JURNAL ILMIAH BERKALA SAINS DAN TERAPAN KIMIA

Jurnal Ilmiah Berkala: Sains dan Terapan Kimia
Vol. 17 No. 1, Januari 2023

Corrosion Inhibition Mechanism Based on Adsorption Isotherm Model From Water Extract of Merkubung (*Macaranga gigantea*) Bark Extract on Mild Steel in Sulfuric Acid Solution

Mekanisme Inhibisi Korosi Berdasarkan Model Isoterm Adsorpsi Ekstrak Air Kulit Kayu Merkubung (*Macaranga Gigantea*) pada Baja Lunak dalam Larutan Asam Sulfat

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ABSTRACT

The phenolic chemicals found in water extract of *Merkubung* bark (WEMB) can be employed as corrosion inhibitors. The corrosion inhibition mechanism by WEMB can be studied using an adsorption isotherm model. The Langmuir adsorption isotherm model has an R^2 value that was closest to 1 one compared to the Freundlich, Temkin, Florry Huggins, and Frumkin adsorption isotherm models, as shown by an analysis of the adsorption isotherm model. Due to the interaction between the WEMB and the steel surface, the adsorption isotherm model reveals that the inhibitor of WEMB on the surface coating of mild steel tends toward chemisorption.

Keywords: extract, Merkubung, corrosion inhibitor, adsorption isotherm model, Langmuir, Freundlich, Temkin, Flory Huggins and Frumkin

ABSTRAK

Ekstrak air kulit kayu merkubung (*Macaranga gigantea*) mengandung senyawa fenolik yang dapat digunakan sebagai inhibitor korosi. Mekanisme inhibisi korosi oleh ekstrak air kulit kayu merkubung (AEMB) dapat dipelajari menggunakan model isoterm adsorpsi. Berdasarkan hasil analisis model-model isoterm adsorpsi diperoleh model isoterm adsorpsi Langmuir memiliki nilai R^2 lebih mendekati 1 dibandingkan model isotherm adsorpsi Freundlich, Temkin, Florry Huggins, dan Frumkin. Model-model isoterm adsorpsi tersebut memberikan gambaran bahwa inhibitor AEMB dalam melapisi permukaan baja lunak cenderung berlangsung secara kemisorpsi dengan adanya interaksi tarik menarik antara AEMB dengan permukaan baja

Kata Kunci: *ekstrak merkubung, inhibitor korosi, model isoterm adsorpsi*

Received: September 14, 2020; **Accepted**: January 4, 2023: **Available online**: February 15, 2023

1. INTRODUCTION

The industrial world faces corrosion problems in steel due to exposure to acids, bases, and salts. Many industries have added a small number of substances known as corrosion inhibitors in process fluid streams to industrial pipes (Gusti *et al.*, 2019; Permanasari *et al.*, 2020; Sibarani *et al.*, 2021). Corrosion inhibitors are substances that can adsorb on metal or steel surfaces, thereby reducing the occurrence of the corrosion process. In general, the inhibitors used are synthetic inhibitors which are toxic and not environmentally friendly. As corrosion inhibitors, plant extracts are currently favored. Much research has been carried out on natural extracts as corrosion inhibitors because they are environmentally friendly (Akinbulumo *et al.*, 2020; D. R. Gusti *et al.*, 2020; Ogunleye *et al.*, 2020).

Natural extracts that have been studied with high corrosion inhibition efficiency and are recommended for use as corrosion inhibitors generally contain phenolic compounds (Gusti *et al.*, 2020). The turtledove plant (*Macaranga gigantea*) has been extensively studied and shown to contain phenolic compounds (Arung *et al.*, 2018; Sulastri *et al.*, 2020). Phenolic compounds contain many OH functional groups. The O atom in the OH group has a lone pair of electrons interacting with Fe on the steel surface (Gusti *et al.*, 2022). Therefore, the phenolic content of the Merkubung plant has the potential to be used as a corrosion inhibitor.

Corrosion inhibitors will be adsorbed to form a layer on the steel surface which can inhibit corrosion. Adsorption behavior can be studied with the help of the adsorption isotherm method, which provides information to estimate what happens in the adsorption layer (Ituen *et al.*, 2017; Jain *et al.*, 2017). Therefore, to find out whether WEMB extract has the potential as a corrosion inhibitor, a study was carried out using the weight loss method to calculate the efficiency of corrosion inhibition (Gusti *et al.*, 2017). The inhibitory effects of various plant extracts show different performances of each extract on metal surfaces (Lin *et al.*, 2021). Several adsorption isotherms models, such as the Langmuir, Freundlich, Temkin, Florry Huggins, and Frumkin, are utilized to evaluate whether the adsorption from WEMB extract is physical or chemical and how the WEMB extract interacts with the steel surface (Ituen *et al.*, 2017; Lin *et al.*, 2021).

2. MATERIALS AND METHODS

2.1 Materials

The materials used were mild steel, merkubung wood sap, and H_2SO_4 (Merck). The tools used were thermometers, water baths, glassware (Pyrex), sandpaper grade 120, calipers, reflux tools, and hot plates.

2.2 Research Procedure

The water extract of merkubung bark (WEMB) is prepared by employing a reflux technique to extract merkubung bark powder in water. The WEMB extract was filtered, and the filtrate was then collected. The filtrate was concentrated by heating at 50°C in a water bath to obtain a concentrated extract. About 1.25 g of WEMB extract was put into a 500 mL volumetric flask, then dissolved with 0.75 M H_2SO_4 to obtain an inhibitor solution concentration of 2.5 g/L. Inhibitor solutions were also prepared for a concentration of 2 g/L; 1.5 g/L; 1, and 0.5 g/L.

A drill with a diameter of 3 mm was used to drill holes in mild steel measuring ± 2 x 1 cm. The steel surface was smoothed with 120-grit steel sandpaper and cleaned with distilled water and acetone. The steel was then dried for ±5 minutes. The length and width of the steel were measured with calipers. Using an analytical balance, the mass of the steel was determined, and the initial mass (W_1) was estimated.

The mild steel was then immersed in a 0.75 M solution of sulfuric acid and a solution of sulfuric acid containing WEMB extract, each with a concentration of 0.5; 1.0; 1.5; 2.0; and 2.5 g/L for 24, 48, and 72 hours, respectively. Mild steel was lifted and cleaned with distilled water and acetone, then dried. Dried mild steel was weighed and referred to as the final mass (W_2).

2.3 Data Analysis

The data were analyzed using the weight loss method, which compares the original weight of the steel before immersion to its final weight after immersion. Weight loss data can be used to calculate the corrosion rate and adsorption isotherm models (Yetri & Jamarun, 2015). The corrosion rate is calculated using the following equation (Gusti *et al.*, 2020):

$$CR = \frac{W1 - W2}{A \times t} \quad (1)$$

CR is the corrosion rate (mg/cm^2 hour). W_2 is the final weight of steel (mg). W_1 is the initial weight of steel (mg). A is the steel surface area (cm^2), and t is the steel immersion time (hours).

The percentage of inhibition efficiency on steel corrosion is obtained by using the equation:

$$\%EI = \frac{CR1 - CR2}{CR1} \, x \, 100\% \quad (2)$$

CR1 is the corrosion rate in the absence of an inhibitor (mg/cm^2 hour), and CR2 is the corrosion rate in the presence of an inhibitor (mg/cm^2 hour).

Adsorption isotherms were determined using the following equation (Ituen *et al.*, 2017; Nwabanne & Okafor, 2012):

Langmuir : $\frac{C}{\theta} = \frac{1}{Kads} + C$ (3)

Freundlich: $\text{Log}\ \theta = \text{Log}\ K_{ads} + n \log C$ (4)

Temkin : $\theta = \frac{-2.303 \log K}{2a} - \frac{2.303 \log C}{2a}$ (5)

Frumkin : $\log \frac{\Theta}{1-\Theta} C = 2.303 \log K + 2a\theta$ (6)

Florry Huggins : $\log\left(\frac{\theta}{C}\right) = \log K + x \log(1-\Theta)$ " (7)

3. RESULTS AND DISCUSSION

3.1. The Effect of Inhibitor Concentration of Merkubung Bark Aqueous Extract (WEMB) on Inhibition Efficiency and Corrosion Rate of Mild Steel

The effect of WEMB extract inhibitor concentration and time on the inhibition efficiency and corrosion rate of mild steel is presented in Fig. 1 and Fig. 2. Fig. 1 and 2 demonstrate that as concentration increases, inhibition efficiency increases and corrosion rate decreases. As a corrosion inhibitor, WEMB extract is likely absorbed and forms a thin layer on the steel surface, preventing corrosive ions in the solution from reacting with Fe on the steel surface. The optimum inhibition efficiency value was found at an inhibitor concentration of 2.5 g/L in 72 hours with a value of 93.41%.

Soaking time affected the inhibition efficiency and corrosion rate of mild steel in a solution of aqueous extract of merkubung bark inhibitor at a concentration of 0.5; 1; 1.5; 2, and 2.5 g/L with variations in immersion time of 24, 48, and 72 hours. Fig. 1 and 2 show that the inhibition efficiency and corrosion rate of mild steel with corrosion inhibitor WEMB extract increased with increasing immersion time in sulfuric acid solution. WEMB extract increases corrosion inhibition efficiency on the surface of mild steel. It protects the steel surface from corrosive ion attack by forming a thin layer on the steel's surface. Gusti *et al.* (2019) reported that increasing the concentration of inhibitors and the length of immersion time will increase the inhibition efficiency and reduce the corrosion rate.

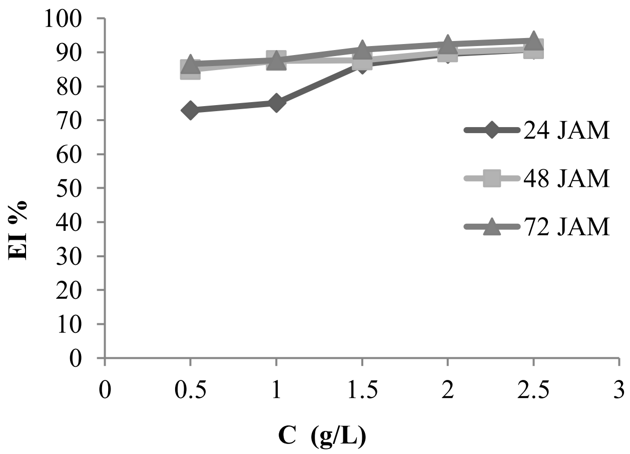

Figure 1. Effect of Concentration and Soaking Time of Mild Steel in the presence of WEMB Extract Inhibitors on the Efficiency of Corrosion Inhibition

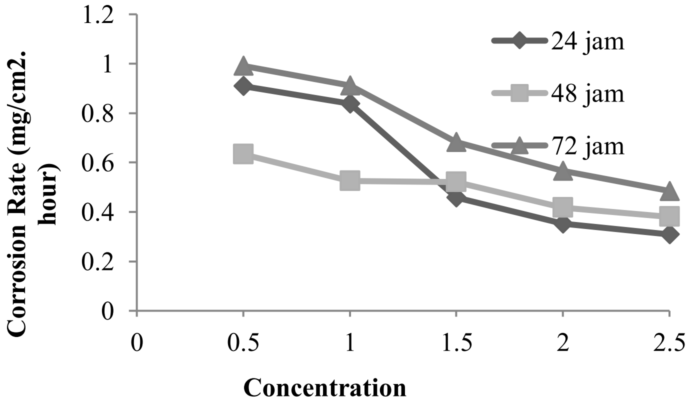

Figure 2. Effect of WEMB Extract Inhibitor Concentration on the corrosion rate of steel in sulfuric acid solution

3.2. Adsorption Isotherm

Adsorption isotherm parameters were used to investigate the behavior and mechanism of corrosion inhibitors. Inhibitor molecules can bind to metal surfaces through adsorption. Adsorption can be divided into physical adsorption (physisorption) and chemical adsorption (chemisorption) (Ituen *et al.*, 2017). The adsorption isotherm theory was applied by linear regression analysis for each adsorption theory, namely the theories of Langmuir, Freundlich, Temkin, Florry Huggins, and Frumkin.

Table 1 shows that linear regression analysis is used to determine the model's suitability for the research data by looking at the correlation coefficient (R^2). If the value of R^2 is close to 1, it can be concluded that there is an increasingly significant influence and a close relationship between variables.

3.3. Langmuir Adsorption Isotherm

Table 1 shows that the Langmuir approach with a regression value of 0.9996 is close to 1, so it is more acceptable to describe the adsorption properties of inhibitor molecules. The Langmuir adsorption isotherm indicates the presence of chemical bonds between the chemical groups of the secondary metabolites present in the inhibitor and the metals present in the mild steel, resulting in the formation of a surface passivation layer that is highly strong. Fig. 3 shows the information on adsorption K values. The adsorption K value at 48 hours in Table 1 shows the highest adsorption value compared to the adsorption K at 24 hours and 72 am. The adsorption K value describes the adsorption strength (Ituen *et al.*, 2017).

Table 1 Adsorption isotherm values of aqueous extract of Merkubung bark on mild steel

Adsorption Isotherm	Soaking Time	R^2	K	
Langmuir	24 hours	0.9956	4,209	
	48 hours	0.9996	15,72	
	72 hours	0.9996	13,10	
		R^2	K	n
Freundlich	24 hours	0.8971	1,261	0.15
	48 hours	0.9325	1,147	0.04
	72 hours	0.9331	1,124	0.05
		R^2	K	*A*
Temkin	24 hours	0.8954	1,562	0.28
	48 hours	0.9295	1,150	0.08
	72 hours	0.9308	1,195	0.10
		R^2	K	X
Flory Huggins	24 hours	0.8500	4,134	1.00
	48 hours	0.8955	306.8	2.84
	72 hours	0.8975	57,45	1.87
		R^2	K	A
Frumkin	24 hours	0.9691	7446	6.21
	48 hours	0.9648	2717	15.3
	72 hours	0.9730	9512	13.9

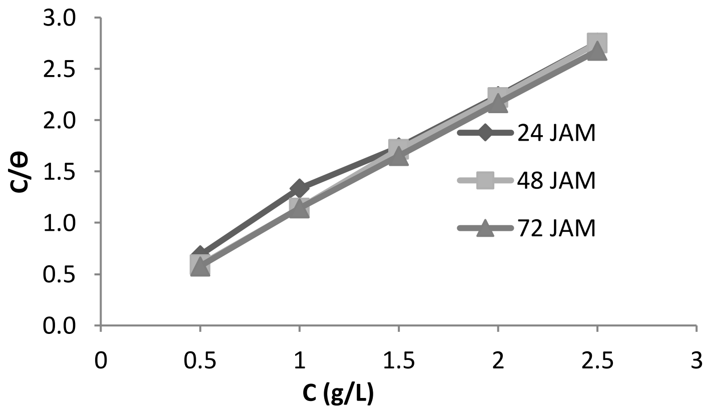

Figure 3. Langmuir adsorption isotherm for mild steel corrosion with immersion times of 24 hours, 48 hours, and 72 hours

3.4. Freundlich Adsorption Isotherm

The Freundlich isotherm model shows that the inhibitor has a heterogeneous surface; each molecule has a different adsorption potential and assumes that adsorption occurs in a multilayer manner on the surface of the inhibitor. The value of n between 1.0 - 10.0 in this isotherm indicates that the adsorption process is going well and easily (Ituen *et al.*, 2017). Based on Fig. 4 and Table 1, the n values of the immersion times of 24, 48, and 72 hours were 0.15, 0.04, and 0.05, respectively.

3.5. Temkin Adsorption Isotherm

The Temkin adsorption isotherm explains the interactions occurring in the adsorption layer (Ituen *et al.*, 2017). The degree of surface covering (θ) is related to the inhibitor concentration (C) in Equation 5, where K is the adsorption equilibrium constant, and a is the molecular interaction parameter. Plotting θ against log C, as presented in Fig. 3, gives a linear relationship. The a value in Table 1 of the Temkin adsorption isotherm is positive. This shows the behavior of the inhibitor attraction on the mild steel surface (Nwabanne & Okafor, 2012).

3.6. Frumkin Adsorption Isotherm

The values for the Frumkin adsorption parameters are presented in Table 1. In Frumkin adsorption, a which has a positive value indicates the attraction behavior of the inhibitor on the mild steel surface. A negative a value indicates inhibitor repulsion on the mild steel surface (Ituen *et al.*, 2017). Table 1 and Fig. 4 show that the a value of the Frumkin isotherm is positive, indicating the presence of attractive inhibitory behavior on the mild steel surface.

3.7. Flory Huggins Adsorption Isotherm

The adsorption isotherm model is a substitution model. The constant parameter (x) in Equation 7 describes the substitution of molecular inhibitors for water (Ituen *et al.*, 2017). Fig. 5 and Table 1 show positive x parameter values, indicating that there is a lot of adsorbed extract from the merkubung bark aqueous extract because it can move more than one water molecule from the mild steel surface (Nwabanne & Okafor, 2012).

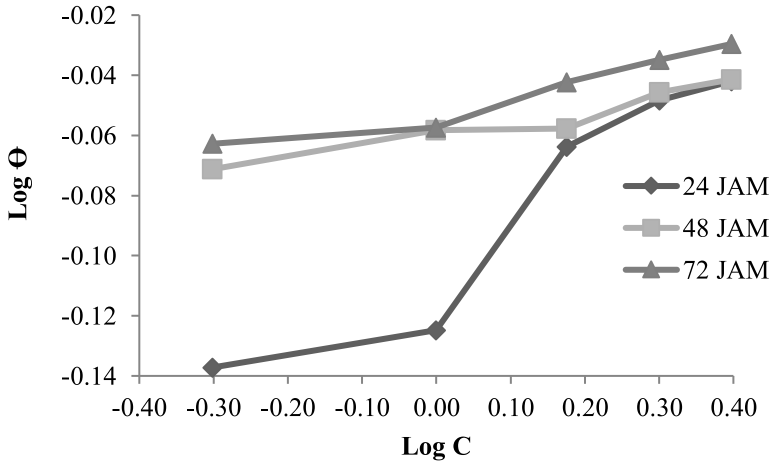

Figure 4. Freundlich adsorption isotherm for mild steel corrosion with immersion times of 24 hours, 48 hours, and 72 hours

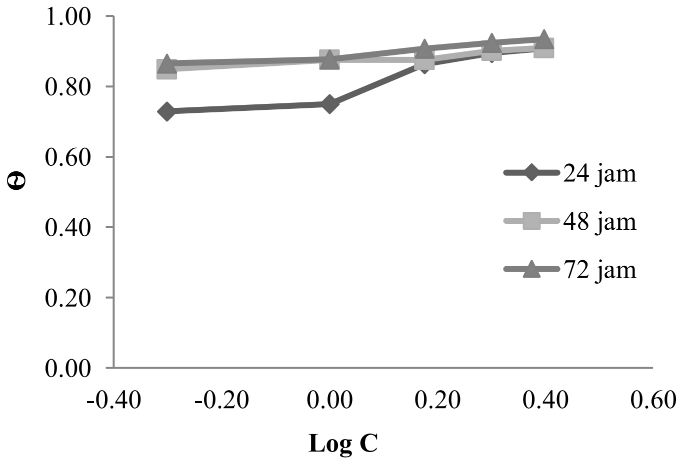

Figure 3. Temkin isotherms for adsorption of aqueous extract of merkubung bark on the surface

of mild steel with immersion times of 24 hours, 48 hours, and 72 hours

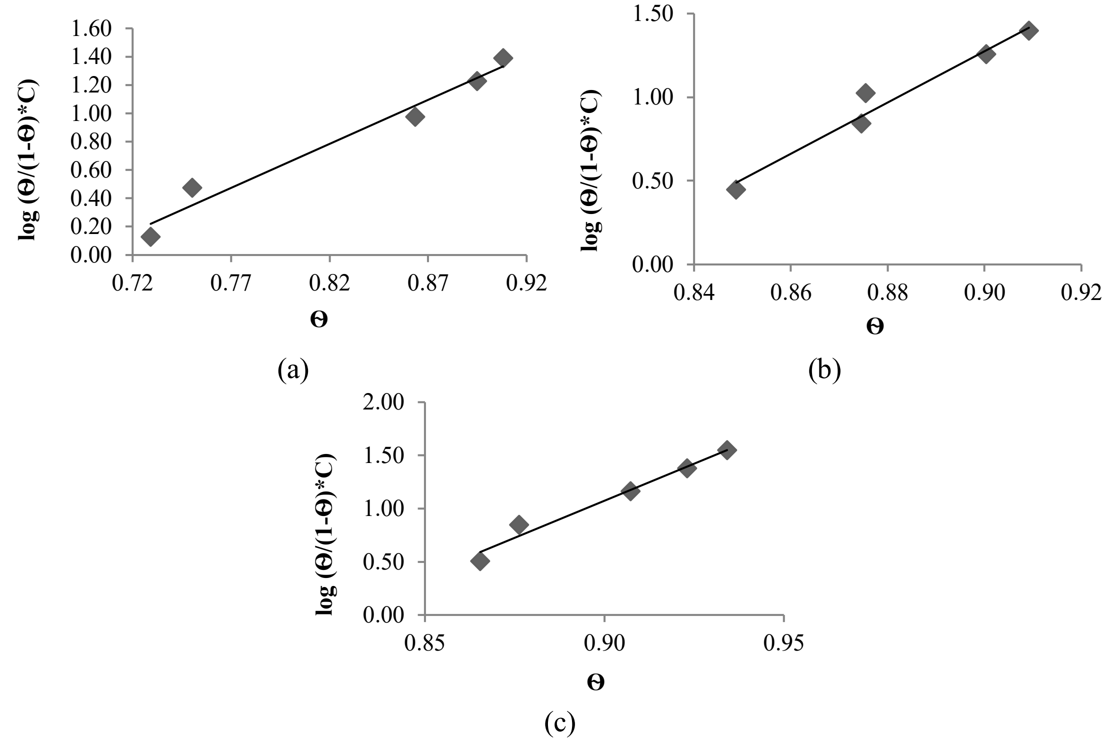

Figure 4. Frumkin isotherm for adsorption of aqueous extract of merkubung bark on a mild steel surface with an immersion time of (a) 24 hours, (b) 48 hours, and (c) 72 hours

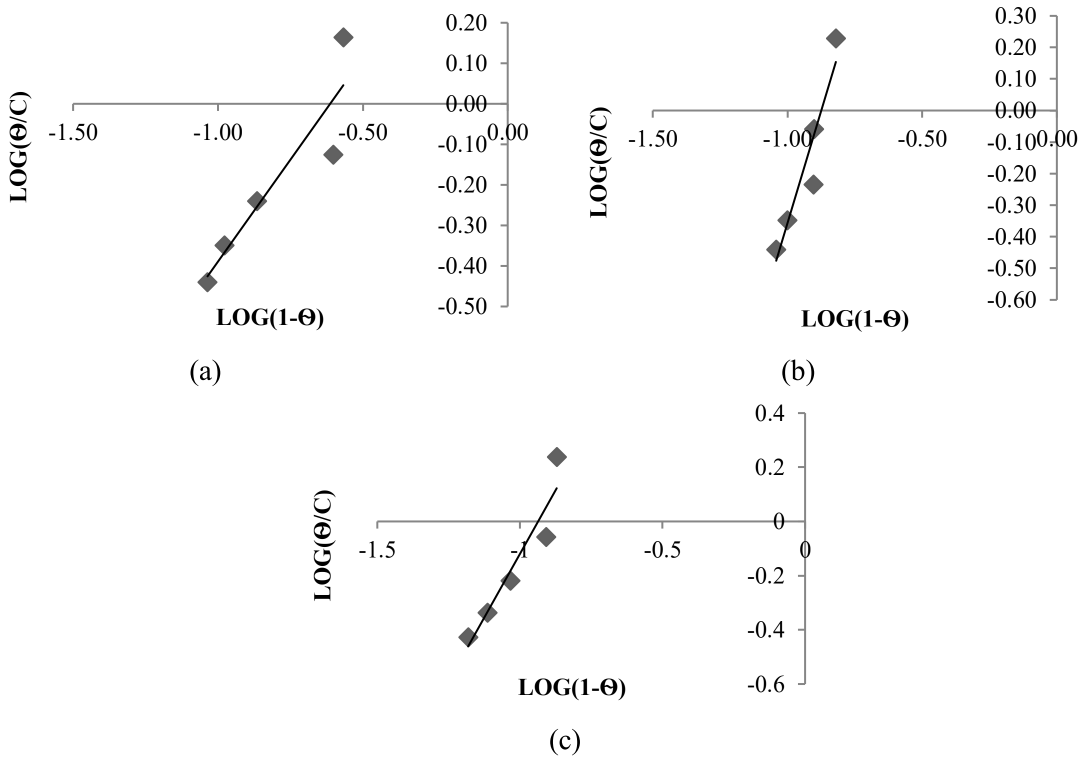

Figure 5. Isotherm Flory Huggins for adsorption of aqueous extract of merkubung bark on a mild steel surface with an immersion time of (a) 24 hours, (b) 48 hours, and (c) 72 hours

4. CONCLUSIONS

The inhibition efficiency increases, and the corrosion rate decreases with increasing WEMB extract concentration. The inhibition efficiency and corrosion rate of mild steel with the corrosion inhibitor WEMB extract increased with the longer immersion time in sulfuric acid solution.

Analysis of the adsorption isotherm model from the Langmuir, Freundlich, Temkin, Florry Huggins, and Frumkin adsorption isotherm models shows that the R2 value of the Langmuir adsorption isotherm model is closer to 1 than the other models. The adsorption isotherm models tested illustrate that the WEMB extract inhibitors in coating the surface of mild steel tend to chemisorb more due to the attractive interaction between the WEMB extract and the steel surface.

LIST OF REFERENCES

Akinbulumo, O. A., Odejobi, O. J., & Odekanle, E. L. (2020). Thermodynamics and adsorption study of the corrosion inhibition of mild steel by Euphorbia heterophylla L. extract in 1.5 M HCl. *Results in Materials*, *5*(October 2019), 100074. https://doi.org/10.1016/j.rinma.2020.100074

Arung, E. T., Amirta, R., Zhu, Q., Amen, Y., & Shimizu, K. (2018). Effect of wood, bark and leaf extracts of Macaranga trees on cytotoxic activity in some cancer and normal cell lines. *Journal of the Indian Academy of Wood Science*, *15*(2), 115–119. https://doi.org/10.1007/s13196-018-0215-4

Gusti, D. R., Lestari, I., Farid, F., & Sirait, P. T. (2019). Protection of mild steel from corrosion using methanol extract of avocado (Persea americana mill) seeds in a solution of sulfuric acid. *Journal of Physics: Conference Series*, *1282*(1). https://doi.org/10.1088/1742-6596/1282/1/012083

Gusti, D. R., Lestari, I., Permana, E., & Anggraini, R. (2020). Exploration o Coffee Bean Husks Waste as an Eco-Environmentally Friendly Corrosion Inhibitor on Mild Steel in Sulphuric Acis Solution. *IOP Conference Series: Earth and Environmental Science*, *483*(1). https://doi.org/10.1088/1755-1315/483/1/012007

Gusti, D.R, Lestari, I., Farid, F., & Sirait, P. T. (2019). Protection of mild steel from corrosion using methanol extract of avocado (Persea americana mill) seeds in a solution of sulfuric acid Protection of mild steel from corrosion using methanol extract of avocado (Persea americana mill) seeds in a solutio. *IOP Conf. Series: Journal of Physics: Conf. Series*, *1282*(1), 12083. https://doi.org/10.1088/1742-6596/1282/1/012083

Gusti, Diah Riski, Emriadi, Alif, A., & Efdi, M. (2017). Corrosion Inhibition of Ethanol Extract of Cassava (Manihot esculenta) Leaves on Mild Steel in

Sulfuric Acid. *International Journal of ChemTech Research*, *10*(2), 163–171. http://www.sphinxsai.com/2017/ch_vol10_no2/1/(163-171)V10N2CT.pdf

Gusti, Diah Riski, Emriadi, E., & Efdi, M. (2022). Thermodynamic and Adsorption Properties of Flavonoid Rutin from Cassava *(Manihot esculenta*) Leaves as a Corrosion Inhibitor on the Mild Steel in Sulfuric Acid Solution. *Defect and Diffusion Forum*, *416*, 183–190. https://doi.org/10.4028/p-fk32yz

Ituen, E., Akaranta, O., & James, A. (2017). Evaluation of Performance of Corrosion Inhibitors Using Adsorption Isotherm Models: An Overview. *Chemical Science International Journal*, *18*(1), 1–34. https://doi.org/10.9734/csji/2017/28976

Jain, S. K., Shakil, N. A., Dutta, A., Kumar, J., & Saini, M. K. (2017). Sorption kinetics and isotherm modelling of imidacloprid on bentonite and organobentonites. *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes*, *52*(5), 326–337. https://doi.org/10.1080/03601234.2017.1281653

Lin, B. lan, Shao, J. jie, Xu, Y. ye, Lai, Y. ming, & Zhao, Z. ning. (2021). Adsorption and corrosion of renewable inhibitor of Pomelo peel extract for mild steel in phosphoric acid solution. *Arabian Journal of Chemistry*, *14*(5). https://doi.org/10.1016/j.arabjc.2021.103114

Nwabanne, J. T., & Okafor, V. N. (2012). Adsorption and Thermodynamics Study of the Inhibition of Corrosion of Mild Steel In H₂SO₄ Medium Using <i>Vernonia Amygdalina</i> *Journal of Minerals and Materials Characterization and Engineering*, *11*(09), 885–890. https://doi.org/10.4236/jmmce.2012.119083

Ogunleye, O. O., Arinkoola, A. O., Eletta, O. A., Agbede, O. O., Osho, Y. A., Morakinyo, A. F., & Hamed, J. O. (2020). Green corrosion inhibition and adsorption characteristics of Luffa cylindrica leaf extract on mild steel in hydrochloric acid environment. *Heliyon*, *6*(1), e03205. https://doi.org/10.1016/j.heliyon.2020.e03205

Permanasari, A. R., Saputra, T. R., Nurul'Aina, A., & Liska, S. (2020). Penentuan Pelarut Terbaik pada Ekstraksi Tanin Kulit Kayu Akasia dan Pengaruhnya Sebagai Inhibitor Laju Korosi pada Baja Karbon [Determination of the Best Solvent in Tannin Extraction from Acacia Bark and Its Effect as a Corrosion Rate Inhibitor in Carbon Steel]. *Jurnal Teknik Kimia Dan Lingkungan*, *4*(1), 7. https://doi.org/10.33795/jtkl.v4i1.129

Sibarani, R. G., Ramadhanti, P., KurniawanSyah, G., & Gusti, D. R. (2021). Eksplorasi Limbah Kulit Nanas Sebagai Biomaterial Dalam Menanggulangi Permasalahan Korosi Pada Baja [Exploration of Pineapple Peel Waste as a Biomaterial in Overcoming Corrosion Problems in Steel]. *Journal BiGME*, *1*(1), 38–45. https://doi.org/10.22437/bigme.v1i1.12312

Sulastri, P., Mariani, Y., Yusro, F., Kehutanan, F., Tanjungpura, U., & Daya, J. (2020). Aktivitas Antibakteri Campuran Ekstrak Kulit Batang Merkubung (Macaranga gigantea) dan Mangpurang (Macaranga triloba) Terhadap *Enterococcus faecalis* dan *Escherichia coli* [Antibacterial Activity of Mixture of Merkubung (*Macaranga gigantea*) and Mangpurang (*Macaranga triloba*) Bark Extracts Against *Enterococcus faecalis* and *Escherichia coli*]. *Jurnal Bios Logos*, *10*(2), 56–62. https://doi.org/https://doi.org/10.35799/jbl.11.2.2020.28323 E-ISSN:

Tang, Z. (2019). A review of corrosion inhibitors for rust preventative fluids. *Current Opinion in Solid State and Materials Science*, *23*(4), 100759. https://doi.org/10.1016/j.cossms.2019.06.003

Yetri, Y., & Jamarun, N. (2015). *Journal of Chemical and Pharmaceutical Research , 2015 , 7 (5): 1083-1094 Research Article Corrosion inhibition of environmental friendly inhibitor using Theobroma cacao peels extract on mild steel in NaCl solution*. *7*(5), 1083–1094.