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Rice Husk Extract and Damar Resin as Corrosion Preventing Bio Coating Materials for Mild Steel in Demineralized Water

Andra Hidayatullah[1,3], Anton Irawan[1,2], Marta Pramudita[1,2,3*]

[1]*Chemical Engineering of Program Magister , University of Sultan Ageng Tirtayasa, 42435 Banten, Indonesia*
[2]*Chemical Engineering Department, Faculty of Engineering, University of Sultan Ageng Tirtayasa, 42435 Banten, Indonesia*
[3]*Biomass Valorization Laboratory, Center of Excellent Faculty of Engineering University of Sultan Ageng Tirtayasa, 42435 Banten, Indonesia*

*Corresponding Author Email: marta_pramudita@untirta.ac.id

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ABSTRACT

Corrosion is one of the main problems in industry, especially in cooling systems, refinery units, pipelines, chemicals, oil and gas production units, boilers and water processing, paints, pigments, lubricants, and others. The research focused on testing the ability of bio-coating materials of rice husk extract and resin gum using the weight loss method. In contrast, the corrosive medium used was demineralized water. The variations used were soaking time (1, 2 and 3 hours), silica concentration in bio-coating (0, 500, 1000 and 1500 ppm) and temperature (40, 60 and 80°C). From the results of this study, the highest efficiency was 87.39% at a soaking time of 1 hour and a concentration of 1500 ppm. The higher the temperature, the inhibition efficiency decreases; this shows the adsorption mechanism is physisorption.

Keywords: *Silica, Damar Resin, Bio-Coating, Rice Husk Extract, Corrosion*

1. INTRODUCTION

Corrosion is a decrease in metal quality due to an electrochemical reaction with its environment. Metals that experience quality degradation involve chemical reactions and electrochemical reactions, namely between the materials concerned with the transfer of electrons. The destruction of materials, especially metals, is due to a reaction between the metal and the environment. The process of material destruction causes a decrease in the quality of the metal material (Pal et.al 2020). Corrosion in metal objects will always happen and cannot be avoided. Corrosion is a process that occurs naturally and will not usually stop if the metal is still in a corrosive environment. This process will damage the metal by eroding the metal, which will then reduce the mechanical properties of the metal. Generally, the corrosion reaction is an electrochemical reaction (Gumelar et.al 2011).

Many ways can be done to inhibit the corrosion rate of metals, one of which is by coating the surface or coating. However, currently, the generally used coatings come from chemicals, which can cause various impacts such as environmental pollution, are difficult to degrade, and can contaminate the fluid in the pipe. Therefore, alternative materials are needed that can prevent these impacts from occurring. Bio coating is a coating on the surface of a material such as metal derived from organic materials to protect the metal from corrosion. The advantages of bio-coating compared to chemical-based coatings include being economical, environmentally friendly, and renewable. In previous research using the electrochemical method, lemon seeds were used as the primary material for bio-coating material to slow down the corrosion rate of mild steel in sulfuric acid media. This case study shows that lemon seed molecule has properties that can be used as a natural coating material for corrosion protection on mild steel in sulfuric acid solution (Pal et.al 2020). Rice husk extract (RHE) and damar resin are alternative natural materials that can substitute synthetic chemicals in coating and protect mild steel metals from corrosion caused by acidic solutions, which is high enough to coat and protect metal materials from corrosion and is a good choice for utilization.

Rice husk (rice husk/rice hull) is the outermost part of the rice grain and contains much silica compared to other rice processing by-products. The by-products of rice processing include straw (4.0±7.0) %; bran (0.6±1.1) %, bran (0.2±0.3) %, and husk (18.0±22.3) %. Rice husk waste can be used to produce coatings for metal materials. It has been noted that the content of rice husk waste contains a lot of compounds that can be used to inhibit the corrosion rate, namely silica, which produces the highest compound. Silica is one of the organic compounds that have the potential as a corrosion coating. Silicate (SiO_2) has good adhesion, a medium for good protection so that it is possible to resist the diffusion of water vapor, ions, and oxygen to the metal surface to protect the metal from corrosion. Resin is a natural polymer that is very flexible, stable, and easy to obtain. Natural resin is also a natural material that is widely used for coating media. The use of latex as a coating material has also been proven by research by Fitrida et al. 2015 which states that damar resin can be used as a varnish coating on building wood, where damar resin can protect against weathering (corrosion).

Research on bio-coating from rice husks and damar resin extracts was previously carried out on mild steel in the pipeline. The results showed that adding silica and damar resin as a corrosion coating can inhibit the corrosion rate significantly. In this study, a corrosive medium in the form of demineralized water was used to see whether the performance of the bio-coating could work well. The use of demineralized water, widely used in industrial equipment such as boiler feed water, is one of the reasons for using demineralized water as a corrosive medium in this study. From this explanation, it is necessary to research coating tests using rice husk extract and damar resin to obtain inhibitory substances and to determine the effect of increasing the concentration of rice husk extract and damar resin on the corrosion rate of low carbon steel (mild steel) in demineralized water media.

2. METHODS

Mild steel was used with the composition (% by weight):0.16C, 0.1P, 0.01S, 0.5Si, 0.54Mn and the balance was Fe. Damar resin was obtained from a local supplier. N-Hexane was purchased from Sigma Aldrich with a purity of 95%. Acetone was purchased from Merck with 70% 70%. Silica from RHE with 1 M NaOH solution (Pellets pure Emplura®). Demineralized water was purchased from a local supplier.

2.1. The Preparation of The Sample

The material used in this study is mild steel. The mild steel is then cut on a grinder to a thickness of 3.09 mm and mild steel dimensions of 29.79 x 19.23 mm. Then, smooth the mild steel with sandpaper. The mild steel was then cleaned with acetone (Merck 70%). The structural steel is then dried and weighed.

2.2. The Preparation Process of Damar Resin Solution

The following step for making damar resin is by crushing the resin in a mortar. And then sieving it through an 80-mesh sieve at the initial stage. It is then dissolved in a beaker and mixed with n-hexane solvent (Sigma Aldrich 95%) in a 1:2 for damar resin: solvent. Then, stir until the solution becomes homogenous.

2.3. The Preparation of Bio-Coating Materials

In the process of making bio-coating products, the initial stage is carried out by mixing silica and the resulting damar resin solution into a beaker with a ratio of 3:1 and then stirring until a homogeneous product mixture is formed.

2.4. The Process of Mild Steel Coating

In the silica-based metal plating method, the dry metal is pre-loaded with a rope as a metal binder to facilitate dipping. Then, a cup coats the metal with bio-coating materials at 500, 1000 and 1500 ppm concentrations. Then, the metal is placed in a jar, taken out, dried, and weighed as bulk data.

2.5. Bio-Coating Test

The coating-coated metal samples are immersed in demineralized water at temperatures of 40°C, 60°C, and 80°C for 1, 2, and 3 hours. The mild steel was then dried and then weighed again after testing.

2.6. Weight-Loss Method

Weight loss, more commonly known as the weight loss method, is used to determine the magnitude of a material's corrosion rate (mmpy) based on initial and final weight loss and to determine corrosion inhibition efficiency. Data were collected using the weight loss method to calculate the corrosion rate. Data were obtained by weighing an initial polished mild steel sample and a final mild steel sample immersed in water. The corrosion rate can be calculated using the following formula (ASTM31):

$$C_{r(mmpy)} = (87500\ x\ \Delta W)/(\rho\ x\ A\ x\ t) \qquad (1)$$

$$I.E\% = \left(1 - (Cr_{inh}/Cr_{blank})\right)x100 \qquad (2)$$

Where Cr is the Corrosion rate (mmpy), Cr_{inh} is the Corrosion rate with inhibitor (mmpy), Cr_{blank} is the Corrosion rate without inhibitor (mmpy), ΔW is Weight loss (g), A is a Surface area (cm2), ρ is Density of mild steel (g/cm3), t is Immersion time (hr), I.E% is Inhibition efficiency (%).

3. RESULT AND DISCUSSION

3.1. The effect of adding silica concentration to the biocoating materials on the corrosion rate

The effect of adding silica concentration to the bio coating on corrosion rate with immersion time of 1,2 and 3 hours and temperature of 40^{o}C can be seen in Figure 1.

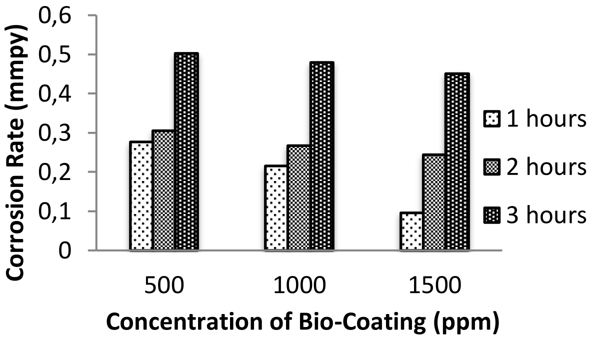

Fig. 1. Corrosion rate vs concentration on immersion time variation at 40°C

Figure 1 shows the calculation results of the effect of corrosion rate on adding silica concentration and immersion time, namely 1, 2, and 3 hours, at 40°C. The graph shows that the higher the concentration of silica added to the bio-coating media, the lower the corrosion rate on the surface of mild steel. It shows that increasing the silica content in the bio-coating media can protect mild steel from corrosion in corrosive media such as demineralized water. Based on the results of the analysis of the corrosion rate that occurs after the material is coated by bio-coating, the quality of the material's resistance to corrosion is generally in the best range, namely "Excellent", with a corrosion rate far below <1 mpy (Fontana 1986).

Furthermore, the effect of corrosion rate on time can also be seen in Figure 4.1, where the corrosion rate that shows the highest results is at the most extensive immersion time, that is, for 3 hours, which, when viewed in the corrosion rate equation in equation (1), it appears that the relationship between the amount of corrosion rate and immersion time is inversely proportional, or in other words, if the immersion time increases, the corrosion rate should decrease.

Yameng Qi et al. stated that the corrosion layer is thicker and tighter with increased immersion time. Moreover, the results of electrochemical measurements show that the corrosion resistance of the coating and the power transfer resistance increase with increasing immersion time [10]. In addition, Osaralube et al. also stated that with increasing immersion time, the corrosion rate tends to decrease due to passivation, namely the formation of corrosion products on the surface. It causes ions that can cause corrosion to be blocked by the rust deposits on the metal surface.

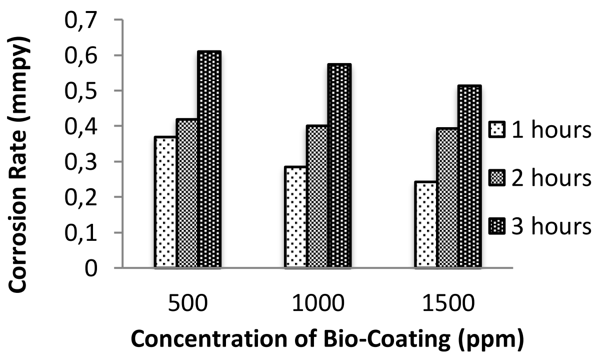

Fig. 2. Corrosion rate vs concentration on immersion time variation at 60°C

The rust deposit that is formed will cover the surface of the mild steel at a certain time, thus preventing the corrosive media from entering the mild steel, until the rust deposit dissolves in the corrosive media.

Figure 2 shows the results of the corrosion rate calculation against the addition of silica concentration and immersion time at 60°C. Similarly, to the effects of the previous comparison at 40° C, adding silica concentration at 60°C also shows a decrease in the corrosion rate (mmpy) as the silica concentration is added to the bio-coating media. However, compared to the graph in Figure 1 before, the overall corrosion rate at 60°C is higher than at 40°C. Still, based on the journal Fontana and Mars Guy, 1986, the quality of bio coating in protecting metals from corrosion is considered "Excellent" because it remains within the range of corrosion rate < 1 mpy.

The immersion time, at concentrations of 500, 1000, and 1500 ppm, also decreased the corrosion rate as the immersion time increased. Just like before, this happens because of the reduction and oxidation reactions. When oxygen undergoes a reduction reaction, the steel metal sample will experience oxidation on the metal surface, which causes the protective layer formed on the metal surface to decrease. This reduction reaction will create more and more as the corrosion formation reaction continues.

Figure 3 shows the results of the comparison graph of the effect of corrosion rate on the addition of silica concentration and time of acquisition at 80°C, which shows results that are also not much different from the previous Figure 1 and Figure 2, where at 80 °C, the effect of adding silica concentration in bio-coating media is also able to reduce the corrosion rate of metals. In addition, the effect of immersion time on the corrosion rate still shows the same results as before. It shows that the bio-coating used in this study can inhibit the corrosion of metals in acidic media when the silica content of the bio-coating is increased. However, the protection by the bio-coating still does not show good results when the metal is immersed in the corrosive medium of demineralized water for a long time because this will increase the corrosion rate of the metal significantly increase.

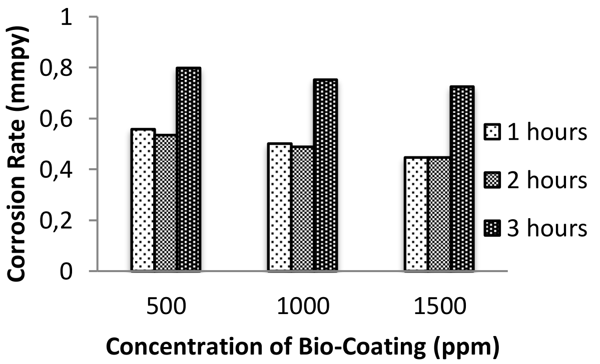

Fig. 3. Corrosion rate vs concentration on immersion time variation at 80°C

The results of this study show a decrease in corrosion rate when the concentration is reduced, the length of immersion time, and the use of high temperatures. It follows the theory that increasing temperature, length of immersion time, and low concentration will cause the speed of the corrosion reaction. It is due to the addition of kinetic energy of the particles in action due to an increase in the temperature of the corrosive media solution, thus exceeding the magnitude of the activation energy. The speed of the corrosion rate is higher if the kinetics price is greater than the activation energy (Melchers et al., 2022). The results of this study indicate that the durability of rice husk extract and resin gum solution mixed into a homogeneous solution can protect mild steel from corrosion in corrosive media demineralized water with an immersion time of 1 hour at 40˚C.

Based on Figure 4, the corrosion rate increases as the temperature of the corrosive media solution increases, namely demineralized water in the same bio-coating concentration. The corrosion rate at a silica concentration of 500 ppm, with an immersion time of 1 hour, when the solution temperatures are 40°C, 60°C, and 80°C is 0.28 mmpy, 0.36 mmpy, and 0.55 mmpy, respectively. The corrosion rate at a silica concentration of 1000 ppm, with an immersion time of 1 hour, when the solution temperatures of 40°C, 60°C, and 80°C were 0.21 mmpy, 0.28 mmpy, and 0.50 mmpy. While the corrosion rate at a silica concentration of 1500 ppm, with an immersion time of 1 hour, when the solution temperatures of 40°C, 60°C, and 80°C were 0.09 mmpy, 0.24 mmpy, 0.44 mmpy, respectively. The resulting corrosion rate at 40°C was lower than that at 60°C and 80°C. The condition of the corrosion media solution at 80°C produced a greater corrosion rate than at other temperatures.

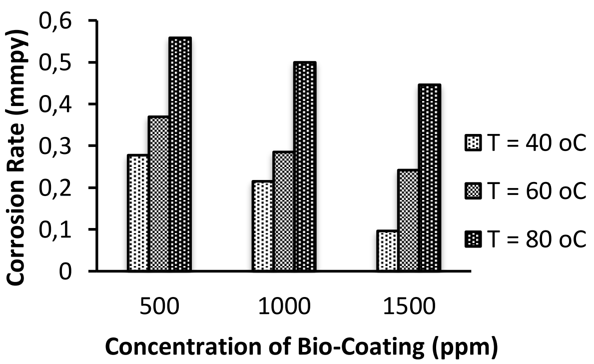

Fig. 4. Corrosion rate vs concentration and temperature variation at immersion time is an hour.

Temperature is one of the factors that can initiate the corrosion process. The temperature increase will increase the corrosion reaction's speed (Mardhani et al., 2013). It occurs because the rise in temperature in the corrosion media solution will cause the addition of kinetic energy of the particles so that it will exceed the magnitude of the activation energy. When the kinetic energy is greater than the activation energy, it will increase the speed of the corrosion rate (Melchers et al. 2019). The corrosion rate highly depends on the k value, a temperature function. When the temperature changes, the k value will also change; when the k value changes, the corrosion rate will change. By the Arrhenius equation, the higher the temperature, the higher the corrosion rate. In addition, based on the collision theory, a high temperature will increase the collision that occurs, so the corrosion rate will be greater. In addition, high temperatures can cause the resin chain to break, so the bio-coating's ability to withstand corrosion rates will be minor. Therefore, the lowest corrosion rate is obtained when the temperature of the corrosive media is 40°C, where the resin is still resistant to low temperatures.

Figure 4 shows silica concentration's effect on corrosion rate, where silica with a concentration of 1500 ppm produced a lower corrosion rate than silica with a concentration of 500 and 1000 ppm. In contrast, silica with a concentration of 1500 ppm had a lower corrosion rate than silica with a concentration of 500 and 1000 ppm. Silica with a concentration of 1500 ppm produced a lower corrosion rate than silica with a 500 and 1000 ppm concentration. It shows that the higher concentration of coating solution will increase the ability of silica content to protect mild steel from the effects of corrosion. However, a silica concentration of 1500 ppm when the temperature is 80oC shows a mismatch where the resulting corrosion rate is relatively high. The corrosion rate on mild steel coated with bio-coating material shows lower results than on mild steel not covered with bio-coating material, according to Figure 4.

Figure 5 shows temperature has a directly proportional effect on the corrosion rate. The higher the temperature in the corrosive medium of demineralized water, the higher the corrosion rate. Vice versa, the lower the temperature, the lower the corrosion rate. The corrosion rate at a silica concentration of 500 ppm, with a soaking time of 2 hours, when the solution temperatures of 40°C, 60°C, and 80°C were 0.305 mmpy, 0.419 mmpy, 0.534 mmpy, respectively. The corrosion rate at a silica concentration of 1000 ppm, with an immersion time of 2 hours, when the solution temperatures of 40°C, 60°C, and 80°C were 0.267 mmpy, 0.400 mmpy, and 0.488 mmpy, respectively. While the corrosion rate at a silica concentration of 1500 ppm, with an immersion time of 2 hours, when the solution temperatures of 40°C, 60°C, and 80°C are 0.244 mmpy, 0.392 mmpy, 0.446 mmpy, respectively. 80°C produces the highest corrosion rate compared to 60°C and 40°C at silica concentrations of 500, 1000, and 1500 ppm.

It happens because an increase in temperature directly leads to an increase in corrosion rate. After all, electrochemical reactions will generally occur faster at higher temperatures. Increased temperature will increase the energy for the response, thus increasing the corrosion rate.

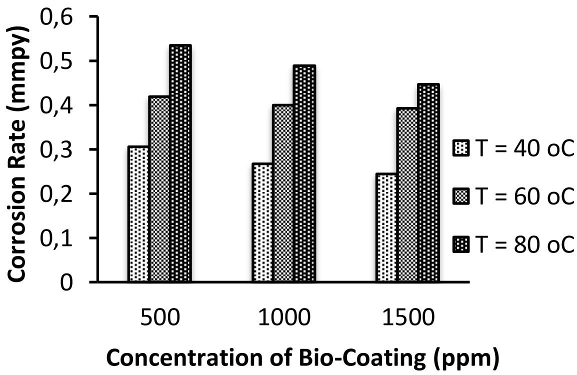

Fig. 5. Corrosion rate vs concentration and temperature variation at immersion time is 2 hours.

Similarly, Figure 5 shows the effect of concentration, which is inversely proportional to the corrosion rate. The higher the silica concentration, the lower the corrosion rate that occurs on the surface of mild steel. The lowest corrosion rate is found at 40°C when the silica concentration of 1500 ppm is 0.115 mmpy. The high silica concentration will increase the ability of bio-coating material to protect the surface of mild steel from corrosion due to demineralized water.

Figure 6 presents a comparison graph of the effect of corrosion rate on adding silica concentration and immersion temperature at 3 hours.

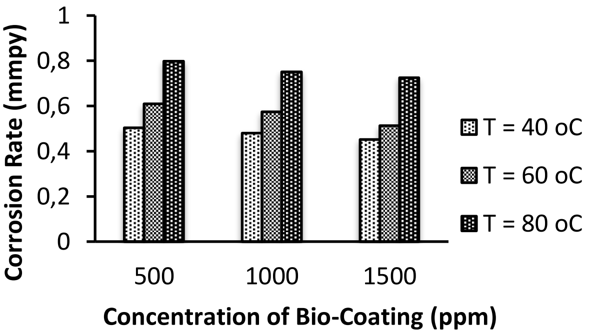

Fig. 6. Corrosion rate vs concentration and temperature variation at immersion time is 3 hours.

The corrosion rate at a silica concentration of 500 ppm, with an immersion time of 3 hours, when the solution temperatures of 40°C, 60°C, and 80°C were 0.502 mmpy, 0.610 mmpy, 0.798 mmpy, respectively. The corrosion rate at a silica concentration of 1000 ppm, with an immersion time of 3 hours, when the solution temperatures of 40°C, 60°C, and 80°C were 0.479 mmpy, 0.573 mmpy, 0.751 mmpy, respectively. While the corrosion rate at a silica concentration of 1500 ppm, with an immersion time of 3 hours, when the solution temperatures of 40°C, 60°C, and 80°C were 0.451 mmpy, 0.512 mmpy, 0.725 mmpy, respectively. Based on the graph presented in Figure 6, the lowest corrosion rate occurs when the corrosive media solution temperature conditions are 40°C and 1500 ppm silica concentration. High temperatures will increase the energy for the reaction, thus increasing the corrosion rate that occurs on mild steel. The higher concentration will increase the ability of bio-coating to protect the surface of mild steel from corrosion.

It is to theory and previous research that the increase in temperature in corrosive media will increase the corrosion rate of mild steel because high temperatures will accelerate the damage to the protective layer (coating) of the material so that it will accelerate and become a place for electrolyte infiltration from outside to interact directly with the specimen. The increase in temperature will cause the process of evaporation of the electrolyte. However, because this is a closed system, the vapour from the corrosive media will be trapped and increase the humidity. The corrosion rate will increase due to corrosive sulfuric acid elements. These corrosive elements are very dominant in improving the corrosion rate.

The effect of concentration on corrosion rate shows the corrosion inhibiting effect due to the attention of rice husk extract bio-coating and damar resin solution; it is caused by bio-coating adsorption on the electrode on the surface of mild steel. The high concentration of bio-coating shows that the silica content and resin gum can inhibit the reduction of hydrogen ions in the cathodic part of mild steel (Sapitri et al. 2016). Silica from rice husk can inhibit corrosion, and the resin gum solution in the mixture has flexible properties and strong adhesion, allowing it to adhere to a homogeneous solution that reacts with demineralized water solution will show the formation of a protective layer covering the surface of the mild steel electrode where the coating will form a film to inhibit the corrosion process. Then, water molecules and other ions are adsorbed on the surface of mild steel and transferred to silica and gum resin, becoming a homogeneous solution.

3.2 The effect of adding silica concentration to the biocoating materials on the Inhibition efficiency of corrosion.

The corrosion rate of a material over time is the corrosion rate. This corrosion rate value can be used to calculate the efficiency value of bio-coating. The bio-coating's efficiency value shows the bio-coating's ability to inhibit the sample's corrosion rate in the corroding medium. This study used weight loss to determine the efficiency and corrosion rate (Cr) values. The efficiency value shows the magnitude of the ability to inhibit the corrosion rate. The following is the data from the calculation of inhibition efficiency in Table 1 using the weight loss method in variations of immersion time, temperature, and bio-coating concentration obtained in the study.

Table 1. Immersion time and temperature on Inhibition Efficiency

Time Immersion (hours)	T °C	Inhibition Efficiency (%)			
		Concentration (ppm)			
		0	500	1000	1500
1	40	0	67.22	76.47	87.39
2		0	52.02	56.08	60.81
3		0	24.89	31.12	36.92
1	60	0	62.09	74.5	78.43
2		0	58.24	60.68	61.53
3		0	47.14	48.09	50.47
1	80	0	68.33	72.33	76.33
2		0	62.67	65.12	66.75
3		0	21.48	28.39	31.35

Table 1 shows the inhibition efficiency value (%IE) produced from bio-coating of rice husk extract and damar resin increases as the concentration of bio-coating additions from Table 1 the best results at a concentration of 1500 Ppm with a soaking time of 1 hour and a temperature of 40°C which is 87.39% while the lowest inhibitor efficiency results at a concentration of 500 Ppm with an immersion time of 3 hours and a temperature of 80˚C of 21.48%. Like the corrosion rate test, immersion time, temperature variation, and bio-coating concentration will affect the resulting inhibition efficiency value. However, the efficiency value is inversely proportional to the corrosion rate value. It is to the literature because when the sample using concentration is added, the temperature and immersion time is reduced, and the greater the inhibition efficiency value (Saratha et al. 2009). There is an inhibition by bio-coating against the attack of aggressive ions present in the corrosive medium. The barrier increases with an increasing degree of coverage by the added bio-coating (Okafor et al. 2010).

The efficiency of using bio-coating at 1 hour has the best value compared to 2 and 3 hours so that the corrosion process will occur, and there will be more weight reduction due to reacting with demineralized water. The passivation layer formed can only last a specific time and starts to disappear so that an active layer will be included, which causes the corrosion process (Pramudita et al. 2019). The smaller the concentration added and the longer the immersion time and temperature used, the layer formed will erode gradually because oxidation events will continue to occur and not even stop attacking mild steel. In addition, in this study, the efficiency value obtained did not reach 100%; this could be because not all parts of the mild steel were inhibited by bio-coating. It indicates that there are still parts that are exposed to oxidation attacks or the occurrence of the rusting process.

The coating protects mild steel from corrosive media as a barrier effect, which functions as a separator or isolates the surface from water, and an oxygen inhibitor effect, which forms a passive layer. The mechanism of mild steel protection with bio-coating is that bio-coating protects mild steel only on its surface from the corrosive media of demineralized water. When mild steel is contacted with corrosive media, the coating protects the mild steel by forming a layer that can separate, block, or isolate between the metal surface and the corrosive media.

4. CONCLUSION

Based on the research that has been done, the following conclusions are obtained:

1. The concentration of silica from rice husk affects the corrosion rate of mild steel in the corrosive medium of demineralized water, where the higher the silica concentration, the lower the corrosion rate. The silica concentration of 1500 ppm produces a lower corrosion rate than the silica concentration of 500 and 1000 ppm in all temperature conditions and immersion times. The lowest corrosion rate was obtained when the solution temperature was 40^{o}C, immersion time was 1 hour, and silica concentration was 1500 ppm.
2. Rice husk and damar resin bio-coatings can protect mild steel surfaces from corrosion. The efficiency of this bio-coating reached 87.39%. The higher the temperature of the corrosive media solution, the lower the corrosion rate. It indicates that the mechanism of bio-coating protection of mild steel occurs by physisorption.

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