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Theoretical Study of Xanthone Derivative Corrosion Inhibitors Using Density Functional Theory (DFT)

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Abstract

The potential corrosion inhibitor properties of xanthone compounds and its derivatives (gartanin, 8-desoxygartanin, α-mangostine, and β-mangostine) can be demonstrated through Density Functional Density Theory (DFT) at the theoretical level B3LYP/6-31G(d, p). Quantum chemical parameters such as the energy of the highest molecular orbital occupied by electrons (E_{HOMO}), the energy of the lowest molecular orbitals not occupied by electrons (E_{LUMO}), energy gap (E_{gap} / ΔE), dipole moment (μ), and total energy (E_{tot}) can be calculated using DFT method. The DFT data analysis equation can determine the value; potential energy (I), electron affinity (A), absolute electronegativity (χ), global hardness (η), global softness (σ), number of transfer electrons (ΔN), electrophilicity (ω), and corrosion inhibition efficiency (IE%) . The results of quantum chemical parameter calculations show the potential inhibitory properties of gartanin > α-mangostine > β-mangostine > 8-desoxygartanin > xanthone, with the calculated corrosion inhibition efficiency value of gartanin of 86.54%.

***Keywords**:* DFT, corrosion inhibitors, inhibitor efficiency, *Xanthones*, *Xanthones* derivatives.

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1. INTRODUCTION

The Density Functional Theory (DFT) method is used as a quantum chemical calculation used by various corrosion scientists for a long time (Gece *et al*., 2008). Quantum chemical calculations have been used recently to explain the corrosion inhibition mechanism using the DFT method with functional B3LYP/6-31G(d, p). Molecular structure and electronic parameters can be obtained by theoretical calculations containing the highest molecular orbital energy occupied by electrons (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}) energy gap (ΔE), and dipole moment (obayes *et al*., 2014).Theoretically, it can be explained that the calculation of ionization potential and electron affinity can be concluded in the theory developed by Koopman which explains the relation of ionization potential (I) with electron affinity (A) and E_{HOMO} and E_{LUMO} orbital energy (Koopman *et al*., 1934).

The DFT method or Functional density theory is an important method in quantum chemical calculations. The DFT method comes with the development of computer technology that enables the accurate calculation of the first principles of various compositions. Associated with an important role in developing a better understanding of the basic properties of molecules and materials (Bickelhaupt *et al*., 2000). This method was successfully applied to illustrate the structural importance of corrosion inhibitors and the efficiency of adsorption of inhibitor compositions on metal surfaces (Obayes et al., 2014). Corrosion is the process of material degradation or loss of a material both in quality and quantity due to the

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process of chemical reactions with the environment. The environment can be in the form of water, air, solution, soil, and biology which are often referred to as corrosive media. Thermodynamic corrosion events occur when the environment has a more positive standard electrode potential than metal (Trethewey *et al*., 1988). Corrosion inhibitors are an excellent method for preventing corrosion. Generally, corrosion inhibitors come from synthetic chemicals which are dangerous chemicals, the price is relatively expensive and not environmentally friendly. One alternative is to use inhibitors derived from extracts of natural ingredients (Umoren *et al*., 2011). Various organic compounds containing heteroatoms (N, S,O) which can donate electrons have been used as corrosion inhibitors. The use of organic inhibitors to prevent corrosion is a promising alternative. These inhibitors are usually adsorbed on the metal surface by forming coordination bonds (chemical adsorption) or electrostatic interactions between metals and inhibitors (physical adsorption) (Obayes *et al*. 2014).

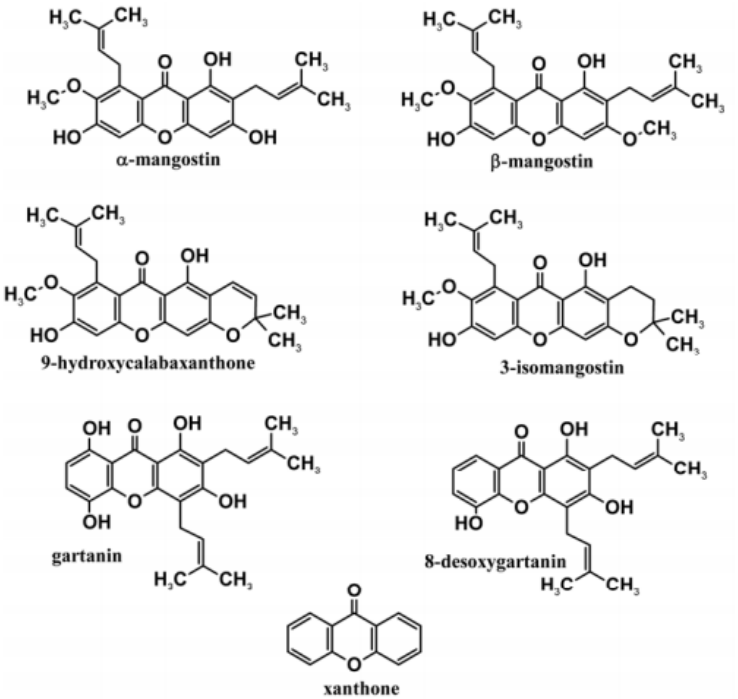


Figure 1. Molecular structure of Xanthones and its derivatives (Walker *et al*., 2007).

In previous studies some plant extracts such as surian leaf extract (Toona Sinensis) (Emriadi *et al*., 2016), brown leaf extract (Cassava Leaf) (Emriadi *et al*., 2015), and also extracts from mangosteen peel (Obot *et al*., 2011) proved to have potential as a corrosion inhibitor. Xanthones or xanthen-9H-ones are secondary plant polyphenols and are not developed by the human body. Xanthones can be isolated from the Gutiferae family including Garcinia mangostana. Parts of the Garcinia mangostana plant that contain xanthones include bark, leaves, fruit and fruit skin. These polyphenols have a special chemical structure that has a tricyclic aromatic ring replaced with isoprene, phenol and methoxy which provides several possible chemical structures. Xanthones contained in mangosteen include 9-hydroxicalabaxanton, 3-isomangostin, gartanin, 8-desoxygartanin, α-mangostine, and β-mangostin (Walker *et al*., 2007). Some xanthones derivatives have not formed as corrosion inhibitors such as gartanin, 8-desoxygartanin, α-mangostine, and the combination of β-mangostine with the molecular structure improved in Figure 1.

Xanthones are organic compounds that play an excellent role in inhibiting corrosion in an acidic atmosphere, have been proven experimentally to have a corrosion inhibitor efficiency of 74.08%, and also xanthones can interact with Fe metals so as to protect Fe from

corrosion, and good inhibition for Fe metals (Obot et al., 2011). Gartanin, 8-desoxygartanin, α-mangostine and β-mangostine are derivatives of xanthone compounds, xanthone compounds and their derivatives have been tested for their compounds contained in mangosteen plants where other content obtained by xanthone derivatives is α-mangostine, β-mangostine, and their derivatives have been tested for their compounds contained in mangosteen plants where other content obtained by xanthhone derivatives is α-mangostine, β-mangostine, 8 - desoxygartanin, and xanthones that have been analyzed using HPLC (Walker *et al*., 2007)

The main objective of this research is to determine the efficiency of inhibition of xanthone molecules and their derivatives (gartanin, 8-desoxygartanin, α-mangostine, and β-mangostine) using the DFT method. Quantum chemical parameters to be calculated namely; E_{HOMO}, E_{LUMO}, gap energy (ΔE), dipole moment (μ), total energy, electron affinity (A), ionization potential (I), global hardness (η), global softness (σ), electronegtivity (χ), electropylicity (A) ω), and the number of transfer electrons (ΔN) of xanthone compounds and their derivatives.

2. MATERIALS AND METHODS

All quantum mechanical calculations have been achieved using the Gaussian09 package (frisch *et al*., 2009). The geometry of all systems investigated by xanthone, gartanin, 8-desoxygartanin, α-mangostine, and β-mangostine shown in Figure 1 is optimized at the level of functional function theory using functional B3LYP (a combination of exchange from Becke with three parameters of hybrid exchange function (B3) using the dynamic correlation function Lee, Yang and Parr (LYP)). The triple-zeta quality base regulated by polarization and diffuse functions denoted 6-31G(d, p) has been used. In this study, the electronic properties of the inhibitors were investigated by calculating the energy of the highest molecular orbitals occupied by electrons (E_{HOMO}), the energy of the lowest molecular orbitals not occupied by electrons (E_{LUMO}), energy gap (ΔE), dipole moment (μ), and energy total.

3. RESULTS AND DISCUSSION

Gartanin, 8-desoxygartanin, α-mangostine, and β-mangostine are derivatives of xanthone composition. As in previous studies, xanthones have been used as antioxidants (Chiang *et al*., 2003; Jung *et al.*, 2006), anti-malaria (Likhitwitayawuid *et al*., 1998), anti-acne activities (Chomnawang *et al.*, 2005), and not only for health, xanthones also have anti-corrosion ability (Obi *et al.*, 2011). All of these xanthones derivatives can be obtained in the garcinia mangostana plant known as mangosteen fruit, which in this plant contains quite a number of xanthones derivatives (Walker *et al.*, 2007). Mangosteen plants themselves are effective as corrosion inhibitors, while the chemical structure of xanthones forms the main core of various natural compositions such as mangostin, which are sometimes collectively referred to as xanthones (Obi *et al.*, 2011).

Experiments have been proven xanthone has good inhibiting properties and environmentally friendly, where xanthone molecules have carbonyl groups, oxygen atoms, and aromatic rings with several bonds that can be used as active sites for the inhibitor process. Xanthones also have a large molecular mass (196.19 g / mol) which effectively has many surfaces for the process of adsorption with mild steel (Obot *et al.*, 2011)

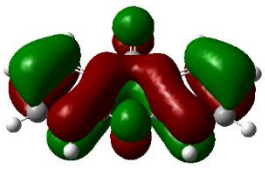
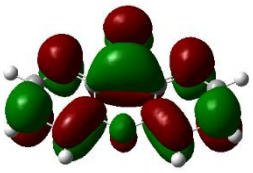
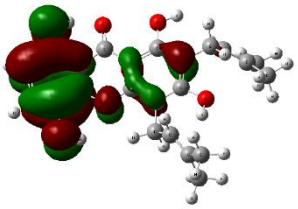
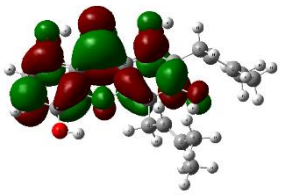
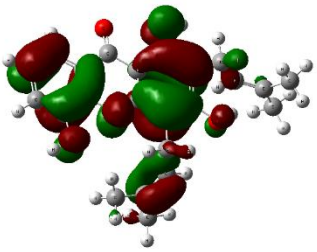
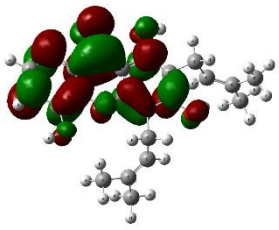
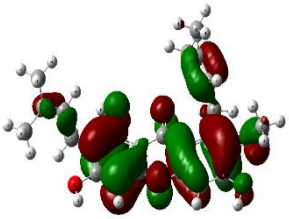
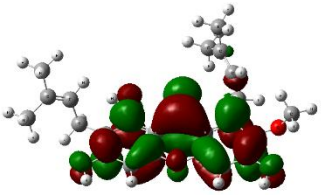
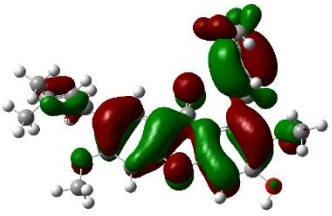
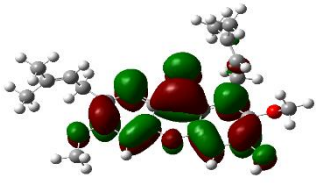
The best-known acid inhibitors are organic compounds that contain nitrogen, sulfur, and oxygen atoms. In general, organic molecules resist corrosion by adsorption on metal surfaces. Furthermore, adsorption depends on the electronic structure of molecular inhibitors, steric factors, aromaticity and electron density at the donor site, there are functional groups such as C=O, N= N, R-OH and other groups, molecular areas, many molecules, and electrochemical potential on metal solutions or interfaces (Obot *et al.*, 2011).

Table 1 distributes HOMO and LUMO energy molecular orbitals in the composition of Xanthones and its derivatives show electrons located in all C=O, O-H, C-O-C bonds and in the benzene ring. The distribution of E_{HOMO} and E_{LUMO} is shown by the two positive and negative phases of the orbitals represented by two colors. The green area represents an increase in electron density and the red color represents a decrease in electron density. The HOMO distribution of xanthones, α-mangostin, and β-mangostin is seen as electrons located in C-C bonds found in the benzene ring, C-O-C bonds, and C=O bonds, whereas in gartanin and 8-desoxygartani

compounds the electrons are not located in the bonds C=O but located in another bond. The distribution of LUMO molecular orbitals in combination of xanthones and electron derivatives is spread throughout the benzene ring, C-O-C bonds, C=O bonds, C-C bonds, C-H bonds and also in O-H bonds.

Table 1 also shows gartanin compounds for the distribution of molecular orbital densities in HOMO showing a very significant difference in form compared to xanthones and other derivatives. In the picture, it can be seen that the electrons are more located in the part of the benzene group that binds O-H, which is caused by another benzene group there is a 2-pentene subtituent that causes electrons to push towards the benzene group which has many O-H bonds. Organic compounds that contain oxygen bonds are in great demand as corrosion inhibitors due to the contribution of π bonds from double or triple bonds they have (Obayes *et al.*, 2017). The existence of this π bond will help the formation of complexes between organic compounds and metal surfaces by coordinating covalent bonds (chemical adsorption) or electrostatically (physical adsorption) (Noor *et al.*, 2005).

Table 1. Frontier molecular orbitals (MO) of Xanthones and its derivatives at B3LYP/6-31(d,p) level of theory

Molecule	HOMO	LUMO
Xanthone		
Gartanin		
8-Desoxygartanin		
α-Mangostine		
β-mangostine		

By using quantum chemical calculations, the values of $E_{HOMO,}$ E_{LUMO}, total energy, and dipole moment values of each compound have been optimized. Table 2 shows the results of quantum chemical properties calculated for Xanthones compounds and their derivatives using the DFT method. Table 2 shows gartanin compounds which have high E_{HOMO} values (-0.19216 eV) and low E_{LUMO} values (-0.05232 eV) compared with Xanthones and other derivatives. For molecular adsorption, both HOMO and LUMO have comparable strengths. A high HOMO value is responsible for donating electrons to electrons in low energy molecules. Increasing the value of E_{HOMO} causes an increase in the value of adsorption and increases the efficiency of the inhibitor. Low LUMO values indicate the ability of molecules to accept electrons (Gece *et al*., 2008).

Table 2 also shows the gap energy value (ΔE), where ΔE is an important parameter as a function of reactivity on inhibitor molecules for adsorption on metal surfaces (Wazzan *et al*., 2014). Gartanin compound has a smaller energy gap value of 0.13984 eV. A low value will provide a good inhibitor efficiency because a large energy gap indicates that it is difficult to add electrons to a low HOMO energy value and it is also difficult to release electrons at high LUMO energy values (Gece *et al*., 2017) . Quantum chemistry states that gartanin has the potential to be a better corrosion inhibitor compared to other compounds.

E_{HOMO}, E_{LUMO} and ΔE values are important parameters in quantum chemical properties, but the dipole moment (μ) is also an important electronic parameter for determining the level of charge circulation around a molecule's surface, which can be used to predict the results of reactivity and stiffness of molecules (Arthur *et al*, 2019). It can be seen in Table 2 that the dipole moment value for gartanin compound is the highest at 8.11 Debye compared to other compounds. A high dipole moment value will cause an increase in adsorption between the inhibitor and the metal surface (Li *et al.*, 2009). So that the high value of gartanin dipole moment will facilitate this inhibitor molecule to be adsorbed on the surface of Fe metal. Volume inhibitors will also increase with increasing dipole moments.

The total energy (E_{tot}) in the gartanin compound is the lowest value compared to the total energy value in other compounds. In Table 2, the value of gartanin is -1342.7624 au. The smaller the total energy value, the better absorption of compounds as inhibitors will have active adsorption absorption on metal surfaces. This total energy supports the argument that the active center of the inhibitor will support the process of adsorption on metal surfaces (Arthur *et al.*, 2019).

From the quantum chemical properties values obtained in Table 2, quantum chemical parameters are calculated using calculated some of the equations mentioned by Koopmans theory (Gece *et al*., 2008). Table 3 shows some quantum chemical parameters, namely Ionization Potential (I), electron affinity (A), electronegativity (χ), global hardness (η), global softness (σ), electrophilicity (ω) and number of electron charges (ΔN).

Ionization potential (I) and electron affinity (A) obtained in equations 1 and 2. Ionization potential (I) is the amount of energy needed to remove electrons from the molecule. Small ionization potential values more easily remove electrons from molecules. With high ionisation energy shows high stability and inert so that molecules are very difficult to bind to metals, but low ionization energy shows high reactivity for atoms and molecules (Pearson, 1986).

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

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

Table 2. Quantum chemical properties of Xanthones and its derivatives using the DFT method

Molecules	$E_{HOMO\ (eV)}$	$E_{LUMO\ (eV)}$	$\Delta E_{\ (eV)}$	Dipole Moment (Debye)	Total energy (au)
Xanthone	-0.23101	-0.06576	0.16525	2.89840	-650.679
Gartanin	-0.19216	-0.05232	0.13984	8.11000	-1342.762
8-Desoxygartanin	-0.20138	-0.04182	0.15956	3.57430	-1267.038
α-Mangostin	-0.20723	-0.04114	0.16609	5.93620	-1381.554
β-Mangostin	-0.21064	-0.04795	0.16269	5.91110	-1345.649

Table 3. Quantum chemical parameters of Xanthones and their derivatives using calculations

Parameters	*Xanthone*	*Gartanin*	*8-desoxygartanin*	α-mangostin	β-mangostin
I (eV)	0.23101	0.19216	0.20138	0.20723	0.21064
A (eV)	0.06576	0.05232	0.04182	0.04114	0.04795
χ (eV)	0.14839	0.12224	0.12160	0.12419	0.12930
η (eV)	0.08263	0.06992	0.07978	0.08305	0.08135
σ (eV^{-1})	12.10287	14.30206	12.53447	12.04166	12.29332
ω (D^2eV^{-1})	50.83645	470.33824	80.06781	212.16491	214.77106
ΔN	0.28306	0.24045	0.27438	0.28550	0.27945

The ionization potential (I) for gartanin compounds shown in Table 3 has a high ionization potential value (0.19216 au). It can be concluded that gartanin can act as a good inhibitor. From Table 3 it is also seen that a low electronegativity (χ) will give a good electrophile where a low electronegativity value will indicate that the compound has a high electronegativity so that it will make it easier to accept electrons. Table 3 shows the electronegativity value of the gartanin compound which has a lower value compared to the xanthone compound which is 0.12224 eV. Another derivative that has a low electronegativity value is the 8-desoxygartanin compound which has the lowest value compared to other derivatives that is 0.12160 eV which can be seen in Table 3.

From the parameters of quantum chemical calculations it is concluded that gartanin can also act as a good inhibitor which will interact with metal surfaces later. With a low potential value of gartanin compounds and a low electronegativity value will provide high stability in the interaction between inhibitors with ferrous metals, and inhibitor compounds will have a higher strength to bind to the surface of Fe metals (Wazzan *et al*., 2014).

In numerical applications, the chemical potential of dipole moments (μ) and global hardness (η) is generally expressed based on differences in estimates in terms of ionization potential I and electron affinity A. In equations 3 and 4. The electropility index (ω) and global softness (σ) can be expressed in equations 5 and 6 (Gece *et al*., 2017).

In Table 3 we can see the value of gartanin compounds for the value of global hardness obtained by the smallest value (0.06992 eV) and high global softness value (14.30206 eV^{-1}) compared to xanthone compounds and other derivatives. This dedicates that gartanin is a compound that will easily interact with metal surfaces.

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

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

$$\omega = \frac{\mu^2}{2\eta} \quad (5)$$

$$\sigma = \frac{1}{\eta} \quad (6)$$

$$\Delta N = \frac{\chi_{fe} - \chi_{inh}}{2\,(\eta_{fe} + \eta_{inh}} \quad (7)$$

Global chemical hardness basically signifies resistance to deformation or polarization of electron clouds from atomic or molecular ions under slight interference to chemical reactions. Global hardness molecules have a small tendency to react, whereas for global softness, molecules have a large tendency to react (Pearson, 1986). Global hardness (η) and global softness (σ) which are also calculated and can be seen in Table 2 show measures of molecular stability and inhibitor reactivity. Global violence has a large ΔE and global tenderness has a small ΔE (Obi *et al.*, 2011). Electron polarizability also called global softness is a measure of the capacity of atoms or groups of atoms to receive electrons (Senet, 1997). The small value of global hardness will make molecules easier to react with metal surfaces and also the high value of global softness will also make molecules easier to react with Fe metal surfaces.

Table 3 also shows the very high electropicity value of gartanin is 470,33824 D^2eV^{-1}. Electrophilicity provides information about the nucleophilic or electrophilic nature of a molecule. High electrophilicity will act as electrophilic while low electrophilicity values will act as nucleophilic (Kalaiselvi *et al.*, 2014). In accordance with the values obtained, gartanin has a high electrophilicity value so that it can act as a good electrophile with the surface of Fe later.

Table 4. Corrosion inhibitor efficiency (IE%) for Xanthones compounds and their derivatives

Molecules	I_{add} %	Ie_{add}%	Efficiency of corrosion inhibitors (IE%)	
			Theoritical (IE_{teori}%)	Experiment
Xanthone	-	-	74.08	74.08
Gartanin	16.8174	0.1246	86.54	-
8-Desoxy*gartanin*	12.8262	0.0950	83.58	-
α-Mangostine	10.2939	0.0762	81.71	-
β-mangostine	8.8178	0.0653	80.61	-

The number of transfer electrons (ΔN) can also be seen in Table 3 which is calculated using equation 7, if ΔN < 3.6, the inhibitory efficiency will increase if the number of electron transfers is not too high, thus increasing the electron contribution of the inhibiting compound to the metal surface (Wazzan *et al.*, 2014). In Table 2 it can be seen that all electron transfer values in Xanthone compounds and their derivatives have values <3.6, but all gartanin optimized compounds are compounds with the lowest electron transfer values compared to other compounds. So it can be concluded that this gartanin compound which will act as an inhibitor, will make an increase in the ability of electron donors on the metal surface.

Xanthones compounds have an efficiency value of 74.08% which has been done experimentally by Obot *et al*., (2011). This value is a reference to get the xanthone derivative value using the equation below.

$$I_{add}\% = \frac{I_{inh}-I_{(x-inh)}}{I_{inh}} x\ 100\% \quad (8)$$

$$I_{eadd}\% = I_{add}\% \, x \, IE_{inh} \quad (9)$$

$$IE_{teori}\% = IE_{inh}\% + I_{eadd}\% \quad (10)$$

Where I_{add}% is the percentage of potential ionization of Xanthone derivatives, obtained from the value of ionization potential (I) in xanthone compounds (I_{inh}) and the value of ionization potential in xanthone derivatives ($I_{x\text{-}inh}$). Whereas for the Ieadd% equation is the percentage of xanthone derivative corrosion inhibitor efficiency obtained by multiplying the percentage value of xanthone derivative ionization potential (I_{add}%), IE_{inh}% is the percentage of inhibitor efficiency (IE%) from the experimental results obtained by Obot et. al, and IE theory is the percentage of Xanthones corrosion inhibitors derived from theoretical calculations using the DFT method (Obayes *et al*., 2014).

Table 4 shows the results of the calculation of the efficiency of corrosion inhibitors of Xanthone compositions with their derivatives. The efficiency value of Xanthones derivatives was obtained using equations 8.9 and 10. According to Obot *et al*, (2011). The calculation results show that the ratio for gartanin composition is the highest compared to the composition of Xanthones and other derivatives. In Table 4 it can be seen that the efficiency of the composition of gartanin is 86.54% which is a higher value compared to the efficiency of the composition of Xanthones and other derivatives. So it can be concluded that the gartanin compound has a very high potential to act as a corrosion inhibitor which will be reacted on the metal surface.

4. CONCLUSION

The DFT method using functional B3LYP / 6-31G (d, p) in the gaussian09 program can be used to determine the potential of xanthone and their four derivatives compounds consisting of gartanin, 8-desoxygartanin, α-mangostine, and β-mangostine as corrosion inhibitors. Inhibition efficiency obtained through quantum chemical calculations from these inhibitors shows an increase with increasing E_{HOMO} values, decreasing E_{LUMO} values and low energy gap values (ΔE) and from this analysis it can be concluded that gartanin is the best inhibitor compared to other compounds in this study. Electronic parameters such as global hardness (η) and global softness (σ) confirm the inhibitory efficiency in the order of gartanin > 8-desoxygartanin > α-mangostin > β-mangostine > Xanthones. Gartanin also showed the highest inhibitor efficiency (IE%) at 86.54%.

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