

Superhydrophobic Silica Ultrasonic Coating Based on Sinabung Volcanic Ash as Anti-Corrosion of Ferrous Metal Materials

Pelapisan Ultrasonik Superhidrofobik Silika Berbasis Abu Vulkanik Sinabung Sebagai Anti Korosi Material Logam Besi

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ABSTRACT

Superhydrophobic materials are substances with a water contact angle exceeding 150° . They can be employed as coatings to prevent corrosion on ferrous metals. This occurs due to the ability of superhydrophobic materials to hinder water adhesion to the metal surface, resulting in less interaction between the metal, water, and oxygen. Ultrasonication is a technique to blend, standardize, and enhance the dispersion of particles. This research uses ultrasonic waves to disperse superhydrophobic silica into a homogeneous mixture. It is then applied as a protective coating material on the surface of ferrous metal to increase its ability to inhibit ferrous metal corrosion. The main material used in this research was Sinabung volcanic ash-based silica, which was synthesized using the sol-gel method. Superhydrophobic silica material was added to the paint by dispersing (0; 0.6; 1.2; 1.8) g with 10 mL of paint using an ultrasonic homogenizer for 15 minutes. The corrosion test was carried out by immersing the sample in a corrosive solution for 96 hours. The results show the effect of sonification and variations in the composition of superhydrophobic silica on the performance of the superhydrophobic silica layer on the surface of iron against corrosive solutions of 15% HCl (v/v) and 3.5% NaCl (w/v). The optimal conditions for varying compositions of superhydrophobic silica were determined to achieve the lowest corrosion rate in different corrosive solutions. Specifically, the corrosion rate was 64.51 mpy at 15% HCl (SS3) and 1.31 mpy at 3.5% NaCl (SS6). These corrosion rates were inversely proportional to the inhibitor efficiency, measured at 83.40% in 15% HCl (SS3) and 93.75% in 3.5% NaCl (SS6). Therefore, the superhydrophobic silica material is highly suitable as an additional component in iron coatings to protect against corrosion effectively.

Keywords: superhydrophobic silica, ultrasonically dip coating, corrosion rate, corrosion inhibitor.

ABSTRAK

Bahan superhidrofobik adalah bahan yang memiliki sudut kontak air lebih besar dari 150° yang dapat digunakan sebagai bahan pelapisan untuk penghambat korosi pada logam besi. Hal ini karena bahan superhidrofobik dapat mencegah air menempel pada permukaan logam, sehingga dapat mengurangi kontak antara logam dengan air dan oksigen. Ultrasonikasi dapat digunakan untuk mencampurkan, menghomogenkan, dan memperluas penyebaran suatu partikel. Penelitian ini memanfaatkan gelombang

ultrasonik untuk mendispersikan superhidrofobik silika dan cat menjadi suatu campuran yang homogen dan mengaplikasikannya menjadi bahan lapisan pelindung dipermukaan logam besi dengan tujuan untuk meningkatkan kemampuannya dalam penghambatan korosi logam besi. Bahan utama yang digunakan dalam penelitian ini adalah silika berbasis abu vulkanik Sinabung yang disintesis dengan metode sol-gel. Penambahan bahan superhidrofobik silika pada cat dilakukan dengan mendispersikan (0; 0,6; 1,2; 1,8) g dengan 10 mL cat menggunakan alat ultrasonic homogenizer selama 15 menit. Uji korosi dilakukan dengan merendam sampel dalam larutan korosif selama 96 jam. Hasilnya terdapat pengaruh sonifikasi dan variasi komposisi superhidrofobik silika pada kinerja lapisan superhidrofobik silika di permukaan besi terhadap larutan korosif HCl 15% (v/v) dan NaCl 3,5% (b/v). Kondisi optimum pada variasi komposisi superhidrofobik silika diperoleh dengan laju korosi terendah dimasing-masing larutan korosif sebesar 64.51 mpy pada HCl 15% (SS3), dan 1.31 mpy pada NaCl 3,5% (SS6), yang berbanding terbalik dengan efisiensi inhibitor yang tertinggi dimasing-masing larutan korosif sebesar 83,40% pada HCl 15% (SS3), dan 93,75% pada NaCl 3,5% (SS6), sehingga bahan superhidrofobik silika cukup layak dipakai sebagai bahan tambahan pada pelapisan besi untuk melindunginya dari korosi.

Kata Kunci: superhidrofobik silika, pelapisan celup ultrasonik, laju korosi, penghambat korosi

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1. INTRODUCTION

Metal possesses numerous benefits but is also susceptible to corrosion (Affandi, 2020). The cause of this phenomenon can be attributed to the elevated levels of humidity and acidic air in Indonesia (Priyotomo, 2020). Applying a protective layer to metal surfaces is a technique to inhibit corrosion (Amri, 2020). However, previous research on metal coating methods has not used practical, efficient, and cost-effective technology (Miranda, 2020). Therefore, further research is needed to develop metal coating methods that are more practical, efficient, and cost-effective, enabling their widespread use to mitigate metal corrosion.

Research on developing hydrophobic coatings employing fluorocarbon compounds like fluoroalkylsilane (FOK) is being discontinued due to its adverse effects on health and environmental contamination (Ilham, 2019). Furthermore, hydrophobic coating studies shifted to using more environmentally friendly compounds such as trimethylchlorosilane (TMCS) and xylene. An inherent drawback of this chemical is its

relatively low hydrophobicity, measuring less than 110. Consequently, water can still permeate the sample's surface (Setyawan D. H., 2014; Setyawan Y. & ., 2015). The next step involves utilizing a blend of hydrophobic and coupling agents to enhance the hydrophobic properties of the material surface by employing silicates. An identified weakness of the superhydrophobic coating method is its lower efficiency, as highlighted by Qiao (2018). Satish (2013) researched superhydrophobic properties in silica-based coatings, specifically focusing on the durability and restoration of these properties. The study utilized sol-gel dip coatings, as described by Mahadik (2013). The resulting superhydrophobic layer had a contact angle of 148.24°. Theoretically, a surface is categorized as superhydrophobic if the contact angle is >150°. The silica coating on iron metal is suboptimal due to the weak adhesion between silica and iron. It is believed to be due to the less efficient coating technique being used. To address this, it is recommended that the technique be updated by employing the ultrasonic dip coating method. This technique

offers the advantage of enhancing the uniformity and stability of the mixture and facilitating the efficient and rapid dissolution of the sample. Adopting this technique allows the coating process to be carried out effectively and smoothly (Haser, 2018).

Research related to hydrophobic materials has attracted researchers' attention because of its lotus effect. The lotus effect is a phenomenon when water droplets that fall on the surface of lotus leaves form dots and roll, carrying pollutants or dust that stick to the surface of the leaves. This phenomenon is often known as the "Lotus effect" (Barthlott, 1997). This is caused by the presence of microscopic structures on the surface of lotus leaves, which are capable of producing high water contact angles ($>150^\circ$) (Putri, 2018). Based on these findings, researchers tried to apply the lotus effect mechanism to coating systems in various ways. The hydrophobic coating offers the benefit of being water-repellent since it can effectively prevent water from adhering to the metal surface. This can minimize corrosion problems because water is a corrosion medium. The hydrophobic coating on a metal surface ensures that water droplets roll off without leaving any marks, thereby maintaining a clean appearance. This makes the metal surface always look clean. Furthermore, hydrophobic coating can reduce friction between the fluid and the metal surface. This can increase work efficiency in equipment that uses fluids. When hydrophobic coatings are used on metal coatings, they can effectively reduce corrosion issues, enhance job productivity, and lower maintenance expenses (Hasanah, 2018).

Silica is an oxide material with potential high-tech applications, including metal coating. Silica particles with small to nanoscale sizes offer several benefits, including chemical resistance, low density, heat resistance, robust atomic bonding, and

high adhesion (Sinaga, 2019). Silica is a material that is strong, durable, and environmentally friendly. Silica can serve as a protective layer for metal, shielding it from corrosion, abrasion, and elevated temperatures. The ash from Mount Sinabung has a high concentration of silicon (Si) and can be easily obtained, making it a promising supply of silica for metal coatings (Simatupang & D., 2019; Manurung, 2019). This research aimed to determine the results of mixing the composition of silica and TMCS-xylene on the coating of the coated material to determine the performance of superhydrophobic silica solutions with various composition variations to inhibit the rate of iron corrosion in 15% HCl and 3.5% NaCl solutions and to analyze the effect of sonification (ultrasonically dip coating) on the effectiveness of coating on iron metal in 15% HCl and 3.5% NaCl solutions.

2. MATERIALS AND METHODS

2.1. Materials

The research material was volcanic ash from Mount Sinabung, Kabanjahe Regency, Beras Tepu Village. Test samples included metal plates (Strip Plate), Iron paint (ABC Brand), velvet cloth (Aura Velvet Brand), metal polish (Autosol Brand), and sandpaper. Other supporting materials were NaOH (E-Merck), 37% HCl (E-Merck), NaCl (E-Merck), xylene (E-Merck), trimethylchlorosilane (TMCS), and aqua DM. The equipment was an oven, furnace, 200-mesh sieve, laser cutting, analytical scales, and grinding equipment (mortar). The analytical instruments used were X-ray diffraction (XRD) (D8 Advance Eco (Bruker), Bragg-Bentano Diffraction), and Scanning Electron Microscopy (SEM) (Zeiss type EPOMH 10 Zss).

2.2. Extraction of silica from the volcanic ash of Mount Sinabung

Silica (SiO₂) extraction from Sinabung volcanic ash was carried out using the sol-gel method. First, the volcanic ash was sieved with 200 mesh and weighed 20 grams. The ash was soaked in 12 M HCl for 24 hours to remove metal ions. After that, the ash was neutralized with distilled water and dried in an oven at 120°C for 6 hours. Second, dry volcanic ash was destroyed by dissolving it in 8 M NaOH. The solution was boiled while stirring until it thickened. After almost drying, the solution was put into the furnace at 750°C for 3 hours. After cooling, the solution was added with 200 mL of distilled water and left for 12 hours. Third, the mixture was filtered, and 20 mL of the filtered solution was taken. The solution was dripped with 3 M HCl while stirring with a magnetic stirrer until the pH approached 7. A white silica precipitate was formed. The precipitate was filtered and washed with distilled water. The precipitate was dried in an oven at 120°C for ± 3 hours (Bariyah, 2020).

2.3. Preparation of superhydrophobic silica materials

Silica with various concentrations (0.6 g, 1.2 g, and 1.8 g) was dispersed in 10 mL of 4M NaOH while heated at 50°C (1 hour) until a completely dissolved Na₂SiO₃ solution was obtained. Next, TMCS 13% (v/v) was added, then xylene solvent (v/v) slowly into the mixture and heated at 50°C (2 hours) until a homogeneous solution was obtained (Silviana, 2021). The next stage was to apply a layer of material on the iron surface. Each superhydrophobic silica solution of various concentrations was added to the paint with a paint volume of 10 mL for each composition variation and dispersed for 15 minutes using Ultrasonic Homogenizers (OMNI SONIC Ruptor 400 with a wavelength of 40 kHz, power 400 watts, amplitude 40%) until a homogeneous mixture was obtained.

2.4. Coating 'Ultrasonically Dip Coating'

The sample used was an iron metal plate measuring 2×2 cm and 3 mm (0.3 cm) thick, which was prepared with 1500 grit to flatten and remove scratches on the sample surface. The coating process was carried out using a simple dip coating method (Ultrasonically Dip Coating) for 15 minutes with a frequency of 40 kHz, power 40% in an Ultrasonic Water Bath — an ultrasonic bath (BANDELIN BactoSonic Type BS 14.2, 800 W, 40 kHz), and drying for 24 hours at room temperature (Haser, 2018).

2.5. Corrosion testing

Iron corrosion testing was carried out by immersing an iron plate that had been coated with superhydrophobic silica material in the test solution for 96 hours. The test solution was a corrosive solution, namely a 15% HCl solution and a 3.5% NaCl solution. The 15% HCl acid solution represents an acidic environment, while the 3.5% NaCl solution represents a salty environment which causes corrosion.

3. RESULTS AND DISCUSSION

3.1. Silica (sio₂) extraction results from mount Sinabung volcanic ash

The silica extraction process from Sinabung mountain ash was carried out in three stages. First, sodium silicate (Na₂SiO₃) from Sinabung mountain ash was prepared using NaOH. The dehydration process will occur in this condition, and the second OH⁻ will bond with hydrogen to form water. The two Na⁺ ions will balance the negative charge formed and interact with the SiO₃²⁻ ion to form Na₂SiO₃ in Equation 3.1. Second was the preparation of silicic acid and Si(OH)₄. At this stage, the sodium silicate solution was reacted with a strong acid (HCl) until a precipitate (silica gel) was formed, which was still mixed with NaCl. In this reaction, the hydroxyl group

(OH) in sodium silicate was replaced by a hydrogen group (H^+). The released hydroxyl groups then react with water to form silicic acid. The silicic acid formed was then hydrated to form silica gel in the chemical reaction Equations 3.2 and 3.3. Third was the preparation of SiO_2 using the $Si(OH)_4$ silica gel drying process (Bariyah, 2020). The final stage was to evaporate the water with an oven. The final result of this drying process was white silica powder, as in Figure 1, with the following formation reaction:

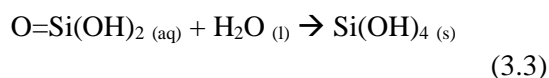
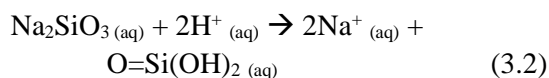
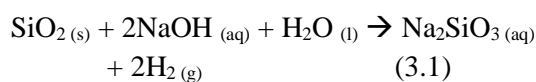


Figure 1. Silica powder extracted from volcanic ash from Mount Sinabung.

Silica gel is a material that has a unique texture and diverse properties. The texture can be hydrogel, xerogel, or airgel, depending on the manufacturing process. The result of this silica extraction is silica xerogel, which has a hard and brittle texture. Silica gel has inert, hydrophobic, and transparent properties (Silviana, 2021). Its inert nature means it does not easily react with other chemicals. Its hydrophobic nature means it does not absorb water easily. Its transparent nature makes it usable for applications that require transparent materials. Silica gel also has other beneficial properties, such as high mechanical strength and thermal stability, and does not expand in

organic solvents (Dirna, 2020). Silica gel is also stable towards hydrogen except fluorine and inert towards all acids except HF. The quality of silica gel is determined by various factors, namely internal structure, particle size, porosity, surface area, resistance, and polarity. Silica gel has several weaknesses: the active site is only siloxane and silanol. This silanol group has low acidity, in addition to having a weak donor atom. However, siloxane and silanol groups are also advantageous because they allow modification (Suchithra, 2012). Silica gel can be modified to improve its properties and be used for wider applications.

3.2. Ultrasonically dip coating of iron plates

Using the Ultrasonically Dip Coating technology, the iron plate's surface was coated with a superhydrophobic silica material. The process involved different versions, including a blank coating without inhibitors labeled as C1/C2 and a coating with superhydrophobic silica material (SS). The variations were determined by the amount of silica used as a superhydrophobic substance, specifically 0.6 g, 1.2 g, and 1.8 g for every 10 mL of paint. Variations in material composition were labeled: SS1/SS4 (0.6:10) g/mL, SS2/SS5 (1.2:10) g/mL, SS3/SS6 (1.8:10) g/mL, each of which represents the test in a corrosive solution of 15% HCl/3.5% NaCl. The documentation for the iron plate that has been coated after drying for 24 hours is presented in Figure 2. The iron plate's surface, solely covered with paint, has greater shine. Conversely, the surface of the iron plate, which is covered with a superhydrophobic silica substance, appears rougher. This is because of the presence of silica particles. In addition, the ultrasonically superhydrophobic silica coating (SS1) findings demonstrate that the superhydrophobic silica material forms a thin layer that tightly and densely adheres to

the iron plate sample's surface, effectively filling any gaps. This coating technique allows the superhydrophobic silica material to conform to the shape of the substrate surface, resulting in a strong bond between the substrate and the coating material through mechanical interlocking (Farid, 2019).

3.3. XRD and EM analysis of superhydrophobic silica coating on iron plates

a. XRD (X-Ray Diffraction) characterization

X-ray diffraction (XRD) was employed to characterize the crystal structure that developed on the iron plate. X-rays with a

wavelength (λ) were directed at the crystal surface at an angle of 2θ . This XRD characterization used a type D8 Advance Eco diffractometer (Bruker), Bragg-Bentano Diffraction, equipped with Automatic Powder Diffraction software, and used a Cu anod tube with a wavelength of 1.54060 Å. The data obtained from XRD analysis was a diffractogram, a graph of the relationship between intensity (I) spectrum peaks and diffraction angles (2θ). The diffractogram shows the spectrum peaks that appear in the sample. Figure 3 presents the XRD test results of iron plate samples before and after superhydrophobic silica coating in the origin program view.



Figure 2. (a) Iron surface with a blank layer (C), (b) Iron surface with a superhydrophobic silica layer (SS1).

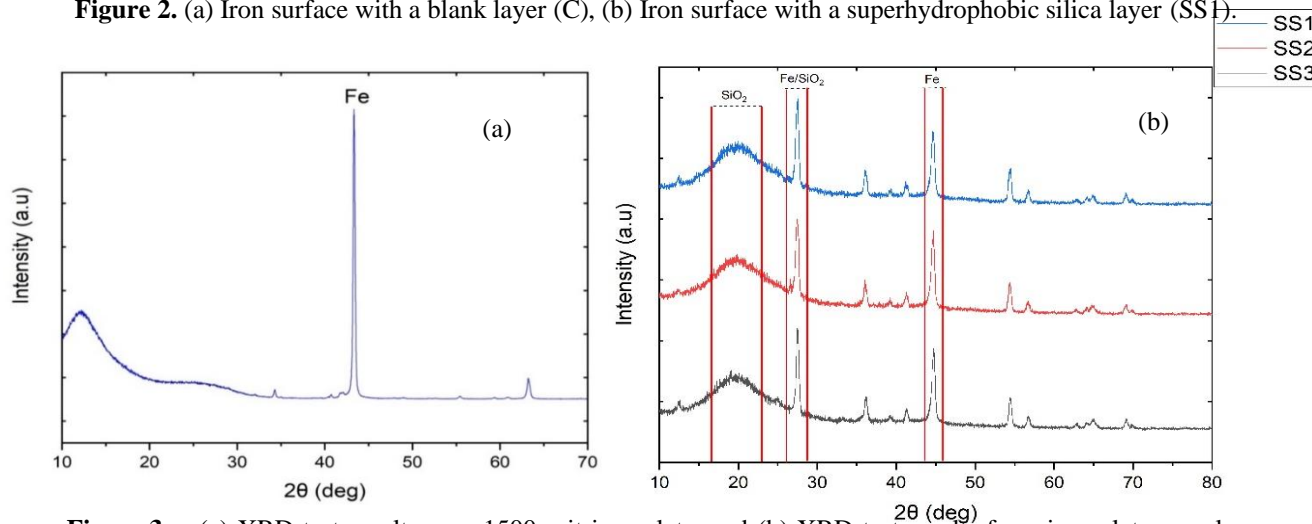


Figure 3. (a) XRD test results on a 1500-grit iron plate, and (b) XRD test results from iron plate samples after superhydrophobic silica coating.

The peak intensity was plotted on the y-axis, and the measured diffraction angle was

plotted on the x-axis, where the diffraction angle was (2θ), which was between $10^\circ - 70^\circ$.

Based on the XRD test results, the highest peak was obtained at the angle $2\theta = 44.081^\circ$ (JCPDS 06-0696), which was the Fe element with an intensity of 10233.5 cps. Specimens that have been coated with superhydrophobic silica material using Ultrasonically Dip Coating are presented in Figure 3(b). Each was labeled according to variations in the addition of silica additives with a combination of paint/silica nanoparticles, namely SS1 (0.6:10) g/mL, SS2 (1.2:10) g/mL, and SS3 (1.8:10) g/mL. Based on the diffractogram graph where the diffraction angle (2θ) was between $10^\circ - 80^\circ$, the XRD pattern for the SiO_2 compound widened at an angle of $2\theta = 20.8^\circ$ (JCPDS 036-1451) which showed an amorphous nature where the pattern was in the shape of a hump. The amorphous nature of the resulting silica gel is beneficial when this material is further modified because it is very reactive. Then, a sharp peak appeared at $2\theta = 26.38^\circ$ (JCPDS 05-0490), the peak of the Fe crystalline phase coated with SiO_2 quarts. The silica phase in the silica paint mixture becomes crystalline due to the influence of

ultrasonication treatment, which, during the cavitation process, will result in bubble collapse, namely the breaking of small waves caused by sound. As a result, a hotspot event will occur, namely very intense local heating, which will cause the crystalline level of silica to increase, resulting in the silica particles becoming more crystallized (Guo, 2016). Then, the appearance of a diffraction peak at $2\theta = 40^\circ - 50^\circ$ indicates that the crystal phase is Fe (JCPDS 06-0696). Based on the description above, variations in the composition of superhydrophobic silica applied to each iron plate do not significantly change its structure. Scientific evidence has demonstrated that sound waves used in the coating process do not alter the chemical characteristics or harm the chemical bonds in iron plates with varying compositions.

Figure 4 presents diffractograms of XRD test results on iron plate samples immersed in 15% HCl and 3.5% NaCl solutions, respectively.

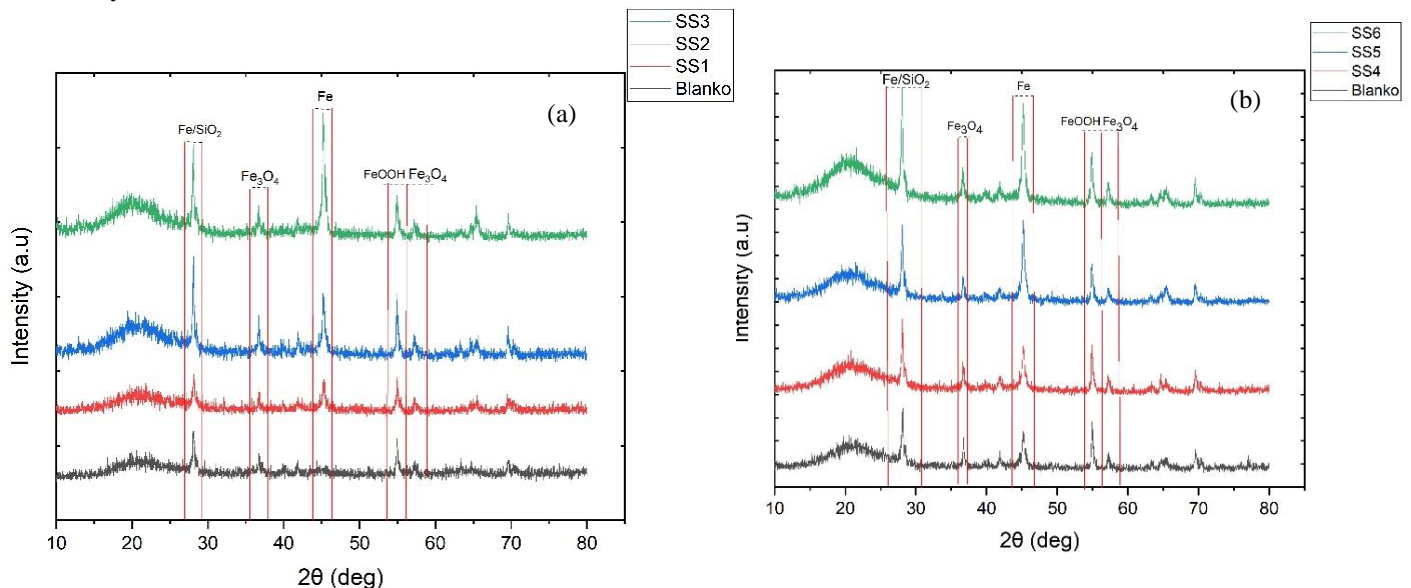


Figure 4. XRD diffractogram of an iron plate in solution, (a) HCl 15% (v/v) and (b) NaCl 3.5% (w/v).

Based on the diffractogram graph in Figure 4, the diffraction angle (2θ) is between $10^\circ -$

80° . The XRD pattern for the amorphous SiO_2 phase compound broadens at an angle of $2\theta =$

20.8° (JCPDS 0.36-1451) with intensity increasing as the composition of the superhydrophobic material is added. In the image above, the diffraction pattern of an iron plate coated with paint (blank) shows the peak of Fe content at $2\theta = 40^\circ - 50^\circ$, the smallest compared to iron plates coated with paint and superhydrophobic silica. This is due to the formation of deposits, which are corrosion products resulting from the interaction between the iron plate and the corrosion environment, namely 15% HCl and 3.5% NaCl solutions. The deposits could be Fe_2O_3 , Fe_3O_4 , and FeOOH , which are corrosion products in the form of a reddish-brown substance that is brittle and porous (Koch, 2017). These deposits would cover the Fe so that the Fe content becomes less. From the composition, the addition of superhydrophobic silica of 0.6 grams, 1.2 grams, and 1.8 grams shows that the Fe peak at $2\theta = 40^\circ - 50^\circ$ is increasing (sharp). This shows that adding superhydrophobic silica mass to the paint will increase the Fe content, as indicated by the higher Fe peak at $2\theta = 40^\circ - 50^\circ$. This indicates that adding silica and surface smoothness greatly influences the corrosion rate. This is in accordance with the theory put forward by Janariah (2022) that the tendency for corrosion is smaller in smooth specimens because the surface is flat. On the iron plate, you can also see the appearance of a new peak that is not too sharp when immersed in a corrosive solution. It can be seen at $2\theta = 60^\circ - 70^\circ$, which is a Fe_2O_3 corrosion product. The appearance of Fe_2O_3 indicates that during the immersion process

with a corrosive solution, the oxidation process of Fe_2O_3 by oxygen occurs (Abdeen, 2020).

b. SEM (Scanning Electron Microscopy) characterization

Scanning Electron Microscopy (SEM) test was carried out to determine the morphology and distribution of sample composition. SEM is utilized to verify the morphological composition of a substance, allowing for the examination of its grain size, surface topography, and structural imperfections (Setyawan D. H., 2014). The iron plate samples included in this study were arranged in a grid pattern of 1500 to homogenize and eliminate any scratches present on the surface of the samples. The results of the 1500 Grid Iron Plate characterization test using SEM referred to Simatupang et al. (2023). Figure 5 (a) shows the presence of lines on the surface of the sample due to the blasting process, which makes the surface of the iron plate sample look smooth and even with a uniform level of roughness so that the sample can be coated with superhydrophobic silica (Simatupang L. S., 2023). SEM testing was conducted on iron plate samples coated with a superhydrophobic silica layer of composition 10:0.6 (SS1). Figure 5(b) shows ultrasonically coating superhydrophobic silica (SS1). The SEM images depict the morphology of several iron plate samples. The coating surface of the iron plate samples appears smooth and devoid of any scratches following the ultrasonic coating process, as opposed to the SEM morphology shown in Figure 5 (a).

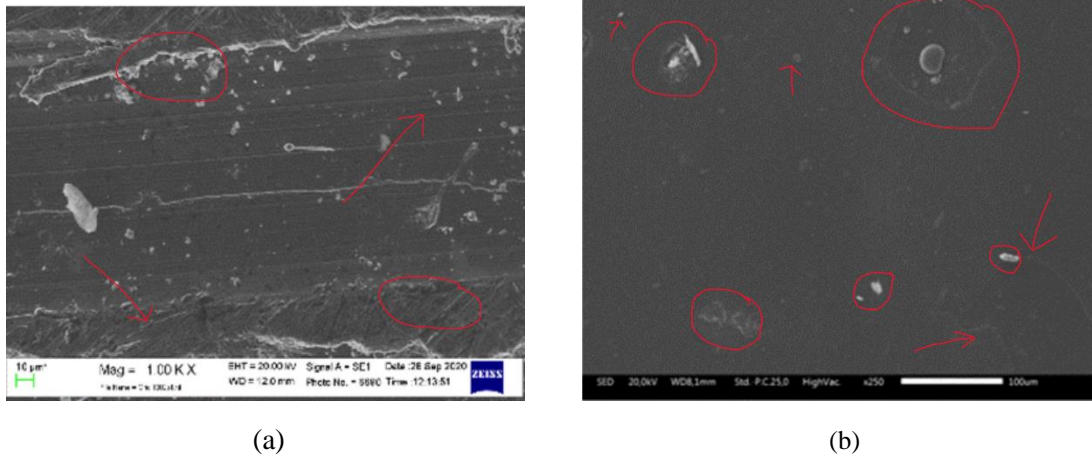


Figure 5. SEM test results of iron plates before corrosion testing (a) Surface of 1500 grit iron plate (Simatupang *et al.*, 2023), and (b) Surface of superhydrophobic silica layer (SS1).

Superhydrophobic silica coating carried out using a simple ultrasonically dip coating method shows that superhydrophobic silica is able to penetrate well into the blasting holes. The ultrasonic coating method enables superhydrophobic silica to conform to the contours of the substrate surface (Marhamah, 2022). The SEM test findings indicate that the interface between the substrate and the superhydrophobic silica layer exhibits a strong connection, allowing for mechanical interlocking between the substrate and the paint/silica nanoparticles.

The process of creating a superhydrophobic silica material protective

layer was achieved by subjecting it to ultrasonic treatment for 15 minutes. The cavitation effect of sound waves will push superhydrophobic silica particles to fill the empty space on the iron plate. SEM characterization shows the morphological appearance of the protective layer of superhydrophobic silica material on the test sample after corrosion testing. The results show that the superhydrophobic silica layer will inhibit the contact of the iron plate with a corrosive environment (Korb, 1992). The results of the SEM characterization test on the surface of the iron plate after coating 10 mL of paint (blank) are presented in **Figure 6**.

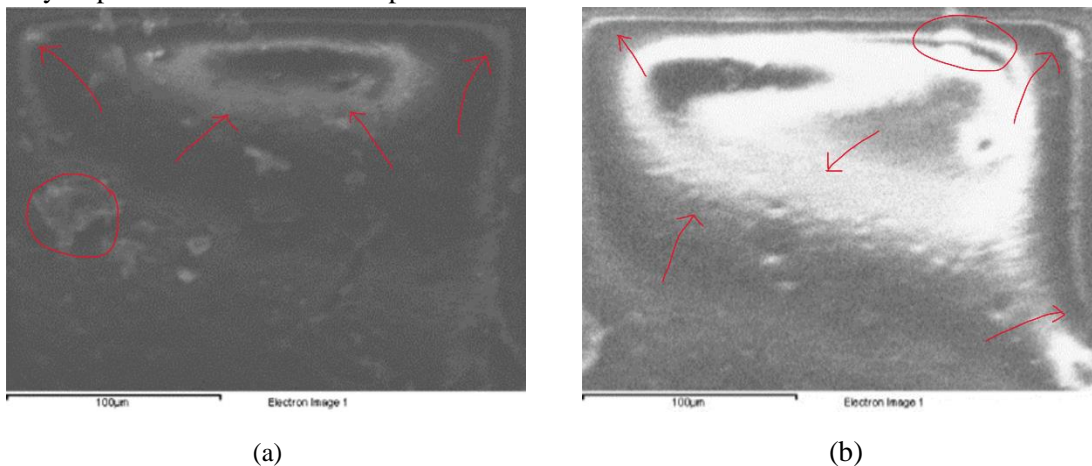
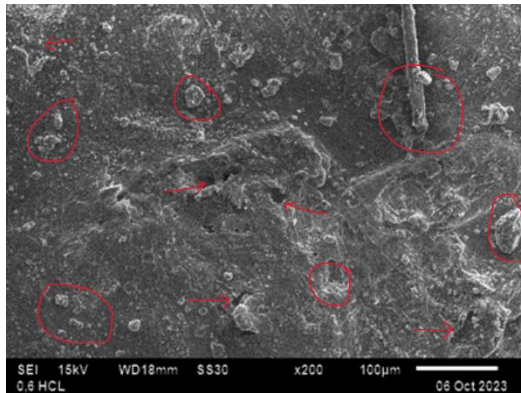


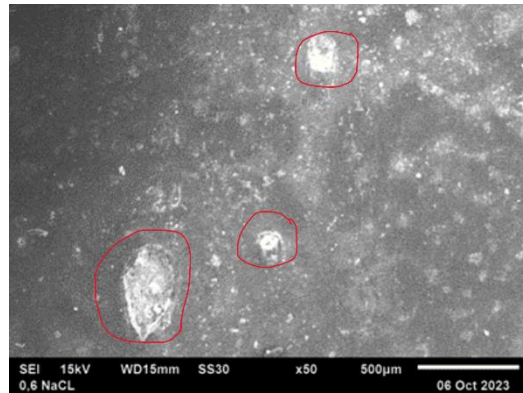
Figure 6. SEM test results of the surface of a blank iron plate after corrosion testing (a) immersed in 15% HCl and (b) immersed in 3.5% NaCl.

Figure 7 shows the results of the SEM characterization test on the surface of the iron plate after it was coated with 0.6 g superhydrophobic silica and 10 mL paint. The results of the SEM characterization test on the surface of the iron plate after being coated with 1.2

g superhydrophobic silica and 10 ml paint are shown in **Figure 8**. **Figure 9** shows the SEM characterization test results on the surface of the iron plate after it was coated with 1.8 g superhydrophobic silica and 10 mL paint.

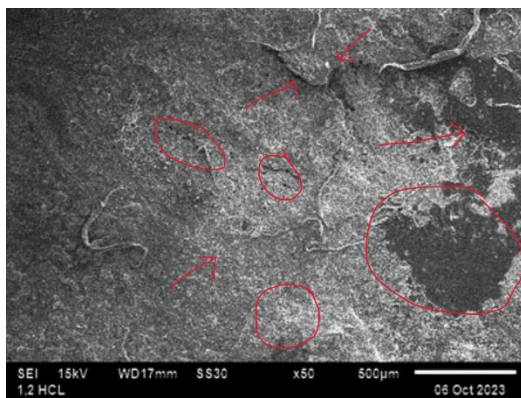


(a)

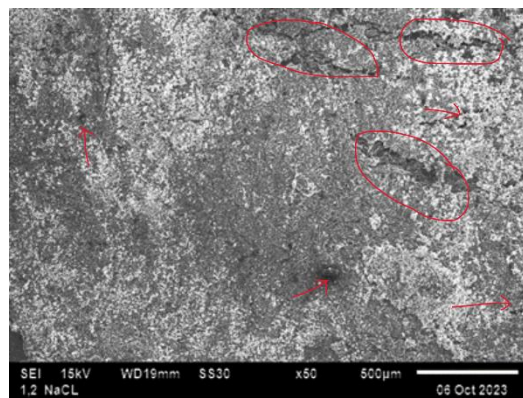


(b)

Figure 7. SEM test results of the surface of an iron plate after corrosion testing (a) sample SS1 in 15% HCl and (b) sample SS4 in NaCl 3.5%.



(a)



(b)

Figure 8. SEM test results of the iron plate surface after corrosion testing (a) SS2 sample in 15% HCl and (b) SS5 sample in 3.5% NaCl.

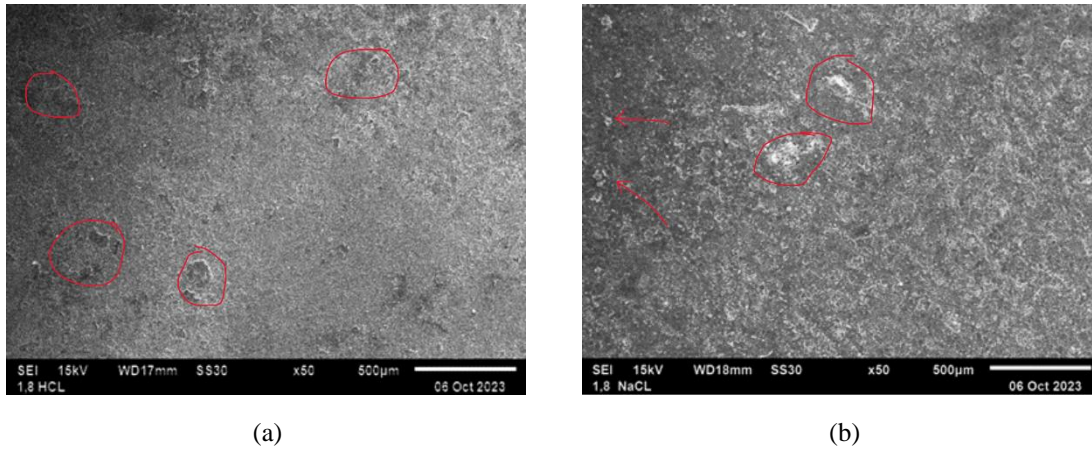


Figure 9. SEM test results of the surface of an iron plate after corrosion testing (a) SS3 sample in 15% HCl and (b) SS6 sample in 3.5% NaCl.

Based on the SEM test results, it can be seen that the layer on the surface of the iron plate only experienced slight cracks, and some small holes appeared, which became a way for Cl⁻ ions to damage the surface of the iron plate. The corrosion caused by the HCl solution is greater than that caused by the NaCl solution due to its highly corrosive nature. The reaction between the iron plate and the environment involves the transfer of electrons, and the metal is oxidized into ions (A. F. 'Adzimaa, 2013). When immersed in a corrosive solution, the difference between an iron plate coated with superhydrophobic silica and paint is clearly visible. Superhydrophobic silica materials can reduce the rate of metal corrosion in a chloride environment by donating silica ions to the iron so that a thin membrane or deposit forms that covers the iron surface. Silica remains stable on the surface; it is proven that silica has stability in acidic media. In other words, to improve the corrosion protection performance of the coating, corrosion inhibitors must be added to the coating system. Superhydrophobic silica mixed with paint can provide maximum protection to iron plates from corrosion attacks by acidic media (Qiao, 2018). The SEM test photo in **Figure 9** shows the distribution of the

white Si element, which is more abundant and evenly distributed as the variation in the composition of the superhydrophobic silica material in the surface layer increases. The wide distribution of the Si element shows the influence of ultrasonic waves in the superhydrophobic silica coating process on the surface of iron plates by filling voids and gaps on the substrate surface, thus creating a strong passive layer between the silica and the substrate.

3.4. Corrosion rate and efficiency of superhydrophobic silica materials

The corrosion rate test assesses the specimen's resistance to rust or corrosion. The corrosion rate was determined by conducting corrosion experiments over a specific duration, during which the alteration in the weight of a material caused by corrosion was measured. Then, the corrosion rate value was calculated. The corrosion rate will provide insight into the effectiveness of applying superhydrophobic silica materials. The corrosion rate (LK) calculation was based on the gravimetric method, specifically the weight loss method. The average corrosion rate using this method was obtained through Equation 3.4 (MF, 2012; A. F. 'Adzimaa, 2013).

$$\text{Corrossion rate (mpy)} = \frac{W \times K}{DA_s T} = \frac{(W_0 - W_1) \times K}{DA_s T} \quad (3.4)$$

Note:

mpy = Corrosion rate in mils per year (mpy)

W = Weight loss (g)

w_0 = Initial sample weight (g)

w_1 = Sample weight after corossion (g)

K = Corrosion rate factor constant 3.45×10^6 (mpy)

D = Specimen density (g/cm^3) for iron metal 7.874 g/cm^3

A_s = Sample surface area (cm^2) of iron plate ($p = 2 \text{ cm}$; $l = 2 \text{ cm}$; $t = 3 \text{ mm} = 0.3 \text{ cm}$)

$$A_s = 2 \cdot (p \times l + p \times t + l \times t)$$

$$A_s = 2 \cdot (2 \times 2 + 2 \times 0.3 + 2 \times 0.3) \text{ cm}$$

$$A_s = 10.4 \text{ cm}^2$$

T = Length of testing time (hours) for 96 hours

Calculating the corrosion rate can be obtained by taking several data such as weight loss, submerged surface area, immersion time, and the density of the metal being tested. By calculating the corrosion rate, the efficiency of the superhydrophobic silica material from each corrosion test solution can be determined. The superhydrophobic efficiency of silica was calculated using Equation 3.5 (Irianty, 2012; A. F. Adzimaa, 2013).

The corrosion activity of the test samples that occurred in an acid solution (HCl 15%) was higher than immersion in a salt solution

(NaCl 3.5%). Acidic solutions are very corrosive. Metals in an acidic medium will easily undergo oxidation because it is an anode reaction. The corrosion rate is influenced by variations in the application of superhydrophobic silica material. The activity of silica as a precursor to additives in paint at micro sizes influences the performance of superhydrophobic silica to inhibit corrosion. The ability of superhydrophobic silica to coat metal surfaces increases due to reduced particle size conditions. This gives the product different properties that can improve its quality and activity.

$$\text{Efficiency (\%)} = \frac{LK_0 - LK_1}{LK_0} \times 100\% \quad (3.5)$$

Note:

LK_0 = Non-additive corrosion rate (mpy)

LK_1 = Additive corrosion rate (mpy)

Table 1. Corrosion Rate and Efficiency of superhydrophobic silica materials

No	Material	Corrosion Rate (mpy)		Efficiency (%)	
		HCl 15%	NaCl 3,5%	HCl 15%	NaCl 3,5%
1	Paint	388.82	21.06	-	-
2	SS1 (0.6:10)	186.51	3.94	52.03	81.25
3	SS2 (1.2:10)	96.54	2.63	75.16	87.50
4	SS3 (1.8:10)	64.51	1.31	83.40	93.75

* Description: C: Paint 10 mL (Blank); SS: Superhydrophobic Silica

The iron plate coated alone with paint (C1-C2) exhibited a higher corrosion rate in comparison to the iron plate coated with superhydrophobic silica (SS1-SS3). Thus, there is an influence of variations in silica composition on the performance of paint coated on an iron surface in a corrosive solution of 15% (v/v) HCl (A) and 3.5% (w/v) NaCl (B), as shown in **Figures 10** and **Figure 11**. As the amount of silica additive increases, the corrosion rate on the iron plate decreases. This relationship is inversely related to the inhibitor efficiency, as stated by Koch (2017) and Janariah (2022), and is directly proportional to the corrosion rate value. The SEM test findings confirm that the superhydrophobic silica layer, applied to the

iron plate samples by ultrasonically dip coating, effectively penetrates the substrate layer. This coating technique employs the cavitation phenomenon generated by ultrasonic waves in a liquid medium. The waves propel the paint/silica nanoparticles into the cavities formed by blasting, conforming to the shape of the substrate surface and forming a protective layer. Ultrasonic wave irradiation improves the efficiency of filling hard-to-reach cavities on the substrate with superhydrophobic silica. This increases the total surface area and creates a strong bond between the substrate and the superhydrophobic silica, enhancing the adhesion strength of the layer during electrochemical reactions.

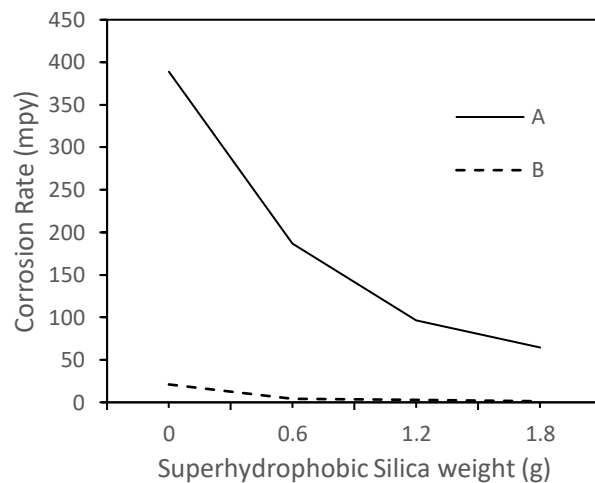


Figure 10. Corrosion Rate of the iron plate for various superhydrophobic silica compositions.

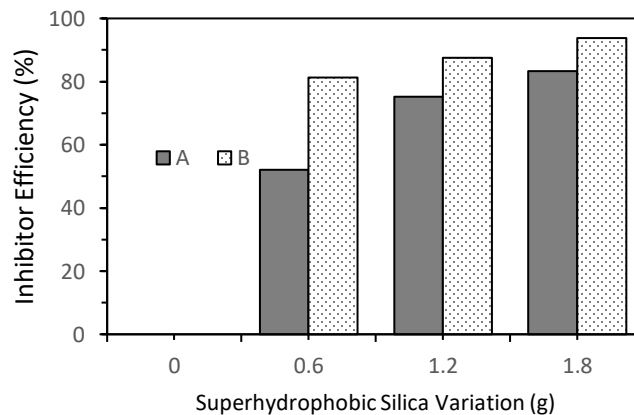


Figure 11. Inhibitor efficiency for various superhydrophobic silica compositions.

4. CONCLUSIONS

There is an influence of sonification (ultrasonically dip coating) and variations in the composition of superhydrophobic silica on the performance of ultrasonic superhydrophobic silica coating on the iron surface against corrosive solutions of 15% HCl and 3.5% NaCl. The most optimum conditions resulting in the lowest corrosion rate for each solution were seen for sample SS3, with a corrosion rate of 64.51 mpy in a 15% HCl (v/v) solution, and for sample SS6, with a corrosion rate of 1.31 mpy in a 3.5% NaCl (w/v) solution. The maximum level of inhibitor effectiveness was observed in the SS3 sample, with an efficiency of 83.40%, when exposed to a 15% HCl (v/v) solution. Similarly, the SS6 sample exhibited the highest inhibitor efficiency of 93.75% when exposed to a 3.5% NaCl (w/v) solution. Ultrasonically coated superhydrophobic silica material could protect against iron corrosion in HCl and NaCl acid solutions. Adding superhydrophobic silica to paint could improve the coating's performance in protecting iron from corrosion. Therefore, superhydrophobic silica material is quite suitable as an additive for iron coatings to provide protection against corrosion. Based on the SEM test results, increasing the concentration of superhydrophobic silica in the paint mixture will form a thicker and more uniform layer. Additionally, this leads to a reduction in the corrosion rate.

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LIST OF REFERENCES

- A. F. 'Adzima, D. R. (2013). Sintesis Natrium Silikat dari Lumpur Lapindo sebagai Inhibitor Korosi [Synthesis of Sodium Silicate from Lapindo Mud as a Corrosion Inhibitor]. *JURNAL TEKNIK POMITS*, 2(2), 384-389. In Indonesian Language.
- Abdeen, D. H. (2020). Corrosion Behaviour of 316L Stainless Steel in CNTs-Water Nanofluid: Effect of Temperature. *MDPI*, 19-27 14(1).
- Affandi, S. A. (2020). Analisa Korosi Atmosferik Baja Karbon Rendah Di Kecamatan Medan Belawan [Analysis of Atmospheric Corrosion of Low Carbon Steel in Medan Belawan District]. *Multitek Indonesia: Jurnal Ilmiah*, 20(01), 80-88. In Indonesian Language.
- Amri, I. A. (2020). Pengolahan limbah cair industri pelapisan logam dengan proses elektrokoagulasi secara kontinyu [Processing liquid waste from the metal plating industry using a continuous electrocoagulation process]. *Chempublish Journal*, 3(01), 15-26. In Indonesian Language.
- Bariyah, S. &. (2020). Activation of Sinabung Mount Volcanic Ash using Various Mineral Acids. *Indonesian Journal of Chemical Science and Technology (IJCST)*, 4(1), 1-4.
- Barthlott, &. N. (1997). *Purity of the sacred lotus, or escape from contamination in biological surfaces (Vol. 39)*. London: Planta.
- Dirna, F. C. (2020). Nanosilica synthesis from betung bamboo sticks and leaves by

- ultrasonication. *Nanotechnology, Science and Applications*, 131-136.
- Farid, R. R. (2019). Enhanced corrosion protection of aluminum by ultrasonically dip coated sodium silicate thin films. *Surface and Coatings Technology*, 355-361.
- Guo, J. G. (2016). Effects of ultrasonic treatment during acid hydrolysis on the yield, particle size and structure of cellulose nanocrystals. *Carbohydrate polymers*, 135, 248-255.
- Hasanah, I. (2018). *Studi Lapisan Anti Air Pe/Sio2 Pada Media Kaca [Study of Pe/Sio2 Waterproof Coating on Glass Media]*. Surabaya: Institut Teknologi Sepuluh Nopember. In Indonesian Language.
- Haser, D. (2018). Ultrasonic Dip Coating of Fibre Ropes with Large Diameters. *Narrow and Smart Textiles*, 21(03), 159-166.
- Ilham, S. (2019). *Studi Pembuatan Lapisan Hidrofobik Berbasis Trimetilchlorosilan pada Preparat Kaca [Study on the Preparation of Trimethylchlorosilane Based Hydrophobic Coatings on Glass Preparations]*. Malang: Universitas Brawijaya. In Indonesian Language.
- Irianty, R. S. (2012). Pengaruh konsentrasi inhibitor ekstrak Daun Gambir dengan pelarut Etanol-Air terhadap laju korosi besi pada air laut [Effect of inhibitor concentration of Gambir Leaf extract with Ethanol-Water solvent on the rate of iron corrosion in seawater]. *Jurnal Riset Kimia*, 5(2), 165-174. In Indonesian Language.
- Janariah, J. O. (2022). Studi Pendahuluan Pembentukan Struktur Komposit Perak Silika (Ag/SiO₂) Berbasis Sekam Padi [Preliminary Study of the Formation of Silver Silica (Ag/SiO₂) Composite Structure Based on Rice Husk]. *Jurnal Teori dan Aplikasi Fisika*, 10(1), 25-30. In Indonesian Language.
- Koch, G. (2017). Part 1 - Trends in oil and gas corrosion research and technologies. In *Cost of corrosion* (pp. 3-30). United Kingdom: Woodhead Publishing, Elsevier.
- Korb, J. L. (1992). *Metals Handbook Volume 13: Corrosion (4th ed.)*. Germany: Philadelphia.
- Mahadik, S. A. (2013). Durability and restoring of superhydrophobic properties in silica-based coatings. *Journal of colloid and interface science*, 405, 462-468.
- Manurung, C. J. (2019). Kajian Dampak Sebaran Abu Vulkanik Terhadap Kesehatan Studi Kasus Gunung Sinabung [Study of the Impact of Volcanic Ash Distribution on Health, Case Study of Mount Sinabung]. *Jurnal Dialog Penanggulangan Bencana*, 7(1), 1-16. In Indonesian Language.
- Marhamah, L. &. (2022). Sintesis Lapisan Hidrofobik Komposit ZnO/PSSiO₂ untuk Aplikasi Self-cleaning Material [Synthesis of ZnO/TiO₂ Composite Hydrophobic Layers for Self-cleaning Material Applications]. *Jurnal Fisika Unand*, 10(1), 508-514. In Indonesian Language.
- MF, F. G. (2012). Pengaruh Kekasaran Permukaan Terhadap Porositas Hasil Hot Dipped Galvanizing (HDG) [The Effect of Surface Roughness on the Porosity of Hot Dipped Galvanizing (HDG) Results]. *Jurnal Rekayasa Mesin*, 3(1), 283-292. In Indonesian Language.
- Miranda. (2020). Analisis Laju Korosi Pada Logam Melalui Proses Dipcoating Larutan Elektrolit [Analysis of Corrosion Rates in Metals Through the Electrolyte Solution Dip

- Coating Process]. *Jurnal Hadron*, 2(1), 29-33. In Indonesian Language.
- Priyotomo, G. (2020). Deteksi Proses Korosi Pada Baja Dengan Menggunakan Lapisan Akrilik Termodifikasi Phenolphthalein [Detection of Corrosion Processes in Steel Using Phenolphthalein Modified Acrylic Coating]. *Jurnal Teknik Mesin*, 3(2), 55-62. In Indonesian Language.
- Putri, T. A. (2018). Sintesis Lapisan Hydrophobic Nanokomposit Mangan Oksida/Polystyrene (Mno2/Ps) Untuk Aplikasi Self Cleaning [Synthesis of Manganese Oxide/Polystyrene (Mno2/Ps) Nanocomposite Hydrophobic Coating for Self Cleaning Applications]. *Pillar of Physics*, 6(1), 1-8. In Indonesian Language.
- Qiao, J. H. (2018). A super-hard superhydrophobic Fe-based amorphous alloy coating. *Surface and Coatings Technology*, 11(02), 286-291.
- Setyawan, D. H. (2014). Pencegahan Korosi Dengan Menggunakan Inhibitor Natrium Silikat (Na_2SiO_3) Hasil Sintetis Dari Lumpur Lapindo Pada Baja Tulangan Beton [Corrosion Prevention Using Sodium Silicate Inhibitor (Na_2SiO_3) Synthesized From Lapindo Mud in Concrete Reinforcing Steel]. Surabaya: Insitut Teknologi Sepuluh Nopember. In Indonesian Language.
- Setyawan, Y. &. (2015). PEG-templated mesoporous silicas using silicate precursor and their applications in desiccant dehumidification cooling systems. *Microporous and Mesoporous Materials*, 22(3), 95-100. In Indonesian Language.
- Silviana, S. D. (2021). Superhydrophobic coating derived from geothermal silica to enhance material durability of bamboo using hexadimethylsilazane (HMDS) and trimethylchlorosilane (TMCS). *Materials*, 530.
- Simatupang, &. D. (2019). The preparation and characterization of Sinabung volcanic ash as silica based adsorbent. *Jurnal Pendidikan Kimia*, 159-163.
- Simatupang, L. S. (2023). Kinerja Ratio Silika-Cat Dengan Metode Dipcoating Pada Permukaan Logam Untuk Penghambat Laju Korosi [Performance of the Silica-Paint Ratio Using the Dip Coating Method on Metal Surfaces to Inhibit Corrosion Rates]. *Journal of Science and Applicative Technology*, 7(1), 43-51. In Indonesian Language.
- Sinaga, N. M. (2019). Dampak Erupsi Gunung Sinabung Terhadap Produksi Dan Harga Cabai Merah (*Capsicum annumL.*) (Desa: Beganding, Kecamatan Simpang Empat, Kab. Karo) [The Impact of the Eruption of Mount Sinabung on the Production and Price of Red Chilies (*Capsicum annumL.*) (Village: Beganding, Simpang Empat District, Karo Regency)]. *Jurnal Darma*, 37(10), 949-959. In Indonesian Language.
- Suchithra, P. S. (2012). Mesoporous organic-inorganic hybrid aerogels through ultrasonic assisted sol-gel intercalation of silica-PEG in bentonite for effective removal of dyes, volatile organic pollutants and petroleum products from aqueous solution. *Chemical engineering Journal*, 589-600.