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Study of Corrosion Inhibition Efficiency of Phenol and Coumarin Compounds from Durian Skin (*Durio zibertinus*) using the DFT (Density Functional Theory) method

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Abstract. In this research, a study has been carried out to investigate the corrosion inhibition efficiency of eight phenolic acid derivative compounds (3,4-dihydroxybenzoic acid (ADB), 4-hydroxy-3-methoxybenzoic acid (AMB), ethyl protocatechute (EP), 3,4-dihydroxybenxaldehyde (DBD)) and Coumarin (Skopeletin (SKP), Fraxetin (FXE), Fraxidin (FXI), 7-hydroxycoumarin (HK)) contained in durian skin (Durio Zibertinus) using the Density Functional Theory (DFT) method. Chemical reactivity parameters such as the lowest molecular orbital energy that does not contain electrons (ELUMO), the highest molecular orbital energy that contains electrons (EHOMO), electron affinity (A), ionization potential (I), energy difference (ΔEgap), global hardness (η), global softness (σ), electronegativity (χ), electrophilicity (ω), number of transferred electrons (ΔN) and back-donation energy (ΔEback-donation) are calculated at the DFT/B3LYP/6-31G (d,p) theoretical level. Based on the research results, it was found that BDB and FXE compounds were better as corrosion inhibitors than other compounds.

Keywords : Inhibitor Corrosion, DFT, Computations Chemistry, Fenolat Acid, Coumarin.

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Introduction

Metal is a material that is widely used in various industrial and construction fields[1]. Protection of metal surfaces from corrosion is a major concern in the metallurgical industry, oil mills, the environment and chemical plants. Corrosion is a decrease in the quality of metal that occurs due to its interaction with the environment [2]. The negative impacts caused by corrosion are very large, ranging from health impacts, economic and safety impacts to environmental impacts. [1]. So that special handling is needed to overcome metal corrosion, one of which is the use of organic inhibitors [3]. Organic compounds are the most efficient corrosion inhibitors because they are environmentally friendly, available in nature and non-toxic [4]. Organic inhibitors with heterocyclic structures containing conjugated π bonds in their molecular structure and having heteroatom groups, such as N, S, O and P, can be adsorbed on the metal surface through physisorption or chemisorption [5].

Durian (Durio zibertinus) is a tropical plant originating from Southeast Asia [6]. In Indonesia, durian harvest production reaches around 700,000 tons each year. However, unknowingly, 65-80% of durian skin becomes unmanaged waste and is left to pile up to rot. This can have a negative impact on environmental health. So that proper processing is needed to obtain new products that have economic value and can reduce the cost of managing this waste [7]. Feng et al, 2017 succeeded in isolating several phenolic acid and coumarin compounds in durian skin. Derivatives of these phenolic acid compounds are 3,4-dihydroxybenzoic acid (ADB), 4-hydroxy-3 -methoxybenzoic acid (MBA), Ethyl protocatechuate (EP) and 3,4-dihydroxybenxaldehyde (DBD). The molecular structure of the phenolic acid and coumarin derivative compounds is rich in electrons, due to the presence of π conjugation bonds and heteroatom groups in the molecule which are good characteristics as corrosion inhibitors. So it is interesting to investigate the potential for corrosion inhibition and as an effort to process durian skin waste into useful products and to find organic molecules with high corrosion inhibition potential.

The development of increasingly sophisticated computing and algorithm development has contributed to the evolution of material modeling techniques at the atomic scale. Computational methods provide insight into the reactivity parameters of a molecule and the relationship between quantum chemical parameters and corrosion inhibition efficiency [8]. The use of quantum chemical methods such as the DFT method can be used to determine the electronic structure and various molecular properties, such as polarization and excitation energy quickly and accurately to evaluate the effectiveness of inhibitors [9].

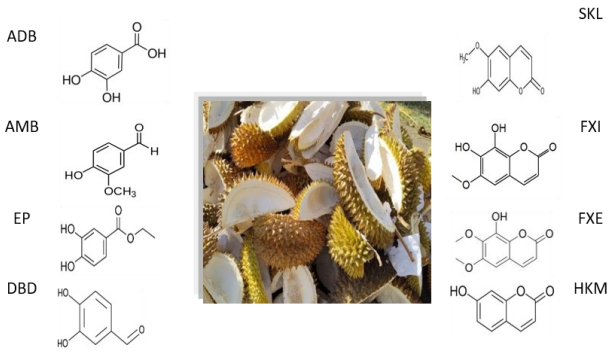

Figure 1. Structure of Duran Compounds

Experimental

The Studi Density Functional Theory (DFT). Geometry optimization of phenolic acid and coumarin derivative molecules (Figure 1) was carried out using the DFT method through three parameters of the hybrid exchange-correlation function Beck, Lee-Yang-Parr (B3LYP) and the nonlocal basis set 6-31G (d, p) implemented in the Gaussian 16 program. The B3LYP hybrid function is a method that combines the Hartree-Fock approximation with energy exchange in the electron correlation function. This method was chosen because the compounds whose electronic properties and structures are predicted are organic compounds. The basis set used is 6-31G (d, p), because based on the literature, this basis set has been proven effective in modeling organic compounds [10]. Quantum chemical descriptors have been extracted from the following equation to predict the corrosion inhibition properties of the investigated molecules [11].

Frontier Molecular Orbital (FMO) such as highest occupied molecular orbital (EHOMO), lowest unoccupied molecular orbital (ELUMO), ionization potential, I (Equation 1), electron affinity, A (Equation 2), energy gap, ΔEgap (Equation 3), electronegativity, χ (Equation 4), chemical hardness, η (Equation 5), softness, σ (Equation 6), global electrophilicity index, ω (Equation 7), fraction of electrons

transferred, (Equation 8) and back donation energy (Equation 9), are calculated (Akinyele; Imran, (2020); Khan [12].

$$I = -E_{HOMO} \quad (1)$$

$$A = -E_{LUMO} \quad (2)$$

$$Energi\ gap\ (\Delta E) = E_{LUMO} - E_{HOMO} \quad (3)$$

$$\chi = \frac{I+A}{2} = -\frac{1}{2}(E_{HOMO} + E_{LUMO}) \quad (4)$$

$$\eta = \frac{I-A}{2} = -\frac{1}{2}(E_{HOMO} - E_{LUMO}) \quad (5)$$

$$\sigma = \frac{1}{\eta} = -\left(\frac{2}{E_{HOMO} - E_{LUMO}}\right) \quad (6)$$

$$\omega = \mu^2 4\eta \quad (7)$$

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \quad (8)$$

$$\Delta E_{back\text{-}donation} = -\eta 4 \quad (9)$$

Result and Discussion

Quantum Chemical Parameters of Durian Peel Chemical Components. Quantum chemical parameters studied such as ELUMO, EHOMO, ΔE (energy gap), total energy and dipole moment in phenolic acid molecules, coumarin and its derivatives are needed to determine the efficiency of corrosion inhibition as done by Gece et al., [13]. The distribution of HOMO and LUMO electron densities is important to observe to determine which part of the molecule is able to donate or accept electrons qualitatively as in Figures 1 and 2.

Figure 1 shows the distribution of molecular orbital densities of phenolic acid derivatives contained in durian skin consisting of ADB, AMB, EP and DBD molecules. The distribution of molecular orbital densities was calculated using the DFT basis set B3LYP/6-31G (d, p) method using the Gaussian program. The overall image shows the distribution of electrons in the HOMO and LUMO regions. HOMO is the highest orbital in the valence band that has been filled by electrons, while LUMO is the lowest orbital in the conduction band that has not been filled by electrons [14]. In the HOMO area, electrons are mainly localized on oxygen atoms and C-C bonds in the benzene ring. Part of these atoms is expected to be the center of interaction between inhibitor molecules and metal surfaces. Atoms in the HOMO area function as electron donors from inhibitor molecules to metal surfaces, forming coordination bonds. On the other hand, analysis of the LUMO area shows that the electron distribution in phenolic acid derivative molecules is focused on the oxygen double bond, the C=C double bond in the benzene ring, and the C-C bond. These atoms function as electron acceptors from the metal orbital to the inhibitor molecular orbital. Gece et al. [13] stated that the adsorption strength of molecules in the HOMO and LUMO orbitals is comparable.

Figure 2 shows the electron distribution in coumarin compound derivatives. In the HOMO region, electrons are spread across the O atom, the C=O double bond, the C-C bond and the hydroxyl group. In the LUMO region, the distribution of electrons is seen in the pyran ring, C=O and C-C. The Frontier Molecular Orbital (FMO) theory of inhibitors shows the adsorption ability of molecules on metal surfaces. The interaction between inhibitor molecules and metal surfaces is dominated by two processes: (i) electron donation from inhibitor molecules to empty d orbitals on metals (transition metals), and (ii) back donation of electrons from filled d orbitals to inhibitor molecules. The two processes complement each other, and both are useful for enhancing the adsorption process of inhibitor molecules on metal surfaces [14]. The results of geometry optimization on the 4 phenolic acid derivative compounds using the DFT basis set B3LYP/6-31G (d, p) method obtained the values of the molecular properties of ADB, AMB, EP and DBD and quantum chemical parameters that indicate chemical reactivity (Table 1).

EHOMO describes the ability of a molecule to donate electrons to acceptors, such as empty metal d orbitals. Conversely, ELUMO indicates the ability of a molecule to accept electrons. Thus, a lower ELUMO value indicates a greater ability of the molecule to accept electrons and this causes the inhibitor efficiency to be better [15]. When the HOMO energy level increases and the LUMO energy level decreases, the binding ability of the inhibitor to the metal surface increases. Table 2 shows that from the 4 phenolic acid derivative molecules, the ELUMO DBD values are greater than other molecules, which is -0.0621 eV.

Theoretical calculation of quantum chemical parameters in a neutral inhibitor molecule is an approach to predict inhibitor efficiency and explain experimental results [16]. The metal acts as a Lewis base while the inhibitor acts as a Lewis acid. So the metal uses HOMO to initiate a reaction with the LUMO inhibitor. Strong covalent bonds can only be

expected if Egap is close to zero[15].

According to the FMO theory, the interaction between the HOMO and LUMO levels is related to chemical reactivity. ΔEgap is an appropriate parameter that shows the reactivity of the inhibitor to adsorption on the metal surface. A low ΔE value indicates an increase in inhibitor reactivity, thereby increasing the inhibitor efficiency value [13]. The ΔEgap values of the 4 inhibitors (Table 1) increased in the order: EP>ADB>MBA>DBD. Other global reactivity parameters were used to study the effectiveness of the inhibitors. Such as: global hardness (η), electronegativity (X), global softness (σ), transferred electrons (ΔN), and electrophilicity index (ω) of the molecules are shown in Table 2. The tendency of inhibitor binding to metals can be used in the Hard-Soft-Acid-Base (HSAB) theory which helps explain the stability of metal inhibitors.

The HSAB theory states that hard acids prefer to coordinate with hard bases and soft acids prefer to coordinate with soft bases. As a result, metal atoms are classified as soft acids, because soft molecules have small ΔEgaps while hard molecules have high ΔEgaps [15]. Therefore, inhibitors that are classified as soft bases will show an effect on metals. So DBD which has the smallest ΔEgap and the highest softness (σ) has a better corrosion inhibitor than other molecules. This result was confirmed by calculating the softness (σ) of the inhibitor so that its reactivity is shown in Table 1 in the order: DBD > MBA > ADB > EP.

Table 1 shows that the global hardness value (η) for all molecules has a greater value than DBD. This tendency is inversely proportional to the global softness (σ). So the highest softness value (σ) and the smallest hardness value (η) of DBD. Phytochemical inhibition of DBD is estimated to have superior performance due to its electron donation ability, high electron back-donation strength (ΔEback-donation), and smaller Egap value and larger

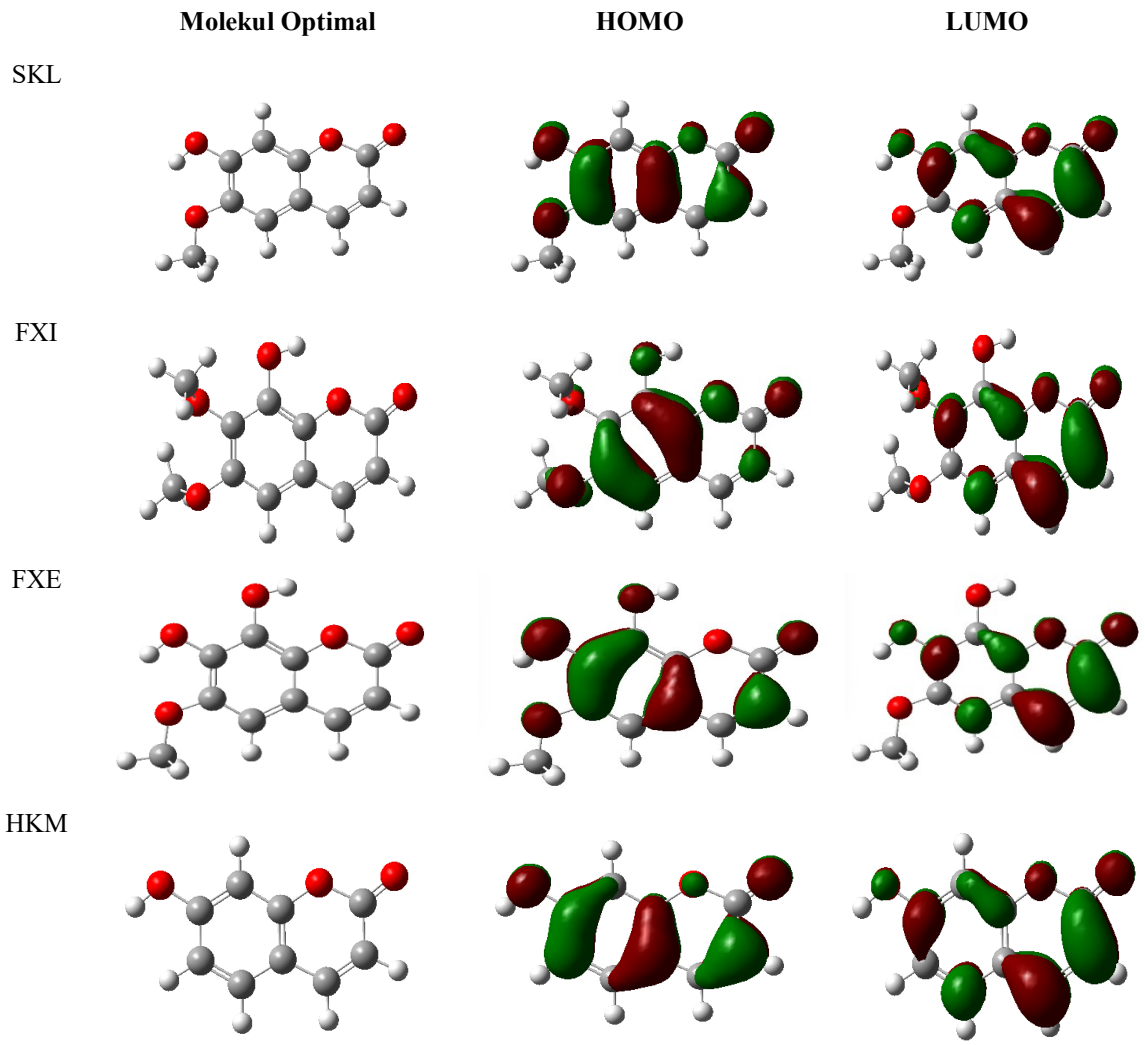

Figure 2. Optimization structure, electron density distribution in the HOMO and LUMO orbitals of phenolic acid compounds (atoms: white=H; red=O; gray=C)

Table 1. Quantum Chemical Parameters of Durian Peel Chemical Components Derivatives of Phenolic Acid

Parameter	Asam Fenolat				Fe[a]
	ADB	AMB	EP	DBD	
E_{HOMO} (eV)	-0,2286	-0,2398	-0,2267	-0,2311	–7.902[a]
E_{LUMO} (eV)	-0,0478	-0,0620	-0,0416	-0,0620	–0.151[a]
ΔE_{gap} (eV)	0,1809	0,1777	0,1851	0,1690	
Momen Dipol (Debye)	2,0851	4,1063	4,5267	2,6308	
Energi total (a.u)	-571,4228	-535,4547	-650,0679	-496,1456	
Potensial Ionisasi / I (eV)	0,2286	0,2398	0,2267	0,2311	
Afinitas Elektron / A (eV)	0,0478	0,0620	0,0416	0,0620	
Elektronegativitas / χ (eV)	0,1382	0,1509	0,1342	0,1466	4.026[a]
Global Hardness / η (eV)	0,0904	0,0889	0,0926	0,0846	3.875[a]
Global Softness / σ (eV^{-1})	11,0619	11,2505	10,8050	11,8273	
Elektrofilisitas / ω (eV)	12,0230	47,4253	55,3522	20,4645	
Energi /$\Delta E_{back\text{-}donation}$	-0,0226	-0,0222	-0,0231	-0,0211	
Elektron Transfer/ ΔN (eV)	0,3102	0,3044	0,3177	0,2897	
Massa Molekul (g/mol)	154,12	168,148	182,175	138,12	

global softness value. According to Saha, 2014 soft molecules are more reactive than hard molecules so they have the highest corrosion inhibition efficiency [11]. Table 1 also shows the value of the fraction of electrons transferred (ΔN) from the 4 phenolic acid derivative molecules.

The electron transfer fraction value describes the interaction between the inhibitor molecule and the metal surface. Where electrons move from molecules with low electronegativity to metal surfaces that have higher electronegativity, until equilibrium is reached. According to Gece et al.[13], if the ΔN value <3.6 the corrosion inhibition efficiency will increase along with the increase in the ability of molecules to donate electrons to the metal surface. So that DBD is a better corrosion inhibitor than other molecules from phenolic acid derivatives. Furthermore, geometry optimization was carried out on the 4 coumarin derivative molecules. The results of the optimization obtained quantum chemical parameters shown in Table 2. Table 2 shows that the FXE molecule has a higher EHOMO value than other molecules in the order: FXE> SKP> FXI> HKM. By comparing the EHOMO values of FXE and other coumarin molecule derivatives, FXE shows higher corrosion inhibition efficiency compared to other molecules. This statement is in line with the report Gece which states that the higher the EHOMO value or the lower the ELUMO value, the stronger the ability of organic molecules to bind to metal cations, which indicates that the organic molecules have high corrosion inhibition efficiency [13].

FXE has the lowest ΔEgap value compared to other molecules, which is 0.1497 eV, indicating that the FXE molecule has higher reactivity and is more effective in being adsorbed on metal surfaces when compared to other molecules. Udowo reported that a larger ΔE value indicates that the molecule requires more energy to be excited from the HOMO orbital to the LUMO orbital [17]. The lower the ΔE value of a molecule, the better its corrosion inhibition efficiency, which is in line with the opinion expressed by [18]. Table 3 shows that FXE has a higher ΔEback-donation value than other molecules in the order: FXE> FXI> HK> SKP.

In addition, the softness value of FXE shows a higher value than the other 4 coumarin derivatives, which is 13.3690 eV-1. This indicates that FXE has high inhibition efficiency as a corrosion inhibitor. The electrophilicity index (ω) indicates the ability of the inhibitor to accept electrons from the metal. FXE shows the highest electrophilicity index (ω) value compared to other inhibitors and its effect on Fe metal. The electrochemical results show that FXE has a fast adsorption process and forms a thick protective layer to cover the Fe surface. The Fe-DBD complex is produced due to the reaction between the oxygen atom and the Fe center which prevents the formation of oxides. As a result, this observation confirms its high capacity to accept electrons from the metal. This means that the metal acts as a Lewis base while all compounds act as Lewis acids (cathodic inhibitors). The metal will accept electrons from the inhibitor to form a coordinated bond. In

addition, the inhibitor can accept electrons from the metal to form a back donor bond depending on the orientation of the inhibitor structure that is optimized in space. The inhibition efficiency will increase because the donation and back donation processes strengthen the adsorption of the inhibitor to the metal surface [15].

The dipole moment value (μ) of FXE is 6.8770 Debye. The SKP molecule has a larger dipole moment value of 7.7303 Debye. A lower dipole moment value can increase the adsorption of inhibitors on the metal surface, so that the corrosion inhibition efficiency becomes higher [19]. However, some researchers argue that the corrosion inhibition efficiency actually increases with increasing dipole moment value [20]. Based on a literature review, several discrepancies were found in the correlation of dipole moment and corrosion inhibition efficiency [21].

Conclusion

In this Based on the results of the analysis of quantum chemical calculations of phenolic acid and coumarin derivatives using the DFT method, a correlation was obtained between the electronic parameters of phenolic acid and coumarin derivative compounds. Analysis of the EHOMO, ELUMO and energy gap (ΔE) values from molecular optimization showed that DBD and FXE molecules were better as corrosion inhibitors compared to other molecules. This is also supported by the values of other quantum chemical parameters such as global hardness (η), global softness (σ), ionization potential (I) electron affinity (A), electronegativity (χ), electron transfer (ΔN), total energy (ET), interaction energy (Eint), and ΔEback-donation values.

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