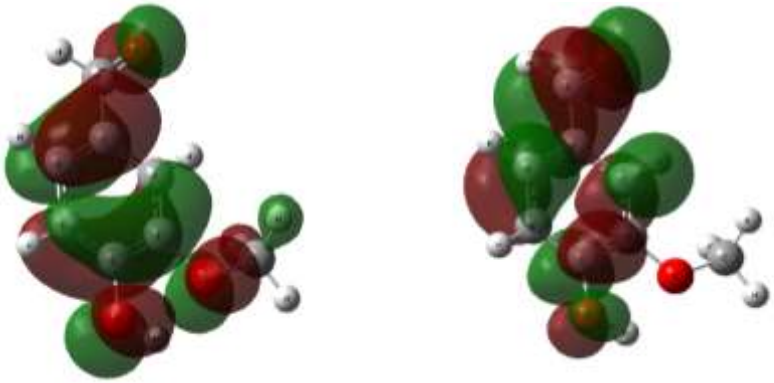
3-Hydroxytyrosol



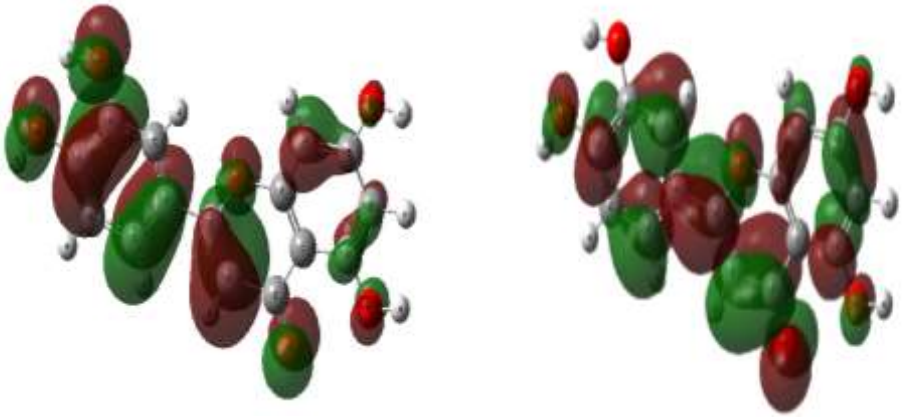
Caffeic acid



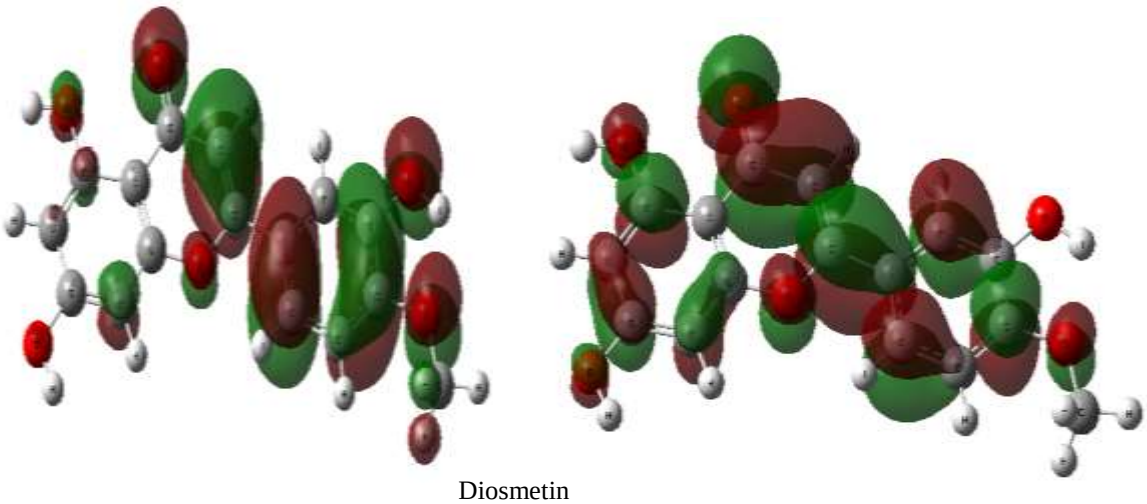
Vanillic acid



Vanillin



Luteolin



Diosmetin

Figure 2. HOMO and LUMO locations of molecules

The absolute electronegativity (χ), absolute hardness (η) and absolute softness (s) and dipole moment (μ) were given in Table 1.

Table 1. The quantum chemical parameters

Molecule	E_{HOMO}/eV	E_{LUMO}/eV	ΔE/eV	χ/eV	η/eV	s/eV	μ/Debye
3 hydroxytyrosol	-5.725	0.054	5.780	2.835	2.890	0.346	2.8572
Caffeic acid	-5.988	-1.941	4.047	3.965	2.024	0.494	4.5529
Vanillic acid	-6.144	-1.352	4.793	3.748	2.396	0.417	1.7446
Vanillin	-6.231	-1.687	4.544	3.959	2.272	0.440	2.4729
Luteolin	-5.883	-1.650	4.233	3.767	2.116	0.473	1.6693
Diosmetin	-5.891	-1.624	4.267	3.757	2.134	0.469	8.7627

As seen from Table 1, band gap values are between 4 and 6 eV for components of olea europae which are signals of higher inhibition ability of molecules. The other parameter of inhibitive behavior is absolute electronegativity, the protection efficiency of maters generally increases with decreasing χ. The inhibitors behave such as soft base and the metal surface acts as a soft acid. Therefore, soft molecules are more reactive than hard ones. In Table 1, low value of softness is signal of high inhibition efficiency and correlate the other parameters. The highest dipole moment is 8.7627 Debye in Table 1, it means that Diosmetin has higher solubility than the others in water phase. Mulliken charge distribution showed that highest negative charge was located on "O" atoms in all molecules. Most probably adsorption occurs on these atoms.

4. Conclusions

According to obtained data 3 hydroxytyrosol, Caffeic acid, Vanillic acid, Vanillin, Luteolin and Diosmetin are suitable inhibitor molecules, they are components of olea europae therefore we can offer using olea europae against corrosion of metals in closed circuit systems or pickling process.

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These molecules may decrease corrosion rate with the help of active adsorption centers. On metal solution interface, adsorption occurs (most probably physically); the inhibitor molecules replace with water molecules. Initially first inhibitor layer occurs, then other molecules may accumulate on this layer and surface effectively protect against corrosion.

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