TiO$_2$-M self-cleaning coating with antimicrobial and superhydrophilic properties

Rizgyandhaka Artha Prawira, Dessy Ariyanti *

Department of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro, Tembalang, Semarang 50275, Indonesia

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ABSTRACT

Self-cleaning coating is an emerging coating technology that has prospect for further development and application. This research is an initial study that is expected to provide knowledge on the effectiveness of TiO$_2$ coating in addition of additives compounds such as graphene, Ag and Fe as self-cleaning coating. This research aimed to develop and characterize the TiO$_2$ based self-cleaning coating that is applied on the glass surface to determine their hydrophilicity, their ability to degrade organic compounds and their antibacterial properties on glass surfaces. The research was carried out by making a TiO$_2$-based coating combined with the addition of additives such as graphene, Ag and Fe at concentrations of 1, 5 and 10% using the simple dip coating method. The results show that the TiO$_2$ coating with 10% graphene gives the lowest water contact angle 13.67° (super hydrophilic wettability properties) with the optimum degradation ability of methylene blue with residual concentration of 0,5497 mg/L at 180 min contact time. Antibacterial properties were performed by TiO$_2$ coating with the addition of 10% Ag reflected in the clear radius of 5.333 mm, which reflected moderate inhibition (clear zone 5–10 mm) against *E. coli*.
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1. Introduction

The development of materials science creates many new high-quality materials in various fields and currently are being developed with the concept of smart materials. Smart materials are defined as materials that have one or more properties that can be changed significantly in response to external stimuli. Physical properties that are generally changed are shape, stress, stiffness, humidity, electric or magnetic field, light, temperature, pH, chemical compounds, viscosity or attenuation. Smart materials can have self-cleaning, self-repairing, self-healing and self-sealing properties. Materials that have been developed as smart materials include Ni, Zn, Ti, Cu, graphene, TiO$_2$ and so on [1–4].

Titanium dioxide (TiO$_2$) is a transparent semiconductor material with high bandgap (3.23 eV), high refractive index and good mechanical performance. TiO$_2$ has photocatalytic properties that can generate electrons when exposed to UV light. One that can be applied from TiO$_2$ is as a self-cleaning coating [5]. Self-

cleaning coating is a coating whose performance depends on solar energy to activate compounds that act as catalysts so that electrons from these compounds are released and used to degrade organic compounds. To obtain self-cleaning properties, the surface of an object must be coated with a material that has photocatalytic and super hydrophilic or superhydrophobic properties [6]. Hydrophobic properties are a combination of surface properties and roughness, the roughness surface morphology can cause an increase in the surface hydrophobicity of the material. A superhydrophobic surface is required to minimize the adhesion between the surface and the liquid [7]. In the research of Won, et al. [8], TiO$_2$ was applied on glass as a coating to see self-cleaning ability. TiO$_2$ with size of < 25 nm and TiO$_2$ type P25 respectively had a contact angle of 18.8° and 14.4° after UV irradiation. Glass coated with TiO$_2$ is more hydrophilic than glass without coating with contact angles of 32.7° and 32.4° after UV irradiation. The self-cleaning ability of TiO$_2$ can be increased by adding other materials, such as graphene, silver (Ag) and iron (Fe).

Graphene has a very regular arrangement of hexagonal carbon atoms forming sheets as thin as one atom. One of the TiO$_2$/graphene composite materials was developed by Padmanabhan

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et al. [9] which was synthesized by the hydrothermal modified sol–gel method and produced a self-cleaning coating with a water contact angle close to 0° within 15 min after UV irradiation and degradation of methylene blue (MB) dye after 150 min of UV irradiation. Graphene-based nanomaterials (GBN) have strong antibacterial properties against a wide variety of microorganisms. This is evidenced in the study of Yang et al. [10], in which a composite layer of graphene nanosheets (GNS)/TiO_2 was produced on a Ti alloy disc to impart antibacterial activity to the surface. The results showed that GNS was maintained after plasma spraying, the number of *E. coli* and *S. aureus* in the TiO_2 - GNS composite layer was 3% less than that of the pure TiO_2 layer.

Silver (Ag) is a material that has antibacterial properties and there has been no research that bacteria are resistant to silver. Ag shows its activity based on its large surface area to volume ratio, chemical stability, good conductivity, catalytic and antibacterial [11]. Ag is often used as a composite raw material in combination with other materials to obtain antibacterial properties. The mechanism of antibacterial properties that is carried out is by metal ion sterilization. In the mechanism, Ag^+ ions produce reactive oxygen species (ROS) when in contact with bacteria. When bacteria come into contact with antibacterial materials containing Ag^+ ion particles on the substrate surface, the normal working system of proteins on the bacterial cell membrane and ion channels will be disrupted by these particles, causing the bacteria to die [12]. Ag can be combined with TiO_2 as a self-cleaning coating [13].

Iron (Fe) is widely used to make composites and modify them with other materials to obtain certain properties. For example, the addition of iron to cement can not only increase the mechanical strength and cell affinity in vitro, but also strengthen bone binding in vivo. Li et al. [14] added iron to brushite cement which not only resulted in longer setting time, larger crystal particles, formation of calcium iron phosphate and changes in chemical groups, but also resulted in good performance in inhibiting the growth of *S. aureus* and *P. aeruginosa*, but less sensitive to *E. coli*. Stan et al. [15] synthesized cotton fiber containing graphene oxide/Fe and N-doped TiO_2 particles as self-cleaning materials. The prepared material showed antibacterial activity against 77% Gram-positive (*E. faecalis*) bacterial strains but could not contain the growth rate of Gram-negative (*E. coli*) strains. In another study, Ismael [16] tested the photocatalytic activity of Fe (III) doped TiO_2 nanoparticles with the precipitation method. The degradation efficiency of methyl orange (MO) reached 95% at 0.1 % mol $FeTiO_2$ (valence band of 2.4 eV) under UV irradiation for 4 h (λ 320 nm).

In this paper, the self-cleaning TiO_2/additive material (graphene, Ag and Fe) preparation with the dip coating method were discussed. The combination of TiO_2 material with additives such as Graphene, Ag and Fe can improve the self-cleaning properties and its antibacterial activity.

2. Experimental methods

2.1. Preparation of coatings

TiO_2 nanoparticle preparation refers to the method carried out by Li et al. [17]. Tetra n-butyl titanate (TNBT) (Merck) was put into Erlenmeyer contains100 mL of ethanol (EtOH) (ROFA) and then stirred using magnetic stirrer for 30 min with heating maintained at a temperature of 30–40 °C.

The preparation of the TiO_2/graphene coating solution refer to the method of Pei et al. [18]. Polyvinyl pyrrolidone (PVP) (BASF) (5 wt%) was dissolved in EtOH with the aid of an ultrasonic homogenizer (Scientz JY99-IIDN) for 30 min and divided into three parts. Graphene powder (Kimiapedia) (1, 5 and 10% by weight) was added to the PVP solution and vigorously stirred using a magnetic

stirrer for 30 min, respectively. The mixture was filtered to take the filtrate. As much as 2% TiO_2 was added to the graphene/PVP suspension and stirred again using a magnetic stirrer for 30 min by keeping the heating at a temperature of 30–40 °C.

The preparation TiO_2/Ag referring the method used in Komaraiah et al. [19]. As much as 2% TiO_2 was added to EtOH and divided into three parts. An amount of 1.5 and 10% (mole ratio of TiO_2) silver nitrate (ROFA) was added to each solution and stirred using a magnetic stirrer for 30 min by keeping the heating at a temperature of 30–40 °C.

TiO_2-Fe coating solution were prepared by following the methods used in Kara et al. [20]. In the preparation of TiO_2 mixture, as much as 2% TiO_2 was added to EtOH and divided into three parts. An amount of 1,5 and 10% (mole ratio of TiO_2) iron (III) nitrate (ROFA) was added to each solution and stirred using a magnetic stirrer for 30 min by keeping the heating at a temperature of 30–40 °C. The blank solution was made as a comparison by making 2% TiO_2 in ethanol.

The glass substrates (50 mm × 50 mm) were prepared by cleaning it with ethanol and distilled water to remove contaminants on the surface. The substrate was dried at 37 °C for 10 min. The dried substrate must be immediately coated with a solution so that no contaminants adhere.

The application of the coating solution was carried out by the dip coating method presented by Pravita and Dahyunir [21]. The substrate was dipped in the coating solution and allowed to stand for 5 min. After that, the samples were dried in an oven at a temperature of 30–40 °C for 10 min. The dyeing and drying process was repeated 5 times.

2.2. Water contact angle analysis (WCA)

The contact angle test is intended to determine the hydrophobic and hydrophilic properties of the substrate surface. The contact angle was measured using the FACE angle instrument - Kyowa Kaimenkagaku Co. Contact Angle Meter. LTD Tokyo Japan, which was measured at three points with ionized-free distilled water at 25 °C.

2.3. Ultraviolet (UV) irradiation of organic compounds

To analyze the photocatalytic activity of the coating, the sample was immersed in a methylene blue (ROFA) solution with a concentration of 4.9999 mg/L (5 ppm) for 180 min while irradiated with a UVC lamp (254 nm 4.9 eV). The results obtained were tested with a UV–Vis spectrophotometer to determine the ability to degrade organic compounds by self-cleaning coatings.

2.4. Antibacterial test

The antibacterial activity testing was modified from Handayani et al. [22] that is carried out by the diffusion method. To begin with, the equipment used is washed, dried and wrapped in paper. The equipment was then sterilized in an autoclave at 121 °C for 15 min. After sterilizing the equipment, the Nutrient agar (NA) (Merck) and Nutrient broth (NB) (Merck) media were made. In the manufacture of NA and NB, 2 g of NA media and 0.8 g of NB media were added to the Erlenmeyer, respectively. The media was dissolved in 100 mL of distilled water and then sterilized in an autoclave at 120 °C for 15 min at a pressure of 2 atm.

The agar medium was made oblique by pouring 5 mL of NB media into a sterile test tube and covered with aluminum foil. The media was sterilized in an autoclave at 121 °C for 15 min, then left at room temperature and placed at an angle until the media solidified. The slanted agar medium was used for bacterial inoculation (bacteria rejuvenation). Bacterial inoculation on the slanted

agar medium was carried out with the test bacteria taken with a sterile ose needle, then implanted on the slanted agar medium by scraping using an osseous needle. Then incubated at 37 °C for 2 days.

Testing of antibacterial activity using the diffusion method was carried out by preparing 10 petri dishes, then ± 10–15 mL of NA medium was poured into each petri dish and spread evenly. The media is allowed to solidify. NB media that has been inoculated with *E. coli* bacteria is poured ± 1 mL onto the NA media and spread evenly. The paper disks were immersed in a coating solution (as antibacterial), then three pieces were affixed as repetitions by adjusting the distance in a petri dish. One petri dish for one antibacterial solution. Petri dishes were incubated for 2 days at 37 °C, then the diameter of the clear zone (mm) of each concentration was measured.

3. Results and discussion

3.1. Visualization of coatings

Glass is used as a common substrate for TiO_2 because of its high transparency, good adhesion, resistance to high calcination temperatures, relatively low cost and resistance to low and high pH wastewater [23]. In this study, the coating solution was applied with dip coating method in layers and the coatings solution containing TiO_2 with graphene, Ag and Fe as additives in various concentration. The result can be seen in Fig. 1. The visualization of TiO_2/graphene coated glass with concentrations of 1, 5 and 10% turns to opaque (Fig. 1A-C). The surface has a smooth surface indicating the glass has been coated perfectly and the adhesive layer appears even and homogen. Meanwhile, the observation of TiO_2/Ag coated glass with concentrations of 1, 5 and 10% resulted opaquer appearance with smooth surface in comparison with TiO_2/graphene and decreased as the increasing concentration (Fig. 1D-F).

The same phenomena found in the coating of TiO_2/Fe with concentrations of 1, 5 and 10%. resulted opaquer appearance with smooth surface in comparison with TiO_2/Ag (Fig. 1G-I). However, the glass becomes more transparent and visible as the concentration increases. The white solution of titania turns to transparent yellow when excess Fe is added. This is dominated by the amount of Fe in the coating solution. The pure TiO_2 coating shows the least opaque with smooth surface (Fig. 1J). Reflected from the result that the multi-layered dip coating method was able to coat glass very well on various types of substrates, as well as increase the thickness of the coating. Coated glass still can maintain its transparency because it is based on the dominant nature of transparent TiO_2 material [5].

3.2. Water contact angle analysis (WCA)

Water contact angle (WCA) measurement is used to understand the surface properties of materials such as wettability, surface energy and adhesion. All samples were tested for surface properties purposes and to examine the addition of the additive components such as graphene, Ag and Fe (Fig. 2).

Fig. 2 shows WCA variations of TiO_2/additives (graphene, Ag and Fe) coatings with different concentrations. The true value of the water contact angle on the graphene monolayer is unknown. Recent experimental literature shows that the contact angle of water on graphene as high as 127° [24]. For samples of TiO_2/graphene and TiO_2/Ag with concentrations of 1, 5 and 10%, the water bubbles that are dripped are unstable, the surface looks like it absorbs water so that the contact angle slowly decreases and becomes more hydrophilic. TiO_2/graphene samples due to the possibility of electron transfer to graphene, photogeneration carrier recombination is reduced. This will help in better photocatalytic superhydrophilicity. This hydrophilic WCA is due to the ability to cancel each other out of graphene, which is more hydrophobic than
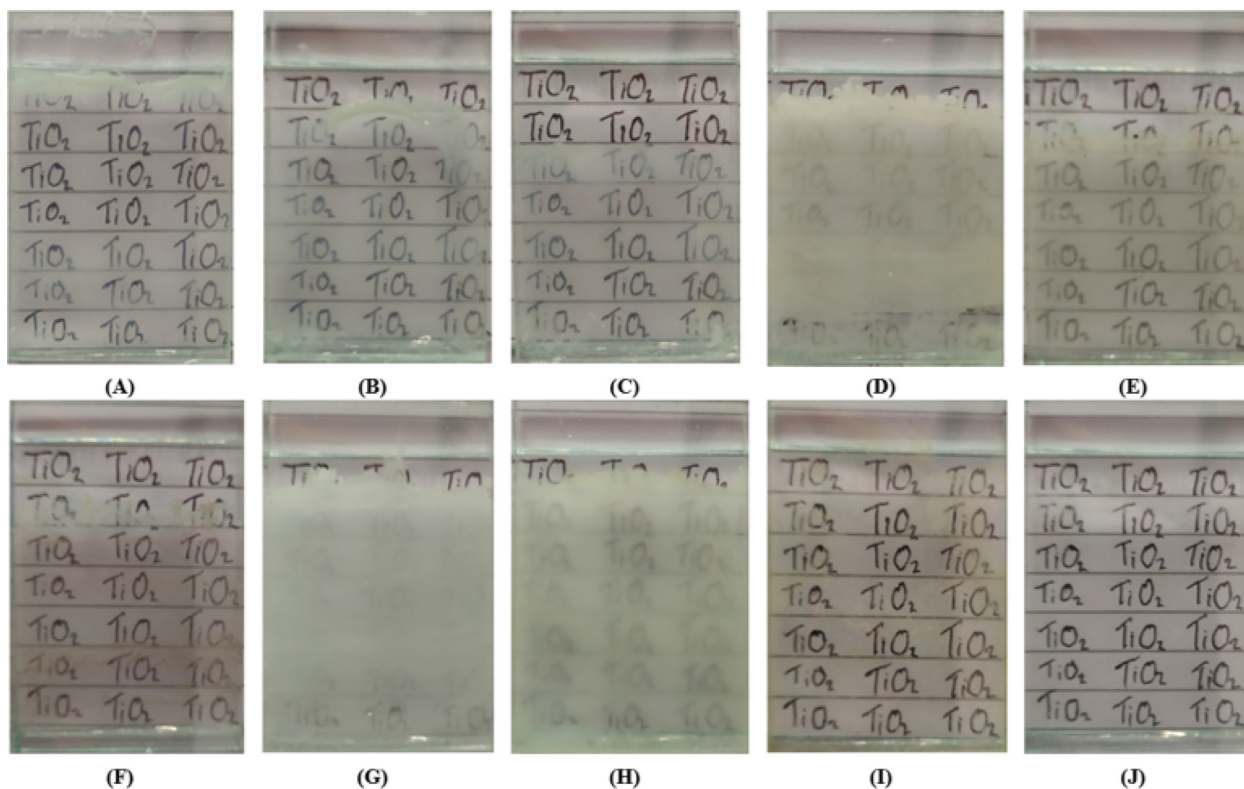

Fig. 1. Appearance of coated glass of TiO_2/graphene (A) 1%; (B) 5%; (C) 10%; TiO_2/Ag (D) 1%; (E) 5%; (F) 10%; TiO_2/Fe (G) 1%; (H) 5%; (I) 10% and (J) pure TiO_2.
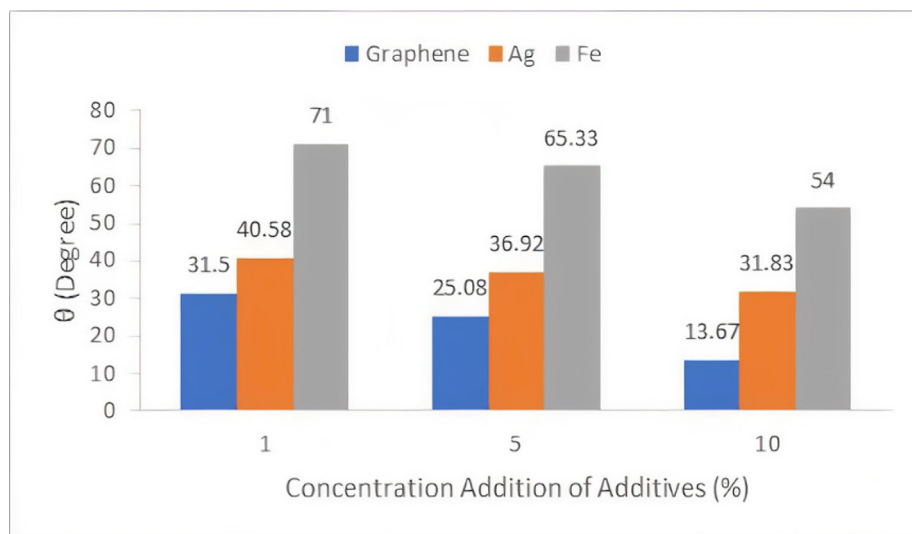
Fig. 2. WCA measurement results TiO_2/additives at various concentrations.

TiO_2. The mechanical properties especially the adhesion of the coating to the substrate are very important for the practical application of super hydrophilic coatings. where the surface tension (ST) between water and the glass surface is stronger than ST between water and water so as to reduce surface roughness [25].

Samples of TiO_2/Ag with concentrations of 1, 5 and 10%, WCA became more hydrophilic with increasing concentration. This can be explained due to the strong adhesion properties of the coating on the substrate. In addition, it is also explained in terms of the effect of silver particles present on the surface of this coating (the contact angles of water in silver are $\sim 90°$ and $\sim 20°$ in TiO_2), resulting in mutually cancelling properties of graphene which is more hydrophobic than TiO_2 and making coatings possible. become more hydrophilic [26]. The decrease in contact angle observed in the samples at each concentration can be assumed also by the aggregation of Ag in the thin film and TiO_2 on the surface [27].

There is literature that discusses water dripping on the surface of iron ore. It is shown that the contact angle of iron ore is 75.42°. This is thought to be because the sample surface becomes impossible to hold droplets on the sample surface. It was also shown that the contact angle becomes large due to the large surface roughness, as well as the higher surface tension of the liquid resulting in a higher contact angle [28]. For samples of TiO_2 /Fe with concentrations of 1, 5 and 10%, the initially dripped water bubbles were more spherical. As the concentration increases, the surface looks like it absorbs water so the contact angle slowly decreases and becomes more hydrophilic. It can be explained that the adhesion force is stronger than the cohesive force. This implies that the ST between water and the glass surface is stronger than the ST between water and water. In addition, due to the surface wettability properties of solids involve surface roughness and modification with materials having high surface energy. The change from a hydrophobic surface to a more hydrophilic one is caused by a combination of the decrease in surface roughness by the TiO_2 nanostructure and the increase in surface energy by Fe.

The blank TiO_2 samples showed WCA values which were more hydrophilic than TiO_2/Fe, but more hydrophobic when compared to TiO_2/graphene and TiO_2/Ag. In addition to the strong adhesion of the coating on the substrate, this is due to the increase in the surface energy of TiO_2. In addition, TiO_2 material is a nanometres-sized material that has a larger surface area than bulk-sized material, causing it to be more hydrophobic than modified TiO_2 coatings [23].

3.3. Self-cleaning properties on the degradation of organic compounds

Photocatalytic degradation of organic compounds was carried out to analyze the potential application of TiO_2/additives (graphene, Ag and Fe) coatings as self-cleaning materials. Photocatalytic degradation of methylene blue (MB) at a concentration of 4.9999 mg/L under UV (254 nm) for 180 min was performed using a UV–Vis Instrument Shimadzu UV-1800. The optimum wavelength for MB dye is 663 nm.

The absorbance data of the MB standard solution is shown in Fig. 3, a linear regression equation can be determined from the solution, namely: y = bx + a, where y = absorbance, x = concentration, b = slope, and a = intercept, and r = linear correlation coefficient. So, the linear regression equation for the MB standard solution is y = 0.1732x – 0.0179 with a linear correlation coefficient (r) of 0.9944. Based on the calibration curve the MB residual concentration was calculated to observe the degradation activities of the TiO2 based coating. As depicted in Fig. 4, it can be seen that the amount of dye remains fluctuates where there is an increase and decrease in coating additives of all concentrations. This is because the coating cannot degrade organic compounds or can be said to be saturated. The saturation of the coating on organic compounds causes the interaction between the coating and organic compounds to be smaller. The greater concentration of additives, the number of degraded dyes increases.

The reaction mechanism that can be explained on the degradation of organic compounds by coating solutions is that, when a photon with energy equal to or greater than the band gap hits TiO_2, it can promote electrons from the valence band (VB) to the conduction band (CB). Thus, producing a positive hole in VB or creating a paired electron hole in CB. During pollutant photodegradation, the photoexcited electrons and holes can react with H_2O to produce radical oxygen species, which can undergo reactions to decompose pollutants such as MB into small molecules. The possible reasons for the increase in photocatalytic activity are the increase in pollutant adsorption and the increase in charge separation and transport in the presence of additives (graphene, Ag and Fe).

TiO_2/graphene has band gap energy of 2.4 eV. Electron transfer via Ti-O-C bonding from TiO_2 to graphene slows photo-induced
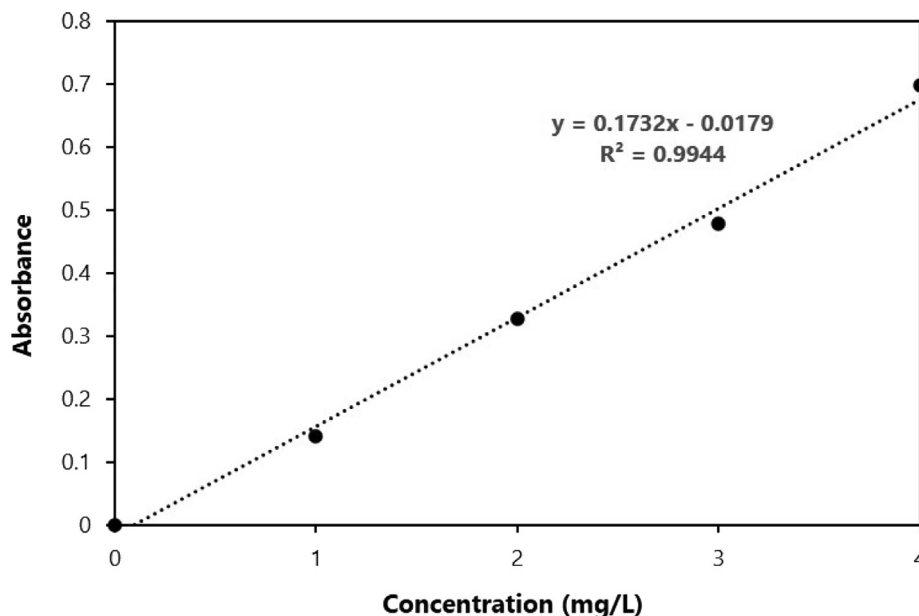
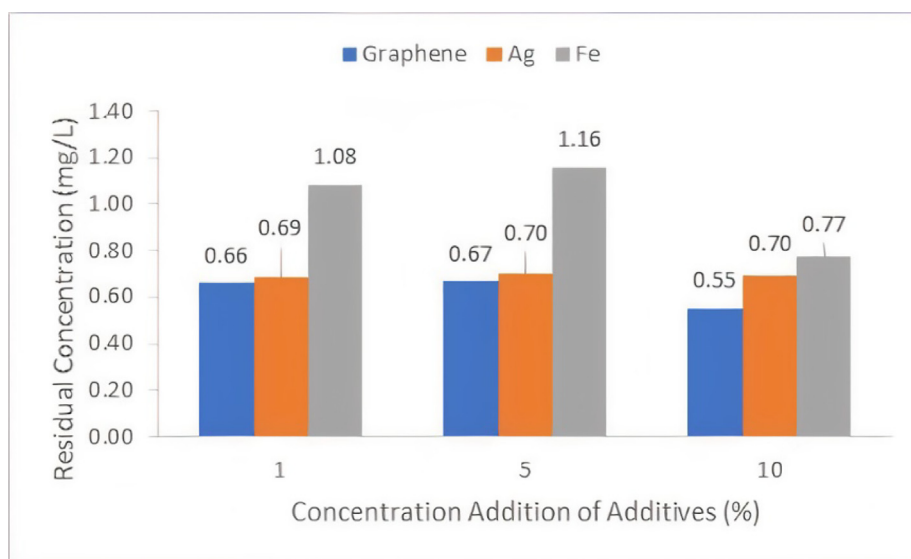**Fig. 3.** Calibration curve of MB standard solution.

Fig. 4. MB residual concentration on degradation ability of TiO$_2$/additives at various concentrations.

charge carrier recombination and promotes ROS production. The significant adsorption capacity of the TiO$_2$/graphene thin film is due to the presence of graphene contained in the coating. The high adsorption of organic pollutants in aqueous solutions is attributed to the electrostatic interactions between the graphene on the coating surface and the dye molecules, due to the cationic properties of the dye molecules and the -π interaction between the phenyl ring of the dye molecules and the graphene surface. In addition, hydrogen bond interactions between graphene carboxyl groups and MB dye molecules can also occurs. The higher photocatalytic efficiency of the TiO$_2$/graphene thin layer compared to the pure TiO$_2$ layer can also be attributed to the charge separation and charge transfer mechanisms that prevent photogenerated electron-hole pair recombination [29]. In the case of TiO$_2$/graphene, graphene contributes to the generation of electron-hole pairs under UV irradiation to produce graphene(e$^-$) and graphene(h +). Graphene(e$^-$) reacts with surrounding oxygen to produce superoxide radicals

(O$_2^-$•) and Graphene(h +) reacts with surrounding water to produce hydroxyl radicals (OH•). The hydroxyl radicals react with MB to form CO$_2$ and H$_2$O. The superoxide radical reacts with the surrounding water to form hydrogen peroxide, which then turns into a hydroxyl radical. Hydroxyl radicals will convert MB into substances that are safe for the environment [29].

The reaction mechanism that can be explained on the degradation of organic compounds by TiO$_2$/Ag is Ag$^+$ ions trap photoinduced holes to form Ag^{2+}, and Ag^{2+} generated in situ can oxidize H$_2$O or OH$^-$ ions adsorbed on the surface to produce OH•. The rate of photoinduced electron-hole pair recombination is reduced by doping because Ag$^+$ can trap photoinduced electrons to form Ag^0, and transfer trapped electrons to O$_2$ or adjacent Ti^{4+} ions, and thereby generate superoxide radicals (O$_2^-$•) and by decreasing the rate of recombination of e$^-$ /h$^+$ pairs with the illumination of light doped with excited Ag, Ag plasmonic electrons migrate to CB titania. Conduction band electrons trapped by the surface adsorb

oxygen to produce $O_2^-\bullet$ which will then react with the adsorbed surface H_2O to produce OH•. Furthermore, for the repeated charge for electro-neutrality in the TiO_2-doped silver ion, O_2^- can easily escape to trap the photo-induced hole and generate OH•. Photo-generated radical's hydroxyl (OH•) have greater oxidizing power and can completely remove organic pollutants [19].

Iron oxide has a band gap of 2.2 ev, TiO_2 anatase is 3.2 ev and TiO_2/Fe is 2.4 ev [16,30]. As the Fe^{3+} dopant concentration increases, the band gap energy will decrease. This is due to the increasing number of Fe^{3+} substituting Ti^{4+} in the TiO_2 structure. In this study, TiO_2/Fe had the lowest ability to degrade organic compounds. Where in the UV wavelength range between 200 and 400 nm, TiO_2 provides a greater absorbance than TiO_2/Fe. According to Othman, et al., if the Fe^{3+} concentration exceeds the optimum amount and produces a band gap energy of 2.00 eV, the photocatalyst activity will decrease [31]. In the study of Pratiwi, et al., [31], Fe^{3+} doping concentrations of 0.05%, 0.125%, and 0.25% had band gap energy values of 2.53 eV, 2.11 eV and 1.33 eV, respectively. However, the 0.25% concentration of TiO_2 Fe^{3+} did not increase the ability of TiO_2 to absorb UV photons. It is feared that the addition of Fe^{3+} concentration that exceeds the optimum in this study will make the band gap value 2.00 eV, thus causing the photocatalyst ability to be not optimal. The proposed charge transfer mechanism during MB dye degradation in the presence of a TiO_2/Fe photocatalyst that is, generation of electron-hole pairs occurs in the presence of UV light. Due to the presence of TiO_2, the electrons that formed will be transferred to TiO_2 because of its higher electron mobility and react with the oxygen molecules present in the dye solution and the formation of $O_2^-\bullet$ occurs. The hole in VB reacts with water molecules and forms OH• radicals. The formed $O_2^-\bullet$ ions and OH• radicals break down the MB dye present in solution. The presence of Fe reduces the rate of electron-hole pair recombination and this enhances the degradation of the MB dye [32].

3.4. Antibacterial test

Testing of antibacterial activity using agar diffusion method. This method was often used compared to other methods because it is makes it easier to determine the antibacterial activity of a preparation by forming a zone of inhibition of bacterial growth from substances that act as antibacterial in solid media. The area of inhibition of bacterial growth is the clear area around the disc. The stronger the antibacterial activity, the wider the inhibition area.

Figs. 5, 6 and 7, shows the antibacterial properties profile of TiO_2 coating with different additives graphene, Ag and Fe respectively. High antibacterial properties of graphene is attributed to
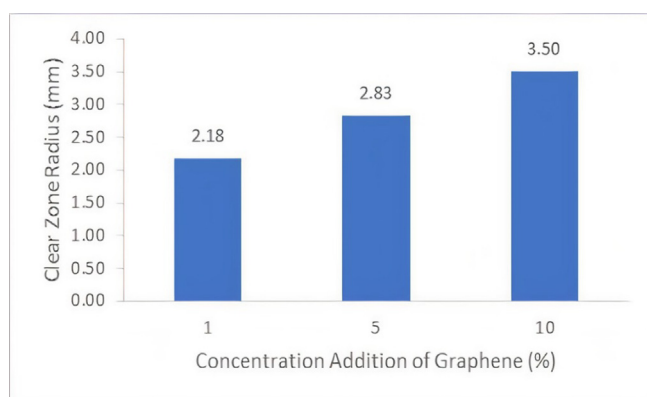
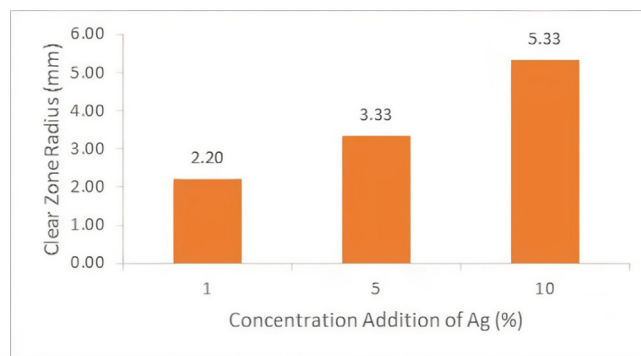**Fig. 5.** Antibacterial properties of TiO_2/graphene at various concentrations.

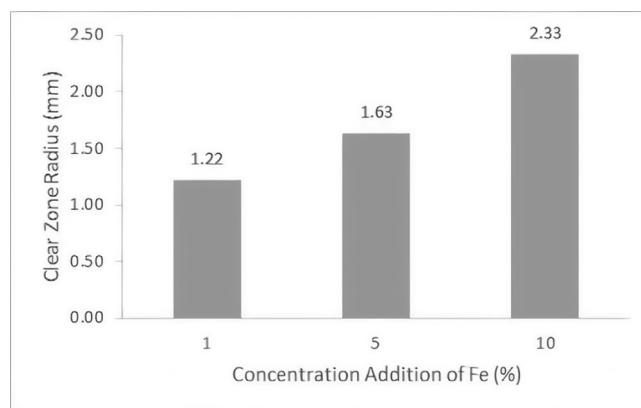**Fig. 6.** Antibacterial properties of TiO_2/Ag at various concentrations.

Fig. 7. Antibacterial properties of TiO_2/Fe at various concentrations.

its effective charge separation in electron transfer. Graphene works as an electron acceptor and transporter. It is known that hydroxyl radicals are the main factors involved in antibacterial performance. Graphene exposed to UV light whose energy is greater than the band gap energy, electrons will move from the valence band to the conduction band to produce holes (hvb^+) in the valence band and electrons (ecb^-) in the conduction band. The electrons will interact with the surrounding oxygen and produce superoxide radicals (O_2^-*), while the holes will interact with the surrounding water to produce hydroxyl radicals (OH$*$) [33]. The OH radicals are capable of oxidizing macromolecules including polysaccharides, proteins, lipids and nucleic acids and causing their dysfunction. As has been investigated $O_2^-\bullet$ generated under UV in the presence of non-metals (C, S, N) doped with TiO_2 has an important impact on bacterial inactivation. The greater antibacterial potential of TiO_2/graphene compared to pure TiO_2 could be due to the ability of graphene to extend the light absorption range and function as an electron acceptor and transporter resulting in increased production of oxides and hydroxyl ions involved in antibacterial activity [34].

The addition of silver not only contributes to the increase in photocatalytic activity, but also complements its antibacterial properties. The antibacterial activity of the doped samples under UV irradiation was due to the synergistic photocatalytic reaction of the antibacterial effect of TiO_2 and silver in the matrix. Silver species (Ag^{2+}, Ag^0) that produced from Ag^+ ions can act as light-generated electron traps and thereby increase photocatalytic efficiency. This mechanism can oxidize H_2O or OH^- ions adsorbed on the surface to produce generates more hydroxyl radicals, by limiting the recombination of charge carriers. The OH radicals are capable of oxidizing macromolecules and causing increased antibacterial activity. The combined effect of silver photocatalyst

and TiO_2 can decompose the peptidoglycan layer and then damage both the cell wall and cell membrane, causing changes in cell membrane permeability and resulting in leakage of intracellular substances [35]. The increase in the antibacterial activity of TiO_2 with the addition of Ag ions can be attributed to the fact that (i) Ag ions directly interact with the thiol groups of vital bacterial enzymes and inactivate them, (ii) Ag ions prolong the absorption of TiO_2 light from UV to visible light range, indirectly inducing photocatalytic antibacterial activity of TiO_2 [36].

The antibacterial activity of TiO_2/Fe samples under UV irradiation was caused by the photocatalytic reaction of the antibacterial effect of TiO_2 and Fe^{3+} in the matrix. Fe^{3+} can inhibit electron-hole recombination best by trapping electrons and holes generated by light, respectively creating Fe^{2+} and Fe^{4+} as light-generated electron traps which will increase photocatalytic efficiency. This mechanism generates hydroxyl radicals, by limiting the recombination of charge carriers and providing increased antibacterial activity [37]. However, TiO_2/Fe coating could not prevent the growth of *E. coli* as well as graphene and Ag. The hydrophobic lipid bilayer on the outer membrane of *E. coli* can prevent TiO_2/Fe from approaching the bacterial surface and damage it. However other parameters such as intracellular ROS concentration, lipid peroxidation level, membrane integrity and DNA damage can be effective [34]. Inhibition according to Davis and Stout (1971) is divided into very strong (clear zone > 20 mm), strong (10–20 mm clear zone), moderate (5–10 mm clear zone) and weak (clear zone < 5 mm). It can be stated that all samples of TiO_2/additive have weak inhibitory power against *E. coli*, except for TiO_2/Ag 10% which has moderate inhibitory power [22].

4. Conclusions

Based on the research that has been conducted, some conclusions can be drawn as follows: The best water contact angle (WCA) obtained with the addition of additives is 54° for 10% Fe addition, 31,83° for 10% Ag addition and the best among others is for 10% graphene addition, which is 13,67°. While the blank TiO_2 has a WCA of 63.58°. The results of the measurement of the contact angle with the addition of additives become more hydrophilic on the glass surface with each increase in concentration. The antibacterial properties of additives can be seen in the clear zone. The clear zone with the addition of 10% graphene is 3.5 mm. The addition of Fe 10% is equal to 2,333 mm. The best results were obtained with the addition of 10% Ag with a clear zone radius of 5.333 mm, which means graphene and Fe have weak inhibition (clear zone < 5 mm) and Ag has moderate inhibition (clear zone 5–10 mm) against *E. coli*. The ability to degrade methylene blue (MB) with the addition of additives obtained the residual concentration of MB 0.6957 mg/L at the addition of 10% Ag, 0.7725 mg/L at the addition of 10% Fe and the best by 10% TiO_2/graphene, with a residual concentration of 0.5497 mg/L from the initial concentration of 4.9999 mg/L at a contact time of 180 min. This proves that the addition of additives can degrade organic compounds even in small amounts.

CRediT authorship contribution statement

Rizgyandhaka Artha Prawira: Methodology, Data curation, Writing – original draft. **Dessy Ariyanti:** Conceptualization, Visualization, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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