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Theoretical study of copper corrosion prevention by terpenoid green inhibitors of thymol, carvacrol, and thymohydroquinone

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Abstract.

It has been predicted by electronic parameters for the corrosion inhibition performance of the green inhibitors of thymol, carvacrol, and thymohydroquinone against copper. Molecular modeling was carried out at the density functional and *ab initio* levels as well as Montre Carlo molecular dynamics. Tymohydroquinone has the ability to prevent copper corrosion better than the other two monoterpenoids. Molecular dynamics studies show that corrosion inhibitors are adsorbed on the metal surface thereby inhibiting corrosion occurring on the metal surface.

Keyword: DFT, *ab initio*, monte carlo, corrosion inhibition, thymol, carvacrol, and tymohydroquinone.

INTRODUCTION.

Terpenoids are a large group of organic compounds found in various organisms, especially plants. Terpenoids have diverse biological functions and varied chemical properties, so they have important roles in ecology, pharmaceuticals, and industry [1-4]. Essential oils containing terpenoids are used in the production of perfumes, cosmetics and food [5-8]. Several terpenoids have potential health effects. Some of them have anti-inflammatory, antimicrobial and antioxidant properties [9-10].

In addition, terpenoids have potential as corrosion inhibiting agents, especially in environments containing metals that are susceptible to corrosion [11-15]. These compounds may form a protective layer on metal surfaces, inhibiting the electrochemical reactions that cause corrosion. Terpenoids can work as corrosion inhibitor agents through several mechanisms, including the formation of a passive layer on the metal surface, absorption on the metal surface to protect against corrosive substances, and changing the electrochemical characteristics at the metal-solution interface. Terpenoids have additional advantages as corrosion inhibitor agents because they are natural and more environmentally friendly compared to many corrosive chemical compounds or synthetic corrosion inhibitors [16-20].

Experimental studies on terpenoids as corrosion inhibitors have not been widely published. On the other hand, molecular modeling can provide an initial insight into the potential of green organic compounds as corrosion inhibitors [21-25]. Samal et al studied lemonal terpenoid as a copper corrosion inhibitor using DFT. The theoretical studies carried out can well differentiate the corrosion inhibition performance of the two lemonal isomers [26]. Theoretical studies can be a bridge in explaining phenomena that are difficult to explain by experimental studies. Simulations can be carried out under conditions that are very similar to experiments using a method that is accurate for the model to be studied, so that the results of computational chemistry calculations can be compared directly with experimental results. In addition, by using computational chemistry, it is possible to calculate the properties of complex molecules with calculation results that correlate significantly with experiments, with computational chemistry the costs and time for research can be reduced [27-30]. This research focuses on studying the monoterpenoid compounds thymol, carvacrol, and thymohydroquinone as copper corrosion inhibitors using DFT and MP2 approaches as well as Monte Carlo Simulation.

RESEARCH METHODS

The electronic properties of thymol, carvacrol, and thymohydroquinone in inhibiting corrosion on copper surfaces were studied using Gaussian 09 [31]. The DFT theory level and MP2 ab initio 6-311++G (d,p) were applied for the calculation of the electronic parameters. Koopmans' theorem [32] is used to measure EHOMO and ELUMO, using equation (1) (2):

$$I = -EHOMO \quad (1)$$

$$A = -ELUMO \quad (2)$$

Elektronegativitas (χ) menurut Pauling adalah ukuran seberapa kuat sebuah atom menarik elektron dalam sebuah ikatan kimia saat berinteraksi dengan atom lain. Ini adalah konsep penting dalam kimia karena mempengaruhi sifat ikatan kimia dan polaritas molekul [33]. Electronegativity values can be calculated using equation (3):

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

Hardness (η) is a measure of atomic resistance to charge transfer [33]. The hardness value can be calculated using equation [33]:

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

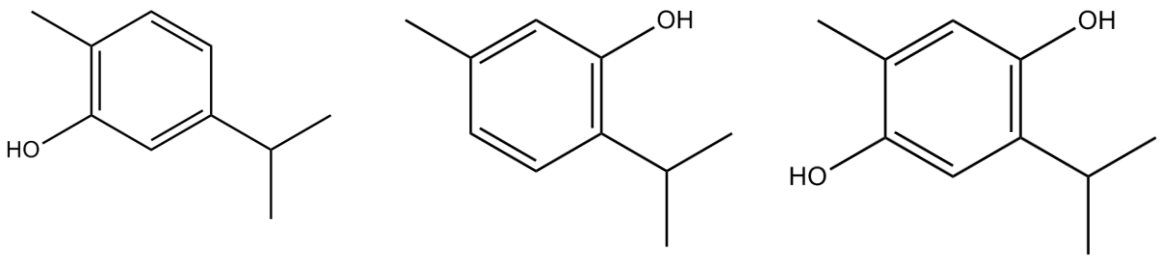
The number of electrons transferred [34.35] can be calculated using equation (5):

$$\Delta\chi=\frac{\chi Cu-\chi Inh}{2(\eta Cu+\eta Inh)} \quad (5)$$

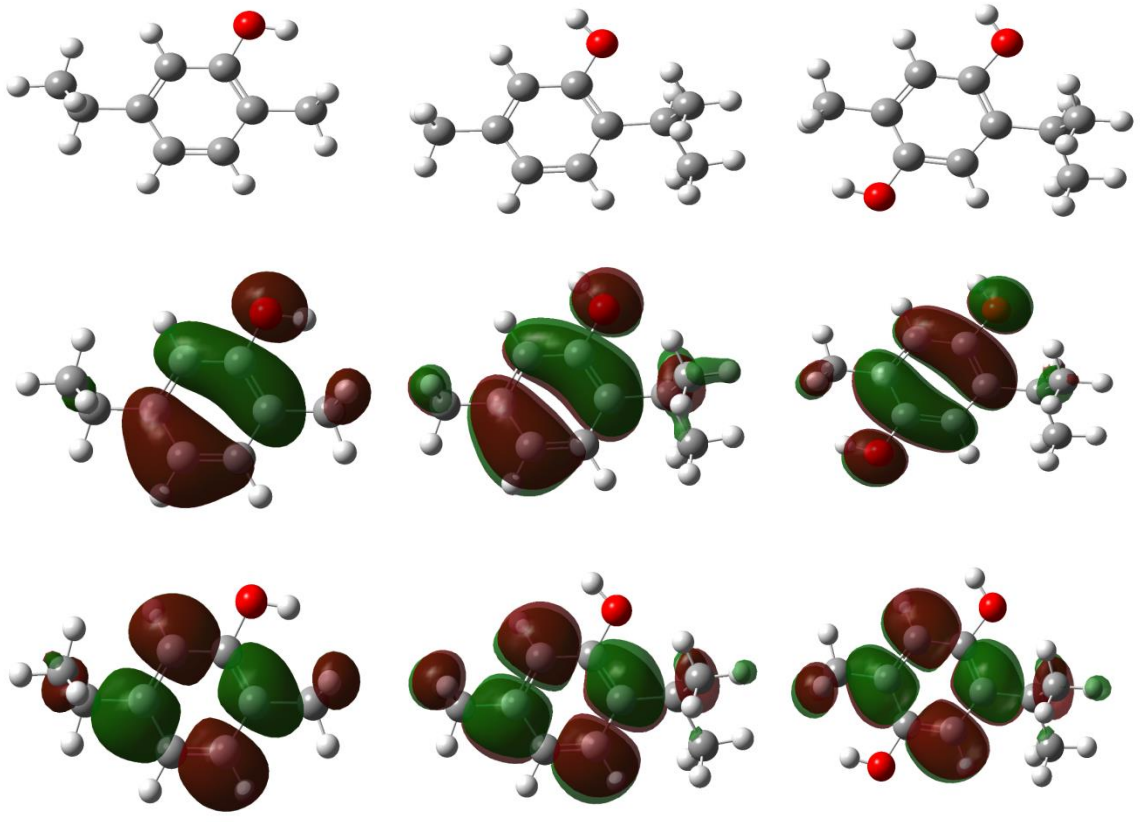
where χCu and χinh denote the absolute electronegativity of copper and organic inhibitors, respectively. ηFeCu and ηinh indicate the absolute hardness of copper and organic inhibitors, respectively. In this study, the theoretical values of χCu = 7.0 eV and ηCu = 0 are used to calculate the number of electrons transferred [36,37].

Monte Carlo Simulation Calculations

Monte Carlo simulation was carried out to be able to imitate the real corrosion environment. Monte Carlo simulation was used to search for the lowest adsorption energy configuration of the interaction of the bioactive molecules thymol, carvacrol, and thymohydroquinone on the surface of copper (Cu) and 100 water molecules. Monte Carlo simulations were carried out using Material studio 7.0 [38,39]. The copper surface can be represented by a Cu(111) plane. Cu(111) planes were used because they are the most stable and have moderate atomic density [40]. The solvent effect of water was simulated by loading 100 geometrically optimized water molecules using the KOMPASS force field into the simulation box along with each organic inhibitor and Cu(111) surface used [41].



carvacrol **thymol** **tymohydroquinone**



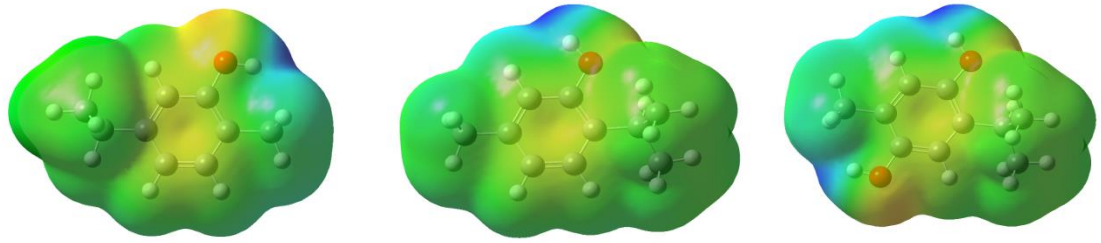


FIGURE 1. Structure of the monoterpenoid thymol, carvacrol, and thymohydroquinone

TABLE 1. Quantum parameters of the thymol, carvacrol, and thymohydroquinone

	carvacrol		**thymol**		**tymohydroquinone**	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
HOMO	-6.0011	-8.2828	-5.9788	-8.2080	-5.4648	-7.8246
LUMO	-0.1578	3.6392	-0.1945	3.5948	-0.1722	3.5415
ΔEgab	-5.8433	-11.9220	-5.7843	-11.8029	-5.2926	-11.3661
I	6.0011	8.2828	5.9788	8.2080	5.4648	7.8246
A	0.1578	-3.6392	0.1945	-3.5948	0.1722	-3.5415
χ	3.0795	2.3218	3.0867	2.3065	2.8185	2.1415
η	2.9216	5.9610	2.8921	5.9014	2.6463	5.6830
ΔN	0.2396	0.1810	-3.0867	0.1841	0.3139	0.2057

EHOMO is related to the capacity of molecules to provide metals with electron donations. High EHOMO values show compounds' propensity to give electrons to acceptor molecules [42]. The strength of the organic inhibitory molecules' attachment to the metal surface is therefore inversely proportional to the EHOMO value. On the basis of the EHOMO value, the prediction of organic inhibitors with the highest corrosion inhibition effectiveness values is possible. The quantum properties of the bioactive compounds thymol, carvacrol, and thymohydroquinone determined using the DFT/6-311++G and MP2/6-311++G methods are shown in Table 1. Table 1 shows that thymohydroquinone had the highest EHOMO values and the highest correlation with the copper metal's corrosion inhibition efficiency. It can be seen that thymohydroquinone EHOMO is -7.8246 eV. The ability of thymohydroquinone to donate electrons to copper metal is improved by the insertion of a double hydroxyl group to the cyclic ring. Figure 1 depicts how the three compounds' HOMO orbitals' electron distributions are distributed.

EHOMO and ionization potential have a direct relationship [42]. Equation 1 can be used to compute the ionization potential value. According to Table 1, thymohydroquinone has a lower ionization potential than thymol (8.2080 eV) and carvacrol (8.2828 eV). It is possible to forecast that thymohydroquinone has a greater inhibitory efficiency value than thymol and carvacrol based on this ionization potential value. The ionization potential value is the least amount of energy needed for electrons to be released from their bonds and bind to the surface of a metal, shielding it from corrosive environments. The inhibitory efficiency value can therefore be increased by a low ionization potential value [43].

The theory of chemical reactivity has been found to be most strongly influenced by electronegativity (χ). For the chemical potential to be balanced when organic inhibitors and copper metal interact, electrons will flow from a lower electronegativity value (organic inhibitor) to a high electronegativity value (Cu) [43]. Equation 3 is used to compute the electronegativity values. The results of computations utilizing the MP2/6-311++G (d,p) approach are shown in Table 1. Thymohydroquinone has the lowest electronegativity value, 2.1415 eV. The other molecules, thymol and carvacrol, had electronegativity values of 3.0867 eV and 3.0795 eV, respectively. The electronegativity value predicts that, when compared to the other three inhibitors, thymohydroquinone has the highest corrosion inhibition efficiency value.

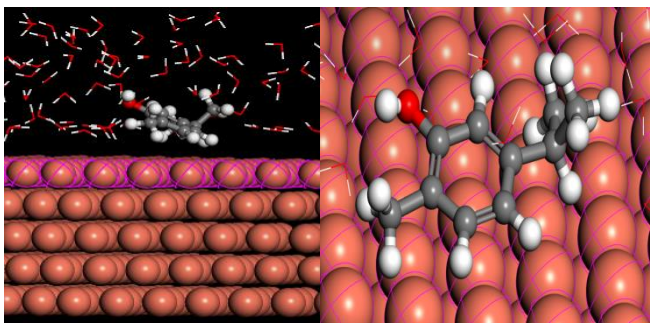
Equation 5 is used to compute the number of electrons that were transported (ΔN) from the inhibitor to the metal. According to the value of electron transfer, the value of inhibitory efficiency is produced by the electron donor [44]. More electrons will coat the Cu surface as the ability to contribute electrons to the Cu metal surface increases. Inhibited corrosion processes can therefore result in electron transfer values [38]. Thymohydroquinone, carvacrol, and thymol are listed in order of their ability to transfer electrons from high to low. Thymohydroquinone's greater contribution to corrosion inhibition effectiveness can be explained by the size of this electron donor.

MEP explains reactivity and the connection between a molecule's structure and its activity. The structure of a molecule is shown by the shape, size, charge density distribution, and location of chemical reactivity in the electron density surface plot mapped with MEP. The MEP surface's color scheme is red, which denotes abundant electrons and a partial negative charge; blue, which denotes a lack of electrons and a partial positive charge; light blue, which denotes a region that is slightly electron deficient; yellow, which denotes a region that is slightly electron rich; and green, which denotes neutrality [44]. Figure 2 displays the MEP plot of the organic inhibitors thymol, carvacrol, and thymohydroquinone. In blue, the electron density is low. In the thymohydroquinone structure, the oxygen atoms that are brownish (red to green) have a higher electron density. This could mean that the oxygen atom in the thymohydroquinone structure has a high electron density, attracting to the Cu surface as a region of low electron density. Fukui function, as opposed to MEP, is a more precise indicator of the portion of the organic inhibitor that is exposed to electrophilic or nucleophilic assault. The MEP merely defines the alteration in an atom's electron density brought on by the addition or subtraction of charges.

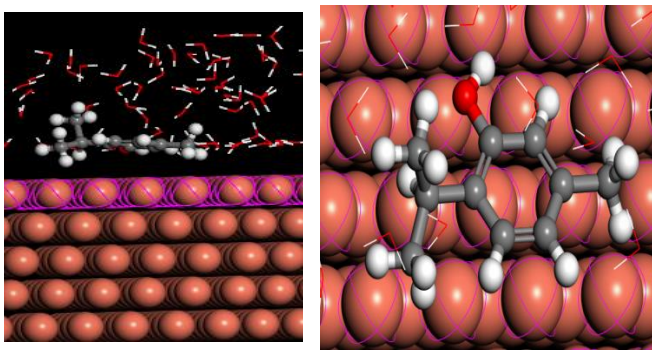
On organic inhibitor systems, water molecules, and metal surfaces, Monte Carlo simulations were performed. The adsorption characteristics of inhibitor molecules and 100 water molecules on the Cu(111) metal surface were investigated using Monte Carlo simulations [45]. Because it possesses the most stable surface, the Cu(111) surface is utilized in the Monte Carlo simulation procedure. Figure 3 demonstrates that the Cu (111) surface, which has 100 water molecules and organic inhibitors (thymol, carvacrol, and thymohydroquinone), has the most stable adsorption pattern. The expected organic inhibitor is adsorbed on the surface of Cu (111) as a result of equilibrium occurring in this system as well. Thymol, carvacrol, and thymohydroquinone are examples of organic inhibitors that can give electrons to the Cu (111) surface because they each include an oxygen atom and a methane cyclic ring. This occurs as a result of vacant orbitals on the Cu (111) surface having the ability to speed up the adsorption process by allowing organic inhibitors to receive electrons and establish stable coordinate bonds. According to Table 2, the systems Cu (111)/thymohydroquinone/100H2O, Cu(111)/thymol/100H2O, Cu(111)/carvacrol/100H2O, and Cu(111)/thymol/100H2O had the highest adsorption energies for the most stable configurations. In comparison to 100 water molecules, monoterpenoid molecules have a greater adsorption energy. Figure 3 displays the organic inhibitor's and water's adsorption energy distributions. It is possible to distinguish between the distributions of adsorption energies for each organic inhibitor and water. This is because monoterpenoid molecules can create a thick coating, making them ideal for use in preventing corrosion on the surface of copper metal. Thymohydroquinone dominates the adsorption energy of organic inhibitors on the Cu (111) surface in the presence of 100 water molecules. It is foreseeable that thymohydroquinone will block more effectively than thymol and carvacrol.

TABLE 2. Adsorption energy of Cu(111)/monoterpenoid/100H2O system with Monte Carlo simulation

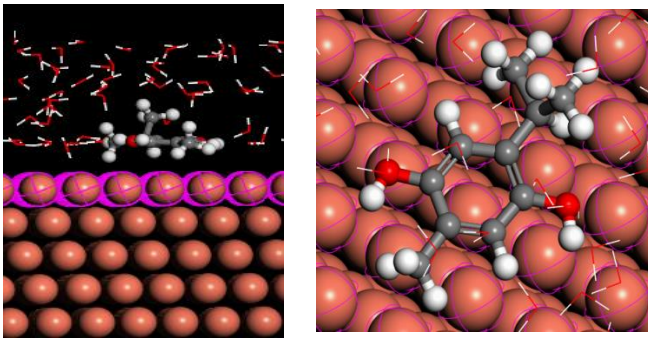
Compound	Metals	Inhibitors (dEad/dNi)	Water (dEad/dNi)
carvacrol	Copper	-63.90	-16.73
thymol	Copper	-67.84	-15.62
tymohydroquinone	Copper	-79.43	-16.83



Carvacrol-Cu(111)



thymol-Cu(111)



tymohydroquinone-Cu(111)

FIGURE 3. Monte Carlo Simulation system of adsorption of thymol, carvacrol and thymohydroquinone in copper surface

CONCLUSION

Thymol, carvacrol, and thymohydroquinone are monoterpenoids with the ability to reduce corrosion. This was explained from the electronic side of the inhibitor molecule using quantum chemistry calculations and Monte Carlo simulations. Quantum chemical parameters are calculated using ab initio MP2 techniques and density functional theory. Thymohydroquinone has the strongest corrosion inhibition potential, which is explained by quantum characteristics. The adsorption energy demonstrates how effective thymohydroquinone is at preventing corrosion on copper metal.

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References

1. Fan, M., Yuan, S., Li, L., Zheng, J., Zhao, D., Wang, C., ... & Liu, J. (2023). Fermentation, 9(2), 119.
2. D. A. Nagegowda and P. Gupta, Plant Science, vol. 294, p. 110457, 2020.
3. Das, D. D., Sharma, N., Chawla, V., & Chawla, P. A. (2023). Critical Reviews in Analytical Chemistry, 1-17.
4. D. A. Septiani, A. Hakim, L. R. Patech, Z. Zulhalifah, and S. Siswadi, Acta Chimica Asiana, vol. 4, no. 1, pp. 108–113, 2021.
5. M. Butnariu, Bioprospecting of plant biodiversity for industrial molecules, 261-292. (2021).
6. Sharmeen, J. B., Mahomoodally, F. M., Zengin, G., & Maggi, F. (2021). Molecules, 26(3), 666.
7. Stephane, F. F. Y., & Jules, B. K. J. (2020). Essential oils-bioactive compounds, new perspectives and applications, 1-15.
8. de Lima, M. C. F., da Silva, L. S., Wiedemann, L. S. M., & da Veiga, V. F. (2019). A Brief History of Terpenoids. In Terpenoids Against Human Diseases (pp. 1-15). CRC Press.

9. Baccouri, B., & Rajhi, I. (2021). Terpenes and terpenoids-recent advances, 53-62.
10. Wu, M., Ni, L., Lu, H., Xu, H., Zou, S., & Zou, X. (2020). Journal of Chemistry, 2020, 1-14.
11. Marciales, A., Haile, T., Ahvazi, B., Ngo, T. D., & Wolodko, J. (2018). *Corrosion Reviews*, *36*(3), 239-266.
12. Vorobyova, V., & Skiba, M. (2022). *Waste and Biomass Valorization*, *13*(7), 3309-3333.
13. Zakeri, A., Bahmani, E., & Aghdam, A. S. R. (2022). Corrosion Communications, 5, 25-38.
14. Burčul, F., Blažević, I., Radan, M., & Politeo, O. (2020). *Current Medicinal Chemistry*, *27*(26), 4297-4343.
15. Idouhli, R., Oukhrib, A., Khadiri, M., Zakir, O., Aityoub, A., Abouelfida, A., ... & Benyaich, A. (2021). Journal of Molecular Structure, 1228, 129478.
16. Bhardwaj, N., Sharma, P., & Kumar, V. (2021). *Corrosion Reviews*, *39*(1), 27-41.
17. Mo, S., Luo, H. Q., & Li, N. B. (2016). *Chemical Papers*, *70*(9), 1131-1143.
18. Shahini, M. H., Keramatinia, M., Ramezanzadeh, M., Ramezanzadeh, B., & Bahlakeh, G. (2021). *Journal of Molecular Liquids*, *342*, 117570.
19. Wati, R., Hadisaputra, S., Asnawati, D., & Hermanto, D. (2018). *Acta Chimica Asiana*, *1*(2), 50-56.
20. Li, W., Tan, B., Zhang, S., Guo, L., Ji, J., Yan, M., & Wang, R. (2022). *Applied Surface Science*, *602*, 154165.
21. S. Hadisaputra, A. A. Purwoko and S. Hamdiani, Int. J. Corros. Scale Inhib. 10, **1**, 419-440 (2021).
22. 23S. Hadisaputra, S. Hamdiani, M. A. Kurniawan and N. Nuryono, Indones. J. Chem. 17, **3**, 431–438, (2017)
23. 24S. Hadisaputra, A. A. Purwoko, L. R. T Savalas, N. Prasetyo, E. Yuanita and S. Hamdiani, Coatings 10, **11**, 1086 (2020).
24. 25S. Hadisaputra, A. A. Purwoko, A. Hakim, N. Prasetyo, S. Hamdiani, ACS omega, 7, **37**, 33054-33066 (2022).
25. 26S. Wirayani, Y., Ulfa, M., & Yahmin, Y. (2018). Corrosion inhibition efficiency of nicotine based on quantum chemical study. *Acta Chimica Asiana*, *1*(2), 37-42
26. Samal, P. P., Singh, C. P., & Krishnamurty, S. (2023). Expounding lemonal terpenoids as corrosion inhibitors for copper using DFT based calculations. *Applied Surface Science*, *614*, 156066.
27. S. Hamdiani, I. H. Rohimah, N. Nuryono, A. A. Purwoko, L. R. T. Savalas and S. Hadisaputra, Asian J. Chem, 31, **2**, 303–308 (2019).
28. M. Murmu, N. C. Murmu, M. Ghosh, P. Banerjee, J. Adhe Sci Tech, 1-29 (2022).
29. S. Hadisaputra, Z. Iskandar, D. Asnawati, Acta Chimica Asiana, 2, **1**, 88-94 (2019).
30. O. E. Oyeneyin, N. D. Ojo, N. Ipinloju, A. C. James, E. B. Agbaffa, Chem Africa, 5, **2**, 319-332 (2022).
31. M. J. Frisch, G.W. Trucks, H.B. Schlegel et al., Gaussian 09 (Gaussian, Inc, Wallingford, CT, 2009)
32. T. Koopmans, Physica, 1(1-6), 104-113 (1934).
33. R. G. Pearson, Inorg Chem, 27, **4**, 734-740 (1988).
34. R. G. Pearson, Coord. Chem. Rev. 100, 403–425 (1990).
35. N. Islam and D.C. Ghosh, Mol. Phys. 109, **6**, 917-931 (2011)
36. S. Martinez, Mater Chem Phys, 77, 1, 97-102 (2003).
37. Ş. Erdoğan, Z.S. Safi, S. Kaya, D.Ö. Işın, L. Guo, C. Kaya, J. Mol. Struct, 1134, 751-761 (2017).
38. D. Frenkel and B. Smit, Understanding Molecular Simulations: from Algorithms to Applications, 2nd ed, (Academic Press, San Diego, 2002)
39. S. Kirkpatrick, C. D. Gelatt, and M.P. Vecchi, Science 220, 4598, 671-680, (1983).
40. E. Junaidi, A. A. Purwoko, S. Hadisaputra, Z. Iskandar, and S. Hamdiani, Asian J. Chem. 33, **7**, 1495-1503, (2021)
41. A. Kasprzhitskii, G. Lazorenko, J. Mol. Liq. 331, 115782 (2021).
42. S. Hadisaputra, L. R. Canaval, H. D. Pranowo and R. Armunanto, Monats. Chem. 145, **5**, 737–745 (2014)
43. S. Kaya, L. Guo, C. Kaya, B. Tüzün, I.B. Obot, R. Touir, and N. Islam, J. Taiwan Inst. Chem. E. 65, 522-529, (2016).
44. R. G. Parr, L. V. Szentpaly, S. Liu, J. Am. Chem. Soc. 121, 1922-1924 (1999).
45. S. Hadisaputra, A. A. Purwoko, F. Wajdi, I. Sumarlan, and S. Hamdiani, Int. J. Corros. Scale Inhib. 8, **3**, 673-688, (2019)).
46. S.A. Umoren, I.B. Obot, A. Madhankumar, Z.M. J. Adhe. Sci. Tech. 29, 271-295 (2015).