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Effect of Bio-Coating Material Concentration of Rice Husk Extract (*Oryza Sativa*) and Damar Resin (*Agathis Dammara*) on Reducing Corrosion Rates in H_2SO_4 Solutions

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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 use of inhibitors has been proven to reduce the rate of corrosion. Still, it is limited by long-term stability, so it is necessary to provide other protection for mild steel, namely coating the metal with a coating material. Coating is the process of covering base material to protect the material from corrosion and provide protection to the material. The silica contained in rice husk extract and damar resin has the potential to be good bio-coating. This research aims to determine the effect of damar resin concentration on the corrosion rate and corrosion rate efficiency. The method used in this research uses several methods, one of which is the weight loss method. The resin and silica sol obtained from ashing rice husks are mixed to form a homogeneous product. Metal samples that have been coated with bio-coating material are soaked in 1 M sulfuric acid solution, with varying resin concentrations of 25, 50, and 75 gr with immersion times of 1, 2, and 3 hours, and at temperatures of 30, 40, 60, and 80 °C, which was then tested for the capability of the bio-coating material. This research obtained the highest corrosion rate value of 0.8860 mmpy using a temperature of 80˚C and a immersion time of 3 hours, with a corrosion efficiency value of 62.96%. Meanwhile, the lowest corrosion rate was 0.2143 mmpy at a temperature of 30˚C and a immersion time of 1 hour, with a corrosion efficiency value of 85.71%.

Keywords: *Bio-coating, rice husk, damar resin, corrosion, silica*

1. INTRODUCTION

Corrosion is the process of material damage due to chemical or electrochemical reactions with the environment(Salensky et al., 1986). Besides that, quite a lot of costs must be incurred as a direct result of this problem. Realizing this situation, controlling and overcoming corrosion problems needs to be done more effectively, especially in applying production support tools so that they can run more effectively, efficiently, and optimally(Raja et al., 2016).

The rate of corrosion itself cannot be stopped but can be minimized. One way to inhibit the corrosion rate is by using a coating method. Coating is a process for coating metal materials to prevent direct contact between the metal and corrosive media. Coating materials consist of adhesives, substrates, and additives. The coating method itself usually uses silica (SiO_2). Silica (SiO_2) is a chemical compound with many applications in various industries, but it also has potential dangers that must be considered(Mor et al., 2017). One of silica's main dangers is exposure to very small crystalline silica dust when used or processed in various industries. Apart from being a health hazard, silica can also potentially be an environmental problem(Nabipour et al., 2020).

Therefore, an alternative that can be made to reduce this impact is to use coatings made from natural ingredients. Coating materials made from natural ingredients is a breakthrough that continues to be researched and developed(Wood, 2007). Apart from its renewable nature, using natural materials is believed to be safe for health and the environment. One of the natural materials that can be used is rice husks and damar resin. According to various studies, rice husk ash has a high silica content, around 87-97%. This high silica content has great potential and can be used as a raw material to replace other silica sources that are cheaper and environmentally friendly(Pramudita et al., 2022). Damar resin has properties including being brittle and easily attached to materials at room temperature, easily soluble in essential oils and non-polar organic solvents, slightly soluble in polar organic solvents, insoluble in water, not heat resistant, flammable, not volatile if not decomposed and can change color if stored for too long in a closed place without good air circulation, and has a weight loss value of approximately 5% at a temperature of 105 °C (Mulyono et al., 2004).

Several researchers have previously researched biocoating from rice husk extract and resin. First, testing the biocoating on a corrosive medium in the form of 1 M NaOH and getting the best results, namely the highest corrosion rate value of 0.8068 mmpy using a biocoating concentration of 500 ppm, temperature of 80˚C, and immersion time of 3 hours(Pramudita et al., 2022). Furthermore, other research using corrosive acid media (acid effect) and producing the best data, namely at a silica concentration of 1500 ppm, makes it more efficient than other concentrations (Hidayatullah et al., 2023). From this presentation, it is necessary to follow research on biocoating rice husk extract and damar resin to determine the effect of the concentration of silica coating material, rice husk extract, and damar resin on reducing the corrosive H_2SO_4 medium.

This research aims to determine the effect of damar resin concentration, time, and temperature of mild steel immersion on the corrosion rate and efficiency.

2. METHODS

2.1 Mild Steel Preparation

The first step is to prepare the Mild Steel, then cut the mild steel with dimensions of 20 x 30 x 1 mm, then sand the mild steel using 250 - 1000 size sandpaper so that the Mild Steel looks cleaner. After that, the Mild Steel was washed using distilled water and acetone for 15 minutes, dried the washed mild steel, and weighed on the mild steel.

2.2 Damar Resin Solution Preparation

The second step is to prepare the ingredients for making gum resin solution, such as n-Hexane and Getah Damar. Put 25, 50, and 75 grams of resin and 80 ml of n-Hexane into a beaker, then heat it to 40°C and stir using a spatula until the resin solution becomes homogeneous.

2.3 Silica Solution Preparation

The third step is to prepare the ingredients for making a silica solution, such as 1 M NaOH and silica. Put 1000 ml of 1 M NaOH and 1.5 grams of silica into a beaker, then heat it to 40°C and stir using a spatula until the solution becomes homogeneous, producing a 1500 ppm silica solution.

2.4 Biocoating Preparation

The fourth step is to prepare the ingredients for the biocoating solution: resin gum solution and silica solution from rice husk extract. Add 80 ml of damar resin solution and 20 ml of silica solution into a beaker, then heat it to a temperature of 40°C and stir using a spatula until the damar resin solution becomes homogeneous, then check using FTIR analysis.

2.5 Dipcoating Process

The weighed Mild Steel is entered into the biocoating solution in the fifth step. After that, immersion for 30 seconds. Then, lift the mild steel and dry it so that the biocoating solution can stick or harden on the mild steel. After that, do the weighing.

2.6 Corrosion Test Process

The coated Mild Steel is entered into the H_2SO_4 solution in the final step. After that, put it in a water bath with temperature variations of 30°C, 40°C, 60°C, and 80°C and time variations of 1, 2, and 3 hours. Then, lift the mild steel and dry it. After drying, weigh it and calculate the corrosion rate using the weight loss method. The formula for corrosion rate is as follows:

$$Cr = (87500*\Delta W)/A\ \rho\ t \quad (1)$$

Where:
Cr = corrosion rate (mmpy)
ΔW = difference between the initial weight and the final weight (g)
A = the surface area (cm^2)
ρ = density of mild steel (g/cm^3)
t = difference in immersion time (h)

3. Results and Discussion

3.1. Characterization of Biocoating Materials

Biocoating is a corrosion coating that comes from available natural ingredients. One of the compounds contained in rice husk extract that can be used as a biocoating is silica. Meanwhile, damar resin is a natural polymer with flexible and stable properties. This biocoating combines flexible and stable resin with silica derived from rice husks, which has strong adhesion to resist water, ions, and oxygen diffusion from the surface. FTIR analysis was conducted to see the functional groups in the biocoating. The test results using FTIR on the biocoating solution are shown in Fig. 1.

Isolate infrared spectrum data shows a wide absorption with strong intensity in the wave number area of 3435.91 $cm^{-1,}$ which is thought to be absorption for the O-H group of the -OH stretching vibration of Si-OH. The presence of a sharp band with strong intensity in the wave number area 2847.67 cm^{-1} and 2909.15 cm^{-1} is thought to indicate the presence of an aliphatic C-H stretching group, which is supported by the presence of absorption in the wave number area 1449.98 cm^{-1} which is believed to indicate the presence of the C-H bending aliphatic. Sharp absorption with strong intensity in the wave number area of 1707.95 cm^{-1} indicates the presence of the C=O stretching group. Absorption in the wave number area of 1571.55 cm^{-1} is thought to be from the aliphatic C=C stretching group. The FTIR absorption pattern analysis showed the presence of the C-H functional group, as indicated by the absorption at a wave number of 2847.67 cm^{-1}. It suggests the possibility of the presence of methyl (CH_3) and methylene (CH_2) groups (Socrates, 1994). This assumption is strengthened by the presence of absorption in the wave number area 1449.98 and 1384.78 $cm^{-1,}$ which is the absorption from the $-CH_2$ and CH_3 bends, which indicates the presence of dimethyl gem groups as a characteristic of triterpenoid compounds. In wave numbers 921.93 and 827.93 $cm^{-1,}$ absorption with strong intensity from the C-H range in the alkene group (Skoog et al., 1998).

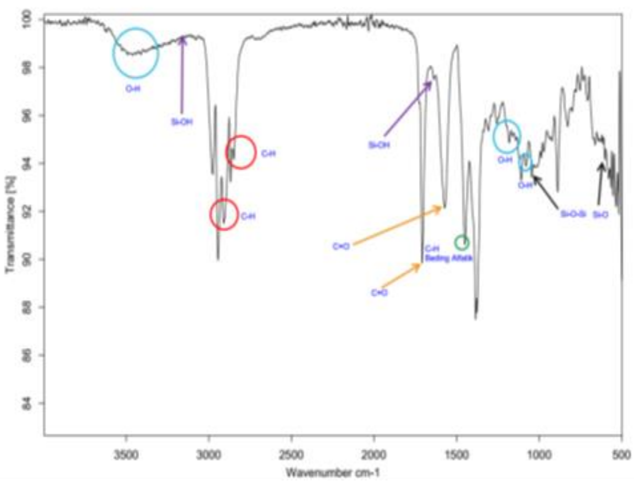
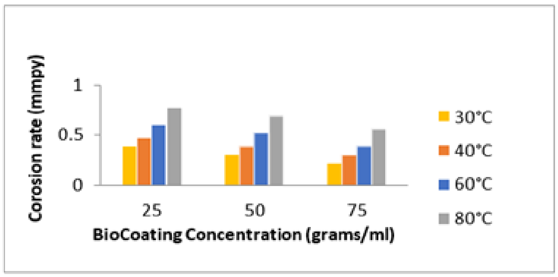


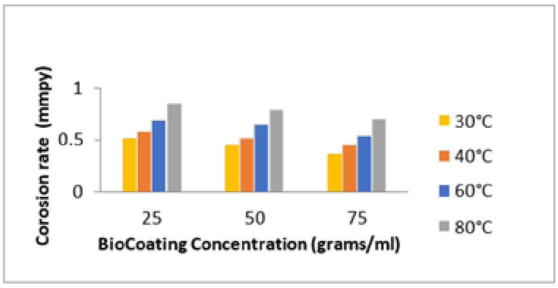
Fig.1 Results of FTIR Analysis of Biocoating Samples of 75 Grams of Damar Resin

3.2 Effect of Temperature vs Concentration on Corrosion Rate at Constant Immersion Time.

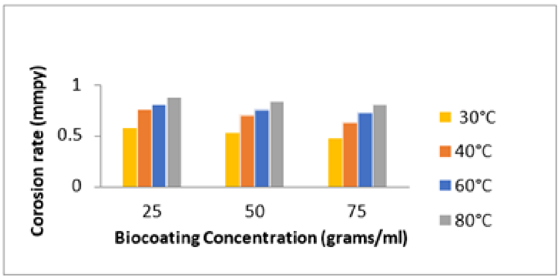
The effect of immersion temperature on the corrosion rate and the optimum conditions for biocoating materials in slowing down the corrosion rate on mild steel for a certain time. The research was conducted by varying the immersion temperature by 30°C, 40°C, 60°C, and 80°C. Based on this research, the overall value of the highest corrosion rate was at an immersion time of 3 hours at a temperature of 80°C, and the lowest corrosion rate was at an immersion time of 1 hour at a temperature of 30°C. It shows an increase in the corrosion rate value, temperature, and immersion time. The increase in the corrosion rate value can be seen in the graph. Fig. 2 presents a comparative graph of the effect of immersion temperature and the addition of resin concentration on the corrosion rate.



(a)



(b)



(C)

Fig.2 Effect of Temperature vs Concentration on Corrosion Rate during Immersion Time (a) 1 Hour (b) 2 Hours (c) 3 Hours

Temperature is one of the factors that can trigger the corrosion process. An increase in temperature will increase the speed of the corrosion reaction(Luqmanulhakim et al., 2023). It happens because an increase in temperature in the corrosion media solution will cause an increase in the kinetic energy of the particles, which will exceed the magnitude of the activation energy. The corrosion rate will increase when the kinetic energy exceeds the activation energy (Williams et al., 2019). The greater corrosion rate value indicates a faster corrosion rate. In this study, the largest corrosion rate occurred at a temperature of 80°C and 3 hours with a corrosion rate value of 0.886 mmpy. It is because the sample experienced a relatively longer immersion time at a high temperature, and there was a reduction in weight due to the reaction of a 1 M H_2SO_4 solution. The smaller corrosion rate value indicates a slower corrosion rate. In this study, the lowest corrosion rate occurred at a temperature of 30°C with an immersion time of 1 hour, and the corrosion rate value was 0.30 mmpy. Because the samples experienced a relatively shorter immersion time, corrosion reactions could be minimized. This shows that the longer the immersion time and the higher the temperature in the 1 M H_2SO_4 solution, the greater the corrosion rate because the mild steel surface will interact with the 1 M H_2SO_4 solution for longer, resulting in a reaction between the mild steel and the 1 M H_2SO_4 solution and produces high corrosion. The low corrosion rate value indicates that the mild steel tested takes a long time to corrode because of the protection from the corrosion bio coating from rice husk extract and gum resin solution. Figure 3 presents the corrosion phenomenon on the surface of mild steel coated with biocoating material without being coated with biocoating material at a temperature of 40^{o}C and an immersion time of 2 hours.

(a)

(b)

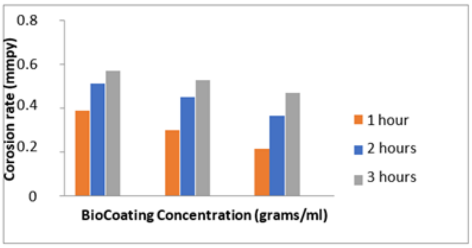
Fig. 3. Corrosion on the surface of mild steel at a temperature of 40oC and an immersion time of 2 hours.
(a) without biocoating
(b) with biocoating

Areas with an acidic tendency will cause the mild steel to react with the sulfuric acid electrolyte, and the mild steel will experience corrosion or erosion. However, coating with biocoating material can protect the surface of mild steel from corrosion. Fig. 3(a) shows the surface of mild steel, which is completely rusted, and the color changes due to oxidation. Fig. 3(b) shows the surface of mild steel, which does not experience discoloration or corrosion because it has been coated with bio-coating material. However, on mild steel that is not coated with biocoating material, sulfuric acid will attack the surface of the mild steel directly, and corrosion will occur on the surface of the mild steel. It shows that bio-coating using rice husks and damar resin is quite effective in protecting the surface of mild steel and slowing down corrosion in 1 M sulfuric acid media. Hence, rice husks have the potential to be used as a corrosion coating on metal surfaces. A greater corrosion rate value indicates a faster corrosion rate. In this study, a large corrosion rate occurred at a temperature of 80°C and 3 hours with a corrosion rate value of 0.886 mmpy.

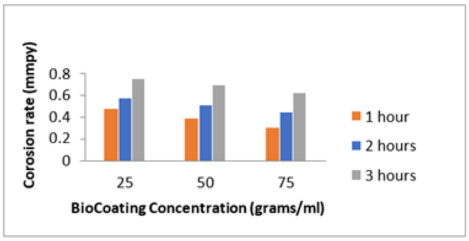
The reason is that the sample experienced a relatively longer immersion time at a high temperature, and weight was reduced due to reacting with a 1 M H_2SO_4 solution. The smaller corrosion rate value indicates a slower corrosion rate. In this study, the lowest corrosion rate occurred at 30° C with an immersion time of 1 hour, and the corrosion rate value was 0.30 mmpy. Because the samples experienced a relatively shorter immersion time, corrosion reactions could be minimized.

3.3 Effect of Immersion Time Vs. Concentration on Corrosion Rate at Constant Temperature

Based on this research, the overall value of the highest corrosion rate was at an immersion time of 3 hours with a temperature of 80°C, and the lowest corrosion rate was at an immersion time of 1 hour with a temperature of 30°C. It shows an increase in the corrosion rate value, immersion time, and high temperatures. The increase in the corrosion rate value can be seen from the graph in Fig. 4, which presents a comparative graph of the effect of immersion time and the addition of damar resin concentration on the corrosion rate.



(a)



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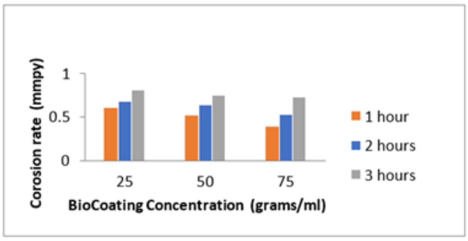
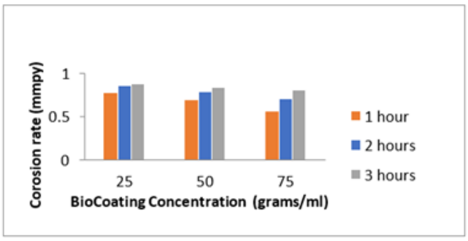


(c)



(d)

Fig. 4. Effect of Immersion Time and Concentration on Corrosion Rate at Constant Temperature (a) 30°C (b) 40°C (c) 60°C (d) 80°C

The rate of corrosion increases with the length of immersion time, temperature, and concentration of the biocoating used. The higher the concentration of biocoating, the lower the temperature, and the longer the immersion time, the lower the corrosion rate value, as the greater the silica content that is present forms complex compounds with corrosive substances and covers the surface of mild steel, so that the corrosion process is increasingly hampered (Zhang et al., 2018). This research shows a decrease in the corrosion rate when the concentration increases, the immersion time is shorter, and low temperatures are used. It is under the theory that increasing the temperature, longer immersion time, and low concentration will cause the corrosion reaction to speed up. The kinetic energy of the acting particles is due to an increase in the temperature of the corrosive media solution, which exceeds the magnitude of the activation energy. The corrosion rate is higher if the kinetic value exceeds the energy activation (Monticelli, 2018). This research shows that the durability of rice husk extract and damar resin solution mixed into a homogeneous solution can protect mild steel from corrosion in a 1 M H_2SO_4 solution with an immersion time of 1 hour at a temperature of 30°C.

(Zhao et al., 2022) stated that with increasing immersion time, the corrosion layer becomes thicker and denser. Moreover, electrochemical measurements show that the corrosion layer and power transfer resistance increase with immersion time (Figueira, 2020). Apart from that, Osaralube et al. also stated that as the immersion time increases, the corrosion rate tends to decrease due to passivation, namely the formation of corrosion products on the surface. It results in ions that can cause corrosion being blocked by rust deposits forming on the metal surface.

However, in the process of immersing mild steel in a corrosive medium in the form of sulfuric acid, a reaction occurs as follows.

$$H_2SO_4 + Fe \rightarrow FeSO_4 + H_2 \qquad (1)$$

The $FeSO_4$ layer will stick to the carbon steel surface and form a layer of protection against further corrosion. However, the relatively fast reaction to form hydrogen gas in gas bubbles causes the protective layer on the metal surface to move to the bulk liquid phase (Gergely, 2018). It causes the corrosion rate in the sulfuric acid solution to continue to increase as the immersion time increases.

It shows that the longer the immersion time and the higher the temperature in the 1 M H_2SO_4 solution, the greater the corrosion rate because the mild steel surface will interact with the 1 M H_2SO_4 solution for longer, resulting in a reaction between the mild steel and the 1 M H_2SO_4 solution and produces high corrosion. The low corrosion rate value indicates that the mild steel tested takes a long time to corrode due to protection from the corrosion biocoating of rice husk extract and damar resin solution.

3.4 Effect of Damar Gum Concentration in Biocoating Materials on Corrosion Rates

Fig. 2 and 4 show that high immersion times and temperatures indicate a decrease in the corrosion rate as the resin concentration increases. It shows that as the concentration of resin in the biocoating material increases, the corrosion process becomes inhibited. The resin can cover the surface of mild steel well so that corrosive media does not directly penetrate the surface of mild steel. Based on the chemical properties of the resin, at a temperature of 105 ^{0}C, it has a weight loss of <1%. Based on Fig. 4.2 and 4.4, it can be concluded that adding silica and resin can inhibit or reduce the corrosion rate.

The effect of concentration on the corrosion rate shows a corrosion inhibitor effect due to the concentration of the biocoating rice husk extract and gum resin solution. The adsorption of the biocoating on the electrode on the surface of the mild steel causes this. The high concentration of bio coating shows that the silica and resin content can inhibit the reduction of hydrogen ions in the mild steel cathodic part.

Silica from rice husks has adhesive power, and the mixed damar resin solution has flexible properties and adheres to a homogeneous solution which reacts with the NaOH solution which will show the formation of a protective layer that covers the surface of the mild steel electrode where the layer will form a film so that it can inhibit the corrosion process. Then, water molecules and other ions are adsorbed on the surface of the mild steel and transferred to the silica and damar resin, becoming a homogeneous solution. The thickness of this protective layer increases as the silica concentration in the rice husk extract increases because more silica is electrostatically adsorbed on the mild steel, decreasing the capacitance value. So, a barrier layer that can form on the surface of mild steel in varying immersion time, temperature, and biocoating concentration can prevent the mild steel from corrosion (Elbakhshwan et al., 2017).

Figure 5 shows the corrosion phenomenon on the surface of mild steel coated with biocoating material with varying concentrations at a temperature of 40^{o}C for an immersion time of 1 hour.

(a) (b) (c)

Fig. 5. Comparison of corrosion that occurs on the surface of mild steel that has been coated with biocoating material at a temperature of 40oC during an immersion time of 1 hour (a) 25 gr (b) 50 gr (c) 75 gr.

Fig. 5 shows the effect of varying biocoating concentrations on the corrosion rate. Low bio-coating concentrations can accelerate corrosive media interacting directly with mild steel, further causing damage to the protective layer or biocoating material quickly, thereby increasing the corrosion rate. In Fig. 5

(c), you can see that the surface of the mild steel has not changed much in color, and only a little rust has formed. Compared to Fig. 5 (a) and (b), you can see that parts of the biocoating layer have worn off, and even the mild steel looks rusty.

This phenomenon can state that the higher the concentration of biocoating, the thicker the layer formed and the better the protection against corrosion. The combination of resin and silica provides good protection against corrosion on metal surfaces. The biocoating layer protects mild steel against corrosion, with one of the materials being resin, where resin has the main function as an adhesive and can inhibit the corrosion rate. Thus, silica from rice husks and damar resin can potentially be used as a biocoating material that protects metals such as mild steel in the corrosive medium of sulfuric acid.

4. CONCLUSION

Based on the research that has been carried out, it was concluded that at the same damar resin concentration, the higher the temperature and the longer the immersion time, the higher the corrosion rate will increase. The greater the concentration of damar resin, the lower the immersion time and temperature, and the lower the corrosion rate. The lowest corrosion rate was obtained at an additional concentration of 75 grams with an immersion time of 1 hour and a temperature of 30°C.

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