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by Saprizal Hadisaputra

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Experimental and Theoretical Study of Pinostrobin as Copper Corrosion Inhibitor at 1 M H_2SO_4 Medium

Experimental and Theoretical Study of Pinostrobin as Copper Corrosion Inhibitor at 1 M H_2SO_4 Medium

Saprizal Hadisaputra[1,*], Agus Abhi Purwoko[1], Aliefman Hakim[1], Rosita Wati[2], Dina Asnawati[2], Yuniar Ponco Prananto[3]

[1]Chemistry Education Division, Faculty of Treacher Training and Science Education, University of Mataram, Jalan Majapahit No 62, Mataram, 83125, Indonesia.
[2]Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Mataram, Jalan Majapahit No 62, Mataram, 83125, Indonesia.
[3]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Brawijaya University, Malang 65145, East Java, Indonesia.

[*]Corresponding author: rizal@unram.ac.id

Abstract. The effect of variations in concentration and temperature on the efficiency of pinostrobin corrosion inhibition of copper in 1M H_2SO_4 was studied using an experimental and theoretical approach. Pinostrobin was isolated from the *Boesenbergia rotunda L* rhizome and was tested for corrosion inhibition of copper in acidic medium. Variations in the concentration of 300 ppm, 400 ppm, and 500 ppm and temperature (308 K, 318 K, and 328 K) were carried out in the weight loss method of corrosion inhibition test. Pinostrobin crystals were isolated with a yield of 57.65 %, a melting point of 98.5 ^{o}C and with a purity of 100 %. The optimum corrosion inhibition efficiency of pinostrobin is 65.71 % at a concentration of 500 ppm and a temperature of 328 K. The activation energy value of Ea < 80 kJ.mol^{-1} indicates the adsorption of pinostrobin on copper surfaces is physical and spontaneously $\Delta G^{o}ads$ < -20 kJ.mol^{-1}. The effect of substituent on the efficiency of corrosion inhibition from pinostrobin was studied using density functional theory. The addition of NH_2 increased the efficiency of corrosion inhibition to 73.07 %, whereas the addition of NO_2 substituents decreased the efficiency of inhibition to 60.97 %. Experimental and theoretical studies have a good correlation in explaining the efficiency of corrosion inhibition from pinostrobin.

1. Introduction

Corrosion is an electrochemical process that occurs between metals and corrosive environments such as sulfuric acid that will reduce the quality of the metal. The corrosion process results in economic and environmental losses [1]. The rate of corrosion can be inhibited by the addition of inhibitors. Of the various types of inhibitors, organic inhibitors are preferred because they are efficient, environmentally friendly and non-toxic. Organic corrosion inhibitors usually have heteroatom N, O, P, S and bonds which allow the inhibitor to coat the metal surface to inhibit corrosion [2-9].

The use of natural ingredients as corrosion inhibitors has been widely used [10-15]. One of them is pinostrobin which is isolated from the Boesenbergia pandurata Roxb rhizome [16]. Pinostrobin qualifies as a good corrosion inhibitor and has not been widely tested as a corrosion inhibitor [17]. Therefore, this study focuses on the application of pinostrobin as a corrosion inhibitor to copper metal in 1 M H_2SO_4 medium by weight loss method. In addition to experimental tests, a theoretical study

was also carried out to examine the effect of substituents on the efficiency of corrosion inhibition of pinostrobin compounds. Theoretical studies have proven capable of bridging aspects that are difficult to explain experimentally [18-21].

2. Methodology

2.1. Experimental Section

2.1.1. Pinostrobin Isolation. Isolation of pinostrobin was carried based on modification of methods from the literatures [17]. The Boesenbergia rotunda L rhizome powder was socleted with n-hexane solvent. The extraction results are then evaporated using a rotary evaporator. The obtained viscous extract was allowed to form crystals and purified by recrystallization with methanol. Pinostronin crystals were further identified by the melting point test and gas chromatography-mass spectroscopy GCMS.

2.1.2. Weight Loss Test. The prepared copper plates were prepared, weighed and then immersed in 1 M H_2SO_4 medium and an inhibitor solution with concentrations of 0, 300, 400 and 500 ppm and at temperatures of 308 K, 318 K and 328 K. Soaking of the copper plate was then washed with distilled water and acetone then dried and weighed. Inhibition efficiency values are calculated based on the equation

$$\%IE = \frac{C_{Ro} - C_{Ri}}{C_{Ro}} x100\% \quad (1)$$

where %IE is the efficiency of inhibition, C_{Ro} is the rate of corrosion without inhibitors and C_{Ri} the rate of corrosion with inhibitors.

2.2. Theoretical Section

All geometry optimizations of pinostrobin compounds are carried out using Gaussian 09 [23]. Geometry optimization is not followed by re-optimization in the solution phase because it has little effect on the structure and energy, so that only a single point of the solution phase is carried out on the gas phase geometry [24-28]. Calculation of quantum chemical parameters based on Koopman's theorem which explains the relationship between ionization potential (I), electron affinity (A) and orbital energy (E_{HOMO} and E_{LUMO})[29-30]. Koopman's equation is as follows:

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

$$A = - E_{LUMO} \quad (3)$$

Electronegativity is obtained based on equation 4 [31]:

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

Furthermore, the inhibition efficiency is calculated based on the equation [32]:

$$I_{add}\,\% = \frac{I_{PI} - I_{\chi-PI}}{I_{PI}} X100\% \quad (5)$$

$$IE_{add}\,\% = I_{add}\,\% - IE_{PI}\% \quad (6)$$

$$I_{theor}\,\% = IE_{PI}\% + \%IE_{add}\,\% \quad (7)$$

where I_{PI} is the percentage of ionization potential, Ieadd% is the percentage of inhibition efficiency, IE_{PI}% is the percentage of inhibition efficiency of experimental results and IE_{theor}% is the theoretical efficiency of inhibition. The structure of pinostrobin is depicted in Figure 1.

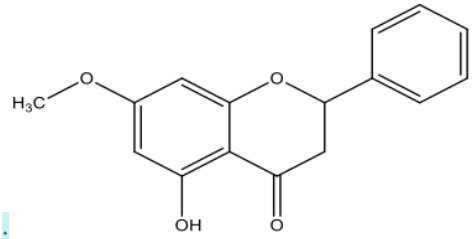

Figure 1. Structure of Pinostrobin (PN).

3. Results and Discussion

3.1. Experimental Study

Pinostrobin was successfully isolated from boesenbergia rotunda L rhizome with a yield of 57.65 %. The melting point test shows that the isolated pinostrobin melting point is 98.5 °C. Pinostrobin identification was continued using GC-MS and the pinostrobin chromatogram is depicted in Figure 2. It shows a peak with a percentage of 100 % which means that pinostrobin has high purity. Spectroscopic results also obtained m/e = 270 according to the relative molecular mass of pinostrobin [33].

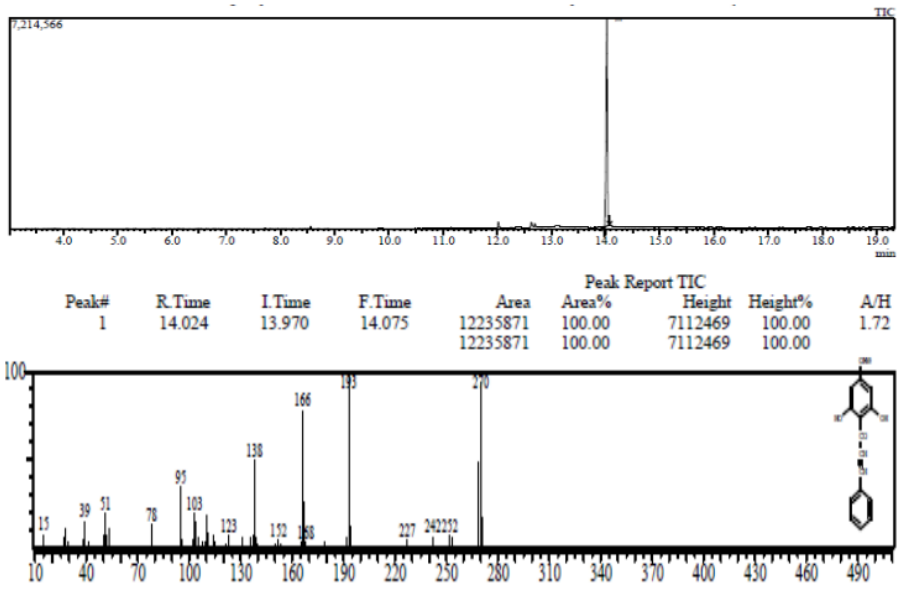

Figure 2. Pinostrobin chromatogram.

Weight loss test begins with the process of immersion of copper plates in a 1 M H_2SO_4 corrosive medium with pinostrobin concentrations of 0, 300, 400 and 500 ppm. Figure 3 shows the effectiveness of pinostrobin inhibition has increased at concentrations of 300 and 400 ppm. The amount of

pinostrobin that coats the copper surface increases so that the attack of corrosive solutions is blocked. The optimum inhibition efficiency of pinostrobin in copper corrosion is 65.35%.

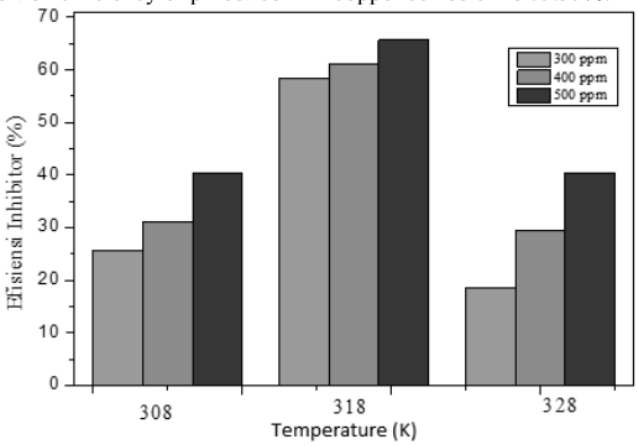

Figure 3. The concentration of inhibitors versus the efficiency of pinostrobin corrosion inhibition.

Activation energy E_a, change in enthalpy values ΔH and entropy ΔS and adsorption free energy $\Delta G^o ads$ are used to determine the overall energy changes in physical and chemical processes between the initial and final states in the corrosion inhibition process. Positive ΔH and ΔS values indicate the reaction is endothermic but takes place spontaneously. This is reinforced by the negative value of $\Delta G^o ads$ indicating the reaction takes place spontaneously shown in Table 1.

Table 1. Activation energy Ea, enthalpy of change ΔH and entropy ΔS values.

Concentration (ppm)	Ea (kJ.mol^{-1})	ΔH (kJ.mol^{-1})	ΔS (J.mol^{-1})
0	-16.35	0.42	50.43
300	-4.89	7.78	71.21
400	-12.45	4.74	60.79
500	12.57	10.39	76.79

Tabel 2. Value of free energy adsorption.

Temperature (K)	K_{ads}	ΔG^0_{ads} (kJ.mol^{-1})
308	0.3607	-7.70
318	1.2555	-11.20
328	0.2205	-6.80

Table 2 shows the process of pinostrobin adsorption on copper surfaces takes place spontaneously because the value of adsorption free energy increases with increasing temperature. At 318 K temperature, there was a decrease in adsorption free energy of -11.2 kJ / mol. A decrease in the value of $\Delta G^o ads$ at 318 K indicates an equilibrium has occurred. A negative $\Delta G^o ads$ value indicates that the adsorption process is a spontaneous process. The value of $\Delta G^o ads$ <-20 kJ / mol indicates that adsorption occurs physically, while the value of $\Delta G^o ads$> -20 kJ / mol indicates the occurrence of chemisorption [34]. Table 3 shows that $\Delta G^o ads$ is negative, which means that the adsorption of pinostrobin on the copper surface is physically adsorption.

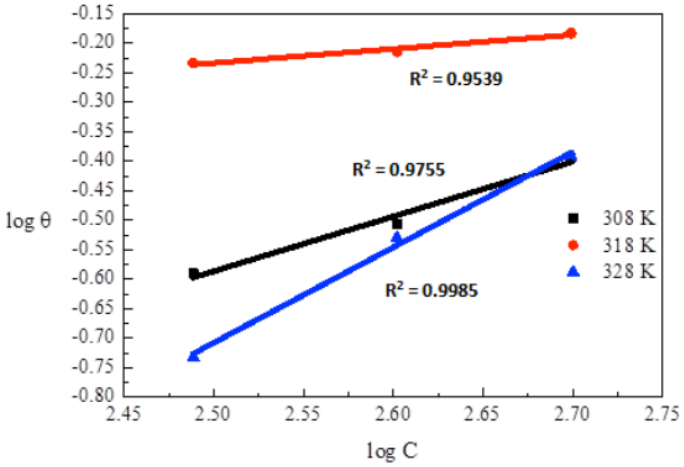

Figure 4. Freundlich isotherm adsorption

The mechanism of interaction between pinostrobin and the copper surface can be determined ba on isotherm adsorption. Figure 4 shows the log θ vs. log C plot at different temperatures showing the adsorption of pinostrobin on the copper surface following the Freundlich adsorption. Adsorption isotherm Freundlich explained that on the surface of the metal a multilayer layer is formed from the inhibitor molecule and is heterogeneous, that is, each active group on the metal surface has a different ability to adsorb. This also corresponds to the negative value of ΔG^0ads which indicates the adsorption occurs physically.

3.2. Theoretical Study

Table 3 shows the validation of the theoretical calculation method by comparing the bonding distance and the binding angle based on theoretical and experimental. The average difference between the bonding distance and the binding angle of pinostrobin between experiment and theoretical is relatively small 0.021 Å and 1.753º, respective This shows a match between theoretical results and experiments. Based on these results, the density functional theory method at B3LYP/6-311++G(d, p) theory level meets the requirements for use in the system under study.

Table 3. Comparison of bond lengths (Å) and angles (º) between experiment [33] and theoretical

Bonds	Exp* (Å)	Theory (Å)	Angle	Exp* (º)	Theory (º)
O1-C2	1.441	1.444	C2-O1-C9	119	116.5
O2-C4	1.232	1.242	O1-C2-C3	112	110.0
C3-C4	1.530	1.518	C3-C2-C1'	114.6	113.0
C5-C6	1.405	1.389	O2-C4-C3	121	120.8
C6-C7	1.384	1.401	C3-C4-C10	118.1	115.7
C8-C9	1.405	1.390	O3-C5-C10	119.8	120.5
C1'-C2	1.353	1.511	C5-C6-C7	115.5	119.5
C2'-C3'	1.400	1.394	O4-C7-C8	125.4	123.3
C5'-C6'	1.390	1.395	C7-C8-C9	119.1	118.5
C3'-C4'	1.400	1.396	O1-C9-C10	121.2	121.6
C1'-C6'	1.406	1.399	C4-C10-C5	124.3	121.1
C9-C10	1.384	1.415	C5-C10-C9	116.8	118.1
C7-C8	1.401	1.405	C2-C1'-C6'	121.5	119.7

Table 4. Quantum chemical parameters the B3LYP method on the 6-311++ G(d, p) basis set.

Parameters	Compounds		
	PN	PN-NH_2	PN-NO_2
E_{HOMO} (eV)	-6.3856	-5.6705	-6.8461
E_{LUMO} (eV)	-1.4756	-1.5943	-2.1891
E*gab* (eV)	-4.9100	-4.7620	-4.6570
I (eV)	6.3856	5.6705	6.8461
χ (eV)	3.9306	3.6324	4.5176
ΔN(Ev)	0.1118	0.2079	-0.0080
IE_{theor} (%)	65.71	73.07	60.09

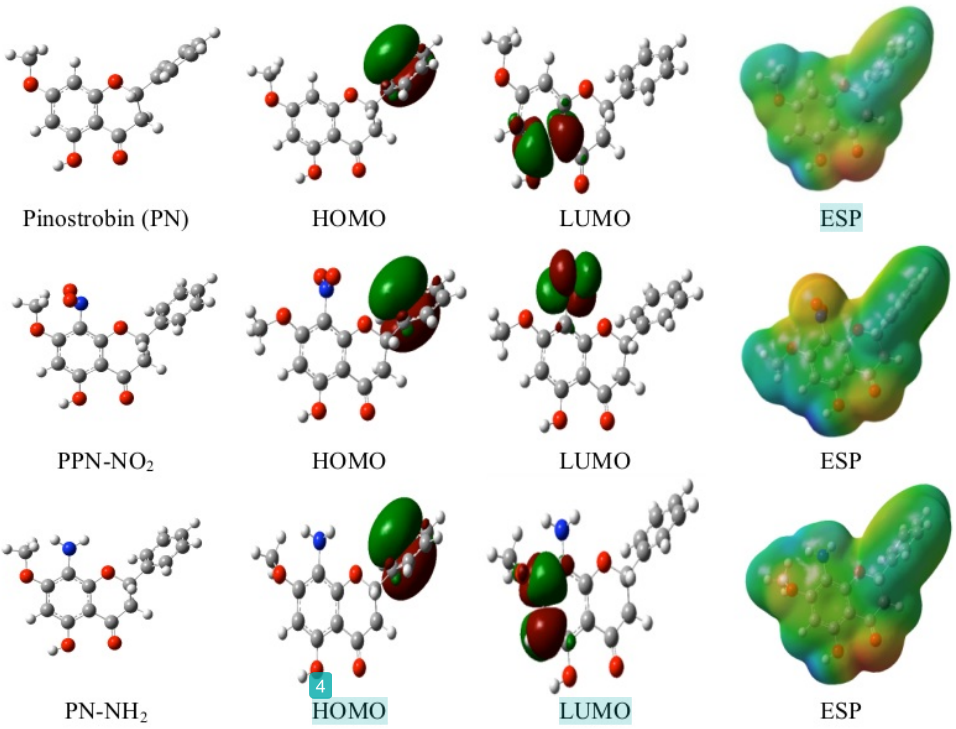

Figure 5. Visualization of pinostrobin HOMO, LUMO, and ESP and their derivatives.

4. Conclusion

The efficiency of pinostrobin corrosion inhibition in acid medium is influenced by concentration and temperature. Weight loss test on isolated pinostrobin produces a maximum inhibition efficiency of 65.71%. The result is less efficient considering the pinostrobin concentration applied is also high at 400 ppm. Pinostrobin adsorption on copper surfaces follows Freundlich isotherm adsorption and physical adsorption. Efforts to improve the efficiency of pinostrobin corrosion inhibition can be done by adding an electron donor group to pinostrobin. The addition of NH_2 for instant increase the efficiency of corrosion inhibition by 8 %. In contrast, the addition of electron withdrawal group NO_2 causes a decrease in efficiency of up to 5%.

Acknowledgments
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