Superhydrophobic coating based on silica derived from bagasse modified with vinyltriethoxysilane and copper (Cu) as antibacterial agent

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Abstract. Prevention of material degradation can be achieved through the coating. Surface coating is an economically advantageous method in producing desired characteristics and auxiliary aesthetics of surface material. Modern coating processes usually use nanomaterial technology made from silica. Silica can be taken from various sources, such as bagasse waste. Bagasse has high silica content up to 88%. Coating material from silica has good adhesion, good protective properties that allow it to withstand the diffusion of water vapor, ions, and oxygen to metal surfaces. Modified silica can be used to produce superhydrophobic surfaces. The addition of vinyl groups to silica can improve the elastic and mechanical properties without much variation in density or thermal conductivity. The addition of vinyltriethoxysilane can create uniform distribution of nanoparticles. Modification of silica can be done to procure anti-bacterial properties. Copper (Cu) is often used as a high activity anti-bacterial with a fairly affordable cost. With the supplementary anti-bacterial properties, material damages attributed to bacteria may be prevented or reduced. This review aims to provide an overview of the production of superhydrophobic coatings using different methods, analyze the characteristics of synthesized materials, and choose suitable methods for producing superhydrophobic coatings. This review proposes the fabrication of silica superhydrophobic coating with the sol-gel method modified through the addition of vinyl and Cu as an anti-bacterial. This recommendation is based on the literature study that has been carried out.

1. Introduction
Degradation of materials is a common problem we often face. Degradation of materials can occur due to materials being exposed to ultraviolet light [1], oxidation reactions [2], or others. To prevent material degradation, a coating is typically used. Surface coating is an economical method to produce surface materials with sought-after surface characteristics, such as anti-corrosion, anti-erosion, and wear resistance [3]. Apart from preventing material degradation, coatings are also used to add aesthetics, especially in a non-reactive atmospheric condition or environment. For instance, coatings are used to coat cars [4] and bridges [5], as the varnish on furniture [6], as well as in paints. Coating development has now advanced onto things from anti-icing coatings on aircraft [7], anti-bacterial coatings [8], superhydrophobic coatings [9], to superoleophobic coatings [10]. Modern coating processes usually use nanomaterial technology [11] made from silica. Silica is a very popular material used in the production of nanoparticle coating technology as it is highly available as a natural polymer [12], has unusual glass-
forming capabilities that can prevent crystallization during cooling and high elastic elongation [13]. Silica also has good adsorption and ion exchange properties, high mechanical and thermal stability, and is easily modified with certain chemical compounds to improve its performance [14].

Silica is a very abundant earth material that can be made into materials of various purposes [15]. In nature, silica is hydrophilic, and nano-sized silica particles will be super-hydrophilic and very easily wetted by water [16]. If the particles are completely modified with hydrophobic compounds, the particles will become superhydrophobic. However, if they are partially modified, then, simultaneously, these particles will have areas of superhydrophobicity and superhydrophilicity [16]. Modified silica can be used to produce superhydrophobic surfaces [17]. Silica, especially in Indonesia, carries the potential as a coating material due to its good adhesion and protective properties, which can withstand the diffusion of water vapor, ions, and oxygen in metal surfaces [18]. Silica as a coating material has been developed in many studies, such as that conducted by Ambarwati and Samsiadi (2010) [19], entitled Hydrophobic Coating of Glass with Waterglass-Based Sol-Gel Method. This study concluded that a considerable increase in hydrophobicity can be expected by coating glass with modified silicic acid. Similar findings were presented by Hamidah et al. (2012) [20] through a study entitled Hydrophobic Coating on Glass through the Sol-Gel Method with Waterglass Precursor.

Commercially, silica precursors that are often used include tetraethylorthosilicate (TEOS), sodium silicate, and tetramethyl orthosilicate [21]. In a study conducted by Nakashima et al. (1998) [22], TEOS and silane (SiH4) are known to be toxic compounds and can cause death. Thus, a safer, cheaper, and environmentally friendly silica precursor is needed [23]. Natural silica can be found in many types of plants and agricultural waste such as rice husks [24–26], geothermal waste [27,28,37,38,29–36], rice straws [39,40], bamboo leaf [41,42], corncobs [43,44], as well as bagasse [45–47]. Bagasse is a sugarcane processing waste that is abundant and is often only used as fuel for steam boilers that produce a significant amount of ash [48]. Bagasse ash contains very high levels of silica (SiO2) at around 68.5% [49].

Silica that has been synthesized and modified can be used as a superhydrophobic coating. Superhydrophobic coating made from silica has been developed into anti-fog coating, anti-freeze surface, and anti-bacterial surface [50]. Chemically modified silica can play a role in inhibiting bacterial growth because it has low surface energy and minimal contact with the surface that bacteria adhere to [51]. Anti-bacterial reagents and chemicals can effectively inhibit bacterial growth. They inversely generate bacterial resistance and thus eventually ineffective over time. Alternatively, surfaces coated with a superhydrophobic coating of modified silica with anti-bacterial properties do not produce bacterial resistance, therefore ideal for preventing the spread of infectious bacteria in addition to the self-cleaning and water-resistant properties of these surfaces [52]. One compound that can act as an antibiotic agent is Cu (II) [4,53–56]. In the previous study [57] entitled Superhydrophobic copper in biological liquids: Anti-bacterial activity and microbiologically induced or inhibited corrosion, copper-modified superhydrophobic surface showed germicidal properties through the copper ions that were able to kill precipitated bacterial cells.

2. Literature Review
2.1. Coating
Coating is the process of superimposing a material onto a surface of another material (or the same material). Coating can also be a method used to create a composite material. In general, coating is intended to obtain specific properties from the surface of a material (metal and non-metal) such as:
1. Surface protection from the surrounding environment that can cause corrosion or deterioration (damage)
2. Increase the wear resistance of a surface (decrease the coefficient of friction)
3. Increase the strength of a material
4. Increase the electrical conductivity of the surface of a material
5. Increase surface electrical resistance
6. Improve surface weldability
7. Improve the aesthetic a material
8. Add shape and repair or improve components of a material
There are various types of coating techniques. Their preferential use is based on the specific outcomes of functions desired (size, shape, and metallurgy of the substrate), the adaptability of the coating material to the technique used, the level of adhesion required, as well as the availability and price of the equipment involved [58]. Several common coating methods used include dip coating, spin coating, electrophoretic deposition, and spray coating. Coating is applied to a material known as a substrate.

The dip-coating technique is a coating method where a substrate is dipped and withdrawn vertically from a coating solution at a certain speed. The affixed solution will flow downward due to gravity and subsequently evaporates, accompanied by a condensation reaction, resulting in a solid film layer. However, this method is not suitable for metal plating because it can corrode the metal to be coated. This method has been widely used, especially to obtain uniform layers with a thickness of approximately 100 nm.

Spin coating is a method for depositing a thin layer by first spreading a coating solution onto a substrate. The substrate is then rotated at a constant speed to obtain a thin layer deposition. The spin coating process is carried out using a coater at high speed (rpm) for a certain time. The faster the rotation, the more homogeneous and thinner the thin layer will be. However, this method requires a large amount of energy, requiring more expensive costs to manufacture.

Thermal spray coating is a process in which a material in the form of a metal powder or wire is deposited in a liquid state on a surface that has been previously prepared to form a spray layer. This technique is one of the most widely used techniques for surface engineering and advanced material development. Feed material is fed into a gun, then heats material into a liquid form, later accelerated by air pressure and sprayed onto a substrate. When the liquid particles from the spray hit the surface of the substrate, the particles then experience cooling and form a (lamellar) layer structure. The basic variations of the thermal spray process are the feed material, the heating method, and the method of spraying the material onto the surface of the substrate. The feed material used can be in the form of powder, wire, or bars.

The thermal heating used to melt coating materials consists of electrical and flame heating. When materials are heated, they plastically transform or melt, and with pressurized gas are accelerated and deposited onto the substrate. These particles will hit the substrate, stick onto it, and form a thin layer (splat) that adjust and adhere to the uneven surface of the substrate with other coating particles. Once cooled, a non-homogeneous layer will form, generally, with a degree of porosity and metal oxides. The feed material can be anything that can be melted, including metals, metal compounds, cement oxides, glass, and polymers, which can be introduced in the form of powder, wire, or rod. The bond between the substrate and the coating can be mechanical, chemical, metallurgical bond, or a combination of the three. The coating properties depend on the type of material, the thermal spray process, the parameters applied, and the treatment after the thermal spray coating process [58].

The flame spray is a coating method that uses thermal energy produced by burning gas fuel (mostly acetylene, propane, or hydrogen) and oxygen which can liquefy coating material particles [59]. The working principle of powder flame spray is as follows: in a flame spray torch, chemical energy from the combustion of oxygen gas is used to produce hot flames.

2.2. Sources of Silica as a Base Coating Material

Silica is widely used in industries to make casting, tires, rubber, plastics, glass, cement, concrete, ceramics, sandpaper, sandblast, etc. Silica has special properties such as low density, an extensive surface area, good adhesion, and excellent heat insulation [60]. Silica presents itself as a good coating material since it has good adhesion. These good protective properties allow it to withstand the diffusion of water vapor, ions, and oxygen in a metal surface so that it can protect the metal from corrosion. The synthesis of silica into coatings can be done through several methods such as the sol-gel process method, the gas phase process method, the coprecipitation method, the emulsion method, plasma spraying and foging process method (polymerization of dissolved silica into organosilica) [61]. Silica coatings can be made using the sol-gel method with DEODMS, MTEOS, TEOS, TMCS, and TPOZ as silica precursors. It was found that the highest amount of silica was found in TEOS at 28%. Silica coatings have previously been made by Kalaphaty (2000) [62] with silica sourced from nature, i.e., rice husk waste found to exist at 48% silica. Shim (2015) [44] has also used silica as a coating material with silica obtained from
corn cobs at a silica content of 99.50%. Silica coating can also be manufactured from silica sourced from bagasse. Bagasse is a sugarcane waste that is commonly found unused in the environment. The use of bagasse as the raw material for silica coating has been explored by Usman (2014) [45] with a silica content of 77.28% and Asfadiyah (2014) [63] with a silica content of 88.28%.

Table 1 summarizes the silica sources, researchers, methods, and silica isolation process results previously carried out.

**Table 1.** Silica raw material source, researcher, method, silica isolation products.

| Raw Materials | Reference | Method          | Product                                                                 |
|---------------|-----------|-----------------|-------------------------------------------------------------------------|
| Rice Husk     | [64]      | Chemical treatment | Rice husk silica gel with a surface area of 258 m$^2$/g and a particle size of <5 to > 40 μm |
|               | [65]      | Chemical treatment | Nanosilica powder with 99% purity, 25 nm particle size, 274 m$^2$/g surface area |
|               | [66]      | Thermal treatment  | Porous silica with a surface area of 1018 m$^2$/g and pore diameter of 2.30 nm |
|               | [67]      | Thermal treatment  | The silica obtained was 99.92%                                           |
|               | [68]      | Microbial treatment | The silica obtained was 49.00%                                         |
|               | [69]      | Microbial treatment | Silica with a size of 55-250 nm                                         |
| Rice Straw    | [39]      | Chemical treatment  | Silica with a size of 50-70 nm                                         |
|               | [39]      | Chemical treatment  | Silica with a size of 16-18 nm                                         |
|               | [70]      | Thermal treatment  | Silica nanodisk with a surface area of 509.50 m$^2$/g and pore size of 5.8 nm |
|               | [40]      | Microbial treatment | Silica with a size of 50-80 nm                                          |
| Corn          | [43]      | Chemical treatment  | Amorphous silica with a size of 50 nm                                   |
|               | [44]      | Chemical treatment  | The silica obtained was 99.50%                                         |
| Bagasse       | [46]      | Chemical treatment  | The silica obtained was 71%                                             |
|               | [45]      | Thermal treatment  | The silica obtained was 77.29%                                         |
2.3. Hydrophobicity

In general, wetting and adhesion interaction between water and surface can be classified into two, namely hydrophobic and hydrophilic interactions. Hydrophobic comes from the words "hydro" (water) and "phobia" (dislike), a nature that is not able to absorb and accept water. Hydrophobic substances are substances that cannot dissolve in water but can dissolve in oil. Meanwhile, the word hydrophilic comes from the words "hydro" (water) and "phile" (like), a property that can absorb and interact with water. Hydrophilic substances can be dissolved in water. The solubilities of these materials are derived from their polarity, where water is a polar compound and oil is a non-polar compound. When a substance is mixed with another substance with the same polarity, the substance can mix (dissolve). It also explains why water and oil do not mix as they have different properties (polar & non-polar). Hence, a surface with hydrophilic properties when in contact with water will become wet, whereas a surface with a hydrophobic nature will not.

The hydrophobicity of a material can be measured from the contact angle of a water droplet on the material's surface [71]. The surface's hydrophobic nature can be observed through the surface formed and the water contact angle, where a greater contact angle indicates greater hydrophobicity. Based on the contact angle, a surface is hydrophilic when the contact angle is 10°–90° and is superhydrophilic when ≤10°. Hydrophobic surfaces have contact angles between 90°-150° and surfaces with contact angles ≥150° are superhydrophobic. Surface roughness can induce a greater contact angle on a hydrophobic surface, indicative of the increase in repellence towards the water. Conversely, the rougher a surface is on a hydrophilic surface, the lower the contact angle will be, meaning that larger interaction with water is taking place [72].

The water-repellent nature of surfaces is influenced by two factors, namely the chemical composition of a surface and its roughness. The chemical composition of the surface of a material affects the hydrophobic nature of a surface as water is polar, meaning that for a surface to be hydrophobic it must be non-polar. Apart from the chemical composition, the interaction between water and a surface that results in a reaction can impact the roughness factor. Premised on the law of equilibrium, the rougher the surface, the lesser the amount of surface in contact with water, the more the water is equilibrated. With this interface equilibrium of water, the water can remain in the form of spheres and helps the surface not to be wet [73].

Recently, superhydrophobic surfaces with contact angles (CA) greater than 150° have attracted the attention of many researchers [74]. A superhydrophobic surface can be obtained by modifying micro and/or nano hierarchical structure on a substrate or modifying surface structure with materials that have low surface energy [75]. Low surface energy will reduce the wettability of a solid surface and generate hydrophobic properties [76]. The hydrophobic nature combines both surface properties and roughness where coarser surface morphology can increase the surface hydrophobicity of a material [77], thus forming round water drops that can collect contaminants and roll down a surface. A surface is said to be superhydrophobic if it exhibits a water contact angle of 150-180° [78].

The hydrophobic property offers advantages such as anti-wetting, self-cleaning, as well as reduction of overloading and friction of fluids on a surface. Accordingly, the surface can be modified to develop a superhydrophobic coating. This superhydrophobic surface can be used on objects exposed to the outdoors as said advantages can be assisted by the presence of rainwater. Rainwater will stick onto the surface of objects that are superhydrophobic and form spherical droplets. It helps contaminants that stick onto the object's surface to attach themselves to the rainwater droplets instead and subsequently roll down along with the rainwater, leaving the object clean. Utilization of these superhydrophobic properties can save costs in the maintenance of objects by eliminating the use of cleaners such as detergents that can pollute the environment [79]. Application on glass generates what is called the self-cleaning property. When the glass is exposed to water, the surface of the glass will be brighter and cleaner. The glass will look clean for longer and its maintenance cost will become cheaper [80].

Many studies have been carried out to understand hydrophobic surfaces’ function, structure, and working principles that exhibit a self-cleaning function. Superhydrophobic properties specified with a water contact angle of more than 150 and a low sliding angle comprise the criteria to obtain a good self-cleaning surface [81]. There are many ways to obtain a hydrophobic surface on a non-metallic material, such as that reported by Lathe et al. (2010) [82] on the making of a hydrophobic layer on a glass surface.
using the sol-gel method using MTES and Tetraethoxysilane (TEOS) as precursors. The dihydrophobic glass had a water contact angle of 160° and a slide angle of 3°.

Fei et al. (2014) [83] performed coating on a glass surface with methyltrimethoxysilane (MTMS) precursor through the dissolving of aerogel synthesized by the sol-gel method. They obtained a water contact angle of 161° and a slide angle of 4°. The research proved that short-chain alkylsilili can produce a hydrophobic coating with a self-cleaning function on a glass surface. Meanwhile, according to Dahlan and Pravita (2013) [84], the manufacture of a hydrophobic layer can be done by making a TiO₂ layer with a solution of titanium tetra-chloride (TiCl₄) and isopropyl alcohol, resulting in a hydrophobic TiO₂ surface with an achieved contact angle exceeding 100°.

Figure 1. Superhydrophobic effect [85].

2.4. Modification of Silica with the Vinyl Group
Silica gel is widely used as an adsorbent because it is easy to produce, very inert, hydrophilic, has high thermal and mechanical stability, and relatively does not swell in organic solvents compared to solid organic polymer resin. Though, it too has weaknesses, namely the types of active sites, which are only limited to silanol (-SiOH) and siloxane (Si-O-Si) groups [86]. The existence of this weakness can be overcome using surface modification. Surface modification of silica gel aims to change the chemical composition of a silica surface. Specifically, the modification process targets transform the –Si-OH group to –Si-OM where M represents other species, both simple and complex, apart from H [87].

Modification of functional groups on the surface of silica gel can be done by using the following techniques [87]:
1. Impregnation
   Impregnation describes the consequent physical interactions between a modifier and the solid surface, either by loading of pores of the solid or by adhesive or electrostatic interactions.
2. Formation of covalent bonds
   This technique can be done by the immobilization of silane reagent and the sol-gel process. In the sol-gel process, the reaction is not carried out with silica gel. It is carried out the base material in the formation silica gel, which is commonly called a precursor.

Suitable modifiers for the above process include [86]:
- Mercaptopropytrimethoxysilane (MPTS) to obtain mercapto or –SH groups as a substitute for –Si-OH.
- Aminopropytrimethoxysilane (APTS) to obtain an amino group or –NH₂ as a substitute for –Si-OH.
- Chloropropytrimethoxysilane (CPTS) to obtain -Cl group as a substitute for -Si-OH.
- Modifiers that are not silane reagents, such as 1-Amino-2-hydroxy-4-naphthalenesulfonic acid.
   Modification using this type of reagent requires another silane reagent as an intermediate. The intermediate that is normally used is glycidoxypropyltrimethoxysilane (GPTMS).
   Another modifier that can be used is vinyltriethoxysilane (VTES), which has three hydrolyzed ethoxy groups and one vinyl group attached to silicon [77]. The addition of vinyl groups to silicon can improve elastic and mechanical properties without much variation in density or thermal conductivity [88]. The addition of VTES can also make the distribution of nanoparticles more uniform [88]. Vinyltriethoxy-silane has a structure [89] as shown in figure 2 below.
2.5. Anti-bacterial

Anti-bacterial materials are substances that inhibit or kill bacterial growth [90]. Bacteria generally can cause disease or damage to the material. Anti-bacterial materials derived from inorganic materials are more developed than anti-bacterial materials derived from organic materials because inorganic materials have advantages in terms of safety, good durability, and better heat resistance [91]. According to Fatmawati et al. (2018) [90], inorganic anti-bacterial compounds usually form a composite with metal ions impregnated or superimposed on the carrying molecules. Several studies regarding the addition of anti-bacterial to coatings that have been done previously are presented in the table 2.

Table 2. Studies on the addition of anti-bacterial to coatings.

| Antibacterial material | Results                                                                 | Reference |
|------------------------|-------------------------------------------------------------------------|-----------|
| Gold-plated (Au) TiO$_2$ nanocomposites. | Good anti-bacterial effect (60-100% killing efficiency), but Au is quite expensive. | [92]       |
| Silica sol with the addition of 0.5-2% Cu nanoparticles. | The number of bacteria decreased dramatically (more than 70% for E. coli and 90% for S. aureus bacteria). | [54]       |
| Superhydrophobic xerogel layer synthesized from a mixture of colloidal silica. | Produced a surface that reduced the adhesion of highly pathogenic S. aureus and P. aeruginosa by ~2 fold compared to controls. | [51]       |
| Addition of silver (Ag) to a superhydrophobic coating | In the anti-bacterial activity test, 88% of the bacteria were killed. However, silver is quite expensive and is a little toxic. | [93]       |
| Coating with Siloxane + AM + SiO$_2$ | There were still a small number of microorganism sites and a small number of spores | [9]        |
| Cotton fiber coated with zinc oxide (ZnO) by sol-gel method | Enhanced anti-bacterial activity against different bacterial species, especially K. pneumoniae, the contact angle achieved was 154° at optimal conditions. | [94]       |

Copper (Cu) is often used as a bacterial control agent because it has high anti-bacterial activity and is quite cheap [53,54]. The metal ion released by the Cu (II) oxide carries a positive charge, creating an electrostatic interaction during the reaction. The metal ions are then reduced to metal atoms by thiol groups in enzymes and proteins which then deactivate metabolic processes necessary for cells and their respiration, leading to cell death [90]. In addition to providing intrinsic anti-bacterial properties, the disintegration of Cu nanoparticles by deposition on SiO$_2$ particles simultaneously leads to an increase
in anti-bacterial efficiency on the surface [54]. Based on research conducted by Tania et al. (2014) [91], a combination of Cu (II)/silica with a concentration of 163 ppm was able to inhibit growth and kill E.coli and S.aureus bacteria. Moreover, research conducted by Berendjchi et al. (2011) [54] showed a drastic reduction in the number of E. coli (gram-negative) and S. aureus (gram-positive) bacteria (more than 70% for E. coli and 90% for S. aureus bacteria).

2.6. Superhydrophobic Coating Application

Superhydrophobic surfaces that exhibit extreme water repellency become scientific and industrial interest due to their wide variety of applications, such as oil-water separation, anti-icing, self-cleaning, drug release, reduced drag on flowing fluids, anti-fouling paints for vessels, anti-bacterial adhesion, windshield coatings, architectural coatings, and so on [95]. Inspired by lotus leaves, salvinia, seaweed, and other natural species, various man-made approaches have been taken to mimic these surfaces and create artificial superhydrophobic surfaces.

Table 3. Superhydrophobic surface application.

| Application | Method | Substrate | Superhydrophobic Agent | CA° | Reference |
|-------------|--------|-----------|------------------------|-----|-----------|
| Electrodeposition | Al | Cu-dodecanethiol complex | 156° | [96] |
| Electrochemical | Al | Silane SAM | 117° | [97] |
| High-intensity ultrasound irradiation | Al | Sodium laurate | 163° | [98] |
| In-situ crystallization | Cu | Zirconium phenylphosphonate (ZrPP) | 134 to 151° | [99] |
| Electrochemical | Cu | Poly(N,N0-dimethylaminoethyl methacrylate) (PDMAEMA) | 119° | [100] |
| Simple Immersion Corrosion Resistance | Mg | Cerium Oxide | >142° | [101] |
| Conventional Curing | Iron | Bionic poly-(tetrafluoroethylene)/poly(phenylene sulfide) (PTFE/PPS) | 165° | [102] |
| Electrochemical deposition | Ti | Fluoralkyl silanes (FAS) | 160° | [103] |
| One-step electrochemical: Ultrafast Electrosynthesis | Zn | Hydrophobic polypyrrole (PPy) | 125° | [104] |
| In-situ growth | Zn | Layered double hydroxide (LDH) | 170° | [105] |
| Chemical replacement deposition | Zn | Platinum | 170° | [106] |
| Anti-Fogging Surface | Grafting | Silica | Polyethylene glycol with short perfluorinated end caps (f-PEGs) | >150° | [107,108] |
| Application               | Method                           | Substrate | Superhydrophobic Agent                                                                 | CA°  | Reference |
|---------------------------|----------------------------------|-----------|----------------------------------------------------------------------------------------|------|-----------|
| Anti-Icing Surface        | Dip-coating                      | Al        | Acrylic urethane resin and polytetrafluoroethylene (PTFE) ZrO$_2$ nanopowder-fluoropolymer, 1H,1H,2H,2H-perfluorodecyl-triethoxysilane (FAS-17) or stearic acid (SA) | 150° | [109]     |
|                          | Dip-coating, spraying or spin-coating | Al | ZrO$_2$ nanopowder-fluoropolymer | $>150°$ | [110]     |
| Water and Oil Separation  | Dip-coating, spraying or spin-coating | Al | Fluorinated thiols | 155° dan 165° | [113]     |
|                          | chemical vapor deposition (CVD)   | CNT sponges | Carbon nanotubes (CNTs) N-dodecanethiol dan Cu(SC$_{12}$H$_{25}$)$_2$ Nitric acid dan 1-Hexadecanethiol (HDT) | 156° | [114]     |
|                          | Solution-immersion               | Cu        | N-dodecanoic acid | 151° | [115]     |
|                          | Solution-immersion               | Cu        | Nitric acid dan 1-Hexadecanethiol (HDT) | 153° | [116]     |
| Self-cleaning Surface     | Electrochemical deposition       | Cu        | Fractal alkylketene dimer | 160° | [95]      |
| Drag Reduction            | Dip-coating                      | Glass     | Carbon nanotubes (CNTs) | 174° | [117]     |
|                          | Chemical vapour deposition (CVD)  | Silica   | Carbon nanotubes (CNTs) (fluoroalkyl)silane | 170° | [118]     |
|                          | Spin-coating                     | Al(C$_5$H$_7$O$_2$)$_3$ Polydimethylsiloxane (PDMS) | SH material | 156° | [120]     |

3. Research Methodology
3.1. Silica Based Superhydrophobic Coating Method of Modification
3.1.1. Spray Coating Method. Spray coating is an easy-to-use spray method developed to make a superhydrophobic layer. According to Qian et al. (2018) [121], thermal spraying is versatile and widely used. Thermal spraying has been used on many occasions to produce coatings that are resistant to corrosion, wear, and oxidation, along with other multifunctional purposes. This method provides smooth and economical mass fabrication of coatings on various steel substrates with desired microstructures. After coating, corrosion current density showed a value of more than two orders of magnitude that was smaller, and the water contact angle increased from $\sim32°$ to more than $155°$. Meanwhile, Jianzhong Ma, et al. (2015) [122], with a similar approach, found that the non-spraying product achieved a contact angle of $123.3°$, whereas the one-time spray layer had a $128.9°$ contact angle and the four layers of spray
achieved contact angle of 152.4°. With the increasing number of spraying layers, the contact angle reached 170.3°.

3.1.2. Sol-Gel Method. Sol-gel is one of the most popular methods to apply mineral layers onto surfaces, adorned with benefits such as low processing temperatures, simplicity of engineering, low costs, and simple process control [123]. This method is used to fabricate SHS on various oxides such as silica, alumina and titania-based on the theory of Wenzel and Cassi Baxter. In Mahadik et al.'s research (2013) [124] on using the sol-gel method, a contact angle of 168 ± 2° and a slide angle of 3 ± 1° were achieved. In Altangerel's (2020) study [125], a contact angle of the coated cashmere surface was achieved and remained almost constant at around 150° and only showed a slight decrease (less than 5 °) after 30 minutes, proving the stability of its water repellent property.

3.1.3. Grafting Method. Taijun, et al. (2010) [126] generated a hydrophobic layer on a fabric surface had insufficiently achieved superhydrophobicity due to the weak inter-surface interaction between the hydrophobic layer and the fabric. The branched nanoscale silica with double bonds was grafted covalently to the surface by graft copolymerization, starting radically with trifluoroethylmethacrylate and divinylbenzene to produce the nanostructures. The results showed that a natural hydrophobic chemical composition and micro/nanostructures provided by the cloth and silica synergistically build a superhydrophobic surface, having a water contact angle and a slide angle of 161° and 8°, respectively. Moreover, in Meng, Long-Yue et al.'s research (2014) [127], with the same method, materials consisting of octanol, electrospun silica nanofibers (SNFs), had produced a contact angle of 150.2 °.

3.1.4. Plasma Treatment Method. In the research of Anupriyanka, et al (2002) [128], superhydrophobic materials were used for superhydrophobic PET fabrics for oil/water separation. Superhydrophobic PET fabrics were made by plasma oxygen treatment with DC light discharge. As a result, the PET fabric had superhydrophobic properties with a contact angle of 163°. In Han and Moon's (2015) study [129], superhydrophobic surfaces were made on glass with CH₄ and C₄F₈-based helium with atmospheric pressured plasma, and water wettability was subsequently observed through the contact angle produced. The results showed that the water droplets spread on the untreated glass, which initially exhibited hydrophilic properties. The contact angle was steadily around 85° and 98° after pre-treatment with CH₄ and C₄F₈ plasma. Later, the contact angle had increased to 152°, becoming superhydrophobic after several successive stages of CH₄ and C₄F₈ plasma treatment.

3.2. Silica Extraction

3.2.1 Base Extraction

3.2.1.1 Sugarcane Bagasse Ash Treatment. Sugarcane bagasse is washed and dried in the sun to dry and is followed by charring. The charcoal obtained is then baked for 4 hours at 700 °C, then cooled and mashed.

3.2.1.2 Sodium Silicate Extraction. A total of 10 grams of ash obtained is dissolved in 50 mL of NaOH of various concentrations and stirred for 2 hours at 300 rpm and 80 °C followed by filtration where the filtrate is sodium silicate [130].

Reaction in the base extraction of silica [131]:
\[
\text{SiO}_2(s) + 2 \text{NaOH}(aq) \rightarrow \text{Na}_2\text{SiO}_3(aq) + \text{H}_2\text{O}(l)
\] (1)

The obtained sodium silicate is dissolved in water assisted by stirring to be used in the second stage, which is the preparation of silicic acid slurry, Si(OH)₄. At this stage, the sodium silicate solution is reacted with a strong acid (HCl) to form a precipitate. The reaction that occurs is:
\[
\text{Na}_2\text{SiO}_3 + 2\text{H}_2\text{O} + 2\text{HCl} \rightarrow \text{Si(OH)}_4 + \text{H}_2\text{O} + 2\text{NaCl}
\] (2)

Si(OH)₄ cannot dissolve in strong acids such as HCl, HNO₃, and H₂SO₄, and will precipitate, making it easy to separate by filtration followed by washing to remove NaCl content. This stage is then followed by the preparation of SiO₂ by heating Si(OH)₄. The reaction that occurs is:
\[
\text{Si(OH)}_4 \rightarrow \text{SiO}_2 + 2\text{H}_2\text{O}
\] (3)

The obtained sodium silicate is dissolved in water assisted by stirring to be used in the second stage, which is the preparation of silicic acid slurry, Si(OH)₄. At this stage, the sodium silicate solution is reacted with a strong acid (HCl) to form a precipitate. The reaction that occurs is:
\[
\text{Na}_2\text{SiO}_3 + 2\text{H}_2\text{O} + 2\text{HCl} \rightarrow \text{Si(OH)}_4 + \text{H}_2\text{O} + 2\text{NaCl}
\] (2)

Si(OH)₄ cannot dissolve in strong acids such as HCl, HNO₃, and H₂SO₄, and will precipitate, making it easy to separate by filtration followed by washing to remove NaCl content. This stage is then followed by the preparation of SiO₂ by heating Si(OH)₄. The reaction that occurs is:
\[
\text{Si(OH)}_4 \rightarrow \text{SiO}_2 + 2\text{H}_2\text{O}
\] (3)
3.2.2 Coprecipitation. The coprecipitation method synthesizes inorganic compounds based on the deposition of more than one substance together when they pass through their saturation point. Coprecipitation is a promising method because the process uses low temperatures, thus requiring a shorter time of around ± 12 hours. Some of the most commonly used substances or precipitating agents in coprecipitation are hydroxides, carbonates, sulfates, and oxalates [132]. Accordingly, this method is the simplest and easiest method to execute. In addition, the coprecipitation process uses easily available tools and materials, meaning the synthesis process can be carried out flexibly [133]. The stages of the coprecipitation method are as follows: Sand sample is immersed in 10 M HCl for 12 hours to dissolve impurities in the sample. The sample is then washed with distilled water to purify it again, followed by drying in the oven. It is then reacted with NaOH and filtered with filter paper. The solution that passes through the filter is titrated gradually with HCl until a final pH. The result of the titration is washed with distilled water up to five times to remove NaCl. After that, it is oven-dried at a temperature of 80 °C for 5 hours. Once the water content is lost, milling is carried out with a mortar to obtain silica powder [61].

3.2.3 Solid-Liquid Extraction. Extraction of silica from rice husk ash can be carried out by a solid-liquid extraction process using an alkaline solution as a solvent. Silica contained in rice husk ash can be taken by dissolving it in an alkaline solution. According to previous research [134], the reaction that occurs between SiO2 contained in rice husk ash and an alkaline solution, in this case the KOH solution, is as follows:

$$\text{SiO}_2 + 2\text{KOH} \rightarrow \text{K}_2\text{SiO}_3 + \text{H}_2\text{O}$$  \hfill (4)

The silica compound that is formed is still in the form of a potassium silicate solution. Hence, the solution is added with 1 N HCl, which binds potassium and produces SiO2. The reaction that occurs is as follows [135]:

$$\text{K}_2\text{SiO}_3 + \text{HCl} \rightarrow \text{SiO}_2 + \text{KCl} + \text{H}_2\text{O}$$  \hfill (5)

3.3 Addition of Antibacterial Cu (II)

Irnaawati et al (2010) [136] conducted a research using copper (Cu) combined with zeolite as an anti-bacterial material. The type of bacteria tested was S. mutans. Cu metal was used as an anti-bacterial because Cu ions have high anti-fungal properties, good chemical stability, and is relatively cheap. The results obtained from the ANOVA test showed that the Cu concentration in Cu-zeolite had a significant effect on the translucency zone of S. mutans. Cu zeolite would release Cu cations little by little and interact with the negatively charged bacterial cell membrane resulting in damage to the cell wall. This study shows that the higher the concentration of anti-bacterial substances, the more bacteria will die, indicative of stronger anti-bacterial properties.

A research was conducted by Chasanah (2015) [137] involving the use of Cu (II) - N-Benzylidine schiff base complexes against E. coli. The schiff base compounds were formed from orthohydroxy benzaldehyde and 4,4-diamino diphenyl ether. The complexes made from the schiff base reaction were formed in combination with the Cu metal. The schiff base compounds and their complex were observed for their anti-bacterial properties, and their strength and anti-bacterial properties were compared. The metal chosen for the complex formation was Cu metal as it is highly available and relatively low in price. The Schiff base compounds that had been formed were successfully complexed with the Cu metal. Both the schiff base compounds and their complex compounds had inhibitory power against the growth of E. coli bacteria. The inhibition of bacterial growth by complex compounds was greater than the resistance provided by the Schiff base compounds.

Tania et al (2014) [91] also conducted research involving the addition of Cu (II) to silica as an anti-bacterial agent. The results obtained were Cu (II)/silica with a concentration of 163 ppm which was able to kill E. Coli and S. aureus from their initial concentration of 1.5 x 106 CFU/mL to 0 CFU/mL with a contact time of 2 hours. Furthermore, silica with the same concentration showed no anti-bacterial effect against E. Coli or S. aureus. From this study, it can be concluded that the addition of anti-bacterial Cu can increase anti-bacterial power.
3.4. Application of Silica Nanoparticles Modified with Vinyl

Several types of silane compounds have been used to modify silica nanoparticles, namely octyltrithoxysilane (OTES), polymethylhydroxylosan (PMHS), tetrathoxysilane (TEOS), methyltrimethoxysilane (MTMS), and hexadecyltrimethoxysilane (HDTMS) (Rohaeti and Zulaikha, 2017). Yuelei Pan et al. (2017) conducted research using silica aerogel made through hydrolysis and water glass condensation with MTMS co-precursors using HCl and NH₂OH catalysts followed by FD. It was found that MTMS volume increased with larger pore volume and pore diameter, but the specific area decreased drastically. Meanwhile, Shuo Hao Li (2016), who conducted a study using flexible silicate aerogel/xerogel synthesized from MTMS and co-precursor dimethyldimethoxysilane (DMDMS), prepared superhydrophobic silicate xerogel by optimizing the ratio of the two silicon precursors (MTMS and DMDMS). The material was used to capture nitrosamines in tobacco extract solutions. The MTMS/DMDMS molar ratio significantly affected the morphology of superhydrophobic silicate xerogels. Moreover, the absence of DMDMS in the synthesis results in a sand-like sample. Thus, the use of MTMS must be accompanied by DMDMS for maximum results. Similarly, the present study used vinyltriethoxysilane to modify the silica nanoparticles in the superhydrophobic coating process.

Previous research [138] has shown silica nanoparticles modified with VTES (vinyltriethoxysilane) were added on superhydrophobic surfaces on a wood substrate. The result of this experiment was that the contact angle of the wood surface became 154°. The addition of VTES also contributed to the prevention of aggregation of silica nanoparticles and had a function in reducing surface energy. From this, it can be concluded that adding vinyl groups can increase the surface contact angle.

4. Discussion

4.1 Silica Content in Sugarcane Bagasse

As one of the sources of silica, Rice straw has a silica content of 4-20% [139]. Bamboo stem, another source of silica, has also been widely used [140]. Ash from bamboo leaves has a silica content of about 58.3% [139,141]. Silica sourced from bamboo leaves typically still has impurities, namely potassium, magnesium, and calcium [140]. Additionally, rice husks are also used to produce silica at the largest scales [135]. Houston (1972) [142] stated that rice husk ash contains silica as much as 86% -97% of its dry weight, while Mittal (1997) [134] stated that it contains much as 90-98% of its dry weight [135]. In Indonesia, there are only two seasons or periods of rice farming, coupled with the reduction of agricultural land and the wide use of rice husk adhesive properties through reacting it with NaOH solution to produce sodium silicate used as a filler material in making soap, detergent, and adhesive in the industrial sector, rice husk stock, as a consequent, is surely depleting [143].

Bagasse is a waste produced from the processing of sugar and is quite abundant in Indonesia. The bagasse is conventionally used as fuel for steam boilers to produce steam power and fuel for furnaces used in sugar productions [144]. In the sugar industry, bagasse has yet been optimal, its leftover is still abundant as it is generated and reused [145]. Based on data from the Indonesian Sugar Plantation Research Center (P3GI), bagasse ash use in Indonesia makes up 2% of the weight of milled sugarcane or around 10,200,000 tonnes/year per season [146].

Bagasse contains several minerals, namely Si, K, Ca, Ti, V, Mn, Fe, Cu, Zn, and P. Because the silica content in bagasse ash is large, bagasse ash can be used as a desirable raw material for making silica gel, implying its added value from its origin as waste produce by sugar factories [144]. Rompas et al. (2013) [49] stated that bagasse contains a high level of silica (SiO₂) at around 68.5%. The use of bagasse as a base material for silica coating has been carried out by Usman (2014) [45] where the silica content in bagasse was found to be 77.28%. Furthermore, Asfadiyah (2014) [63] also conducted a similar study that obtained a silica content of 88.28%. The contents found in bagasse were high enough that it can thus be used to make silica-based materials [47].

Hariharan and Sivakumar (2013) [147] stated that the use of bagasse as industrial waste is not only economical but can also contribute towards the control of environmental pollution. Silica from bagasse that is at excess and is then unused can be stored for a long time because of the stable nature of silica against mechanical influences, organic solvents, and extreme pH conditions [145].
4.2 Influence of Vinyltriethoxysilane (VTES) Addition

One of the ways that can be executed to improve the properties of a material is through modification that entails the addition of certain chemical compounds. Silica gel, unexceptionally, exhibits weakness in the fact that the active sites that it possesses are only limited to the silanol (-SiOH) and siloxane (Si-O-Si) groups [86]. This weakness, though, can be overcome using surface modification. Surface modification of silica gel is the process that aims to change the chemical composition of the silica gel surface. The modification process changes the –Si-OH group into –Si-OM, where M represents several species, either simple or complex, other than H [87]. Some examples of the modifier used are Mercaptopropyltrimethoxysilane (MPTES), Aminopropyltrimethoxysilane (APTS), and Chloro propyltrimethoxysilane (CPTS), in which modification with the addition of these compounds requires silane reagent as an intermediary. The silane reagent that is commonly used is glycidoxypropyltrimethoxysilane (GPTMS) [86]. Vinyltriethoxy-silane (VTES) has three hydrolyzed ethoxy groups and one vinyl group attached to the silicon [77]. The addition of vinyl groups to silicon can improve elastic and mechanical properties without much variation in density or thermal conductivity [88]. The addition of VTES can also make the distribution of nanoparticles more uniform [88].

In Xue et al. (2009) [148], it was explained that the limitations of a solid surface are determined by the chemical composition and geometric microstructure of its surface. One study suggested that high contact angles (CA) exist are predominated by materials that had undergone surface chemical modification rather than their inherent surface roughness. Xue et al. (2009) [148], with the use of excess VTES to replace most of the hydroxyl groups in silica nanoparticles with vinyl groups, when applied to V-SiOx-NP 85 nm could only produce CA of 120 ± 1°. Meanwhile, film at 167 nm of the V-SiOx-NPs had a larger CA at 160°. It was implied that the chemical modification of silica nanoparticles only changed the surface from hydrophilic to hydrophobic, but not superhydrophobic. The rough surface, specifically the V-SiOx-NP microstructure and the irregular nanostructures on the V-SiOx-NP surface, had a bigger influence on superhydrophobicity. It could happen because the particle diameter was getting bigger and thus the surface became rougher. Rougher surfaces can increase hydrophobicity because air can be trapped between solid surfaces and water droplets can minimize their contact area [148].

4.3 Cu Antibacterial Agent

Copper (Cu) is often used as a bacterial control agent, especially at the nanoscale, due to the high antibacterial activity of Cu with its comparatively lower cost compared to other similar anti-bacterial metals [53,54]. Au anti-bacterial can kill bacteria with an efficiency of 60-100%, but has the disadvantage of being expensive [92]. The use of Ag as an anti-bacterial is able to kill 88% of bacteria. However, the price is still quite expensive and it possesses the risk of having a certain amount of toxicity [93]. Moreover, silver as an anti-bacterial also has a weakness of being unstable [149]. Alternatively, ZnO as an anti-bacterial was found not to have been able to kill bacteria effectively, as it was found that the leftover medium still had a small number of microorganism sites and a small number of spores [94].

Copper (Cu) was chosen as an anti-bacterial in the silica modification discussed in this paper because it has good chemical stability and relatively cheap price [149]. It is excellent in terms of electrical and thermal conductivity (lower in this case only for silver), good performance in cold and hot conditions, and high corrosion resistance [55]. Copper (Cu) was proven to have high anti-bacterial power and low toxicity further emphasizing that Cu (II) ions can be used as an alternative to silver anti-bacterial material [150].

In addition to providing intrinsic anti-bacterial properties, the disintegration of Cu nanoparticles through the deposition onto SiO2 particles will addly result in the increase in anti-bacterial efficiency of the surface [54]. This anti-bacterial activity has previously been tested against two types of bacteria, namely gram-positive bacteria (S. aureus) and gram-negative bacteria (E. coli) [91]. Previous research [54] has shown a drastic reduction in the number of E. coli (gram-negative) and S. aureus (gram-positive) bacteria (more than 70% for E. coli and 90% for S. aureus bacteria).
5. Conclusion

Bagasse possesses sufficiently high silica content up to 88%, making it adequate to be used in the fabrication of superhydrophobic coatings. The use of bagasse in the fabrication of superhydrophobic coatings is economical and can also contribute to the control of environmental pollution. The weakness of silica-based materials is that the active sites established are only of silanol (-SiOH) and siloxane (Si-O-Si) groups. Therefore, it requires a modification to improve their characteristics. One of the ways that can be executed to improve the properties is through modification that entails the addition of certain chemical compounds such as vinyltriethoxy-silane (VTES). The addition of vinyltriethoxy-silane (VTES) can improve the elastic and mechanical properties without much variation in density or thermal conductivity and make the nanoparticles more uniform. However, the superhydrophobic surface can only reduce the adhesion of bacteria but cannot sterilize them. The surface will get wet after being exposed to a humid environment for a long time. In addition, the superhydrophobic surface will lose its superhydrophobicity after the presence of a biofilm layer formed by bacteria. The method that can be applied to overcome these problems is the addition of an anti-bacterial agent. Copper (Cu) was chosen as an anti-bacterial agent discussed in this review paper because it has good chemical stability and relatively cheap price. Copper has self-sanitizing capabilities and can contribute to infection control, with its inherent low toxicity.

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