Efficiency of Ilmenite Photocatalyst Material as Modelling for Antimicrobial Activity

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Preparation of ilmenite (FeTiO_3) composite for antimicrobial under UV-visible lights irradiation was carried out to appropriate as a new antimicrobial material. The preparation of FeTiO_3 by using sol-gel method was conducted by the titanium tetra-isopropoxide (TTIP) as precursor titania and added $\text{Fe}(\text{NO}_3)_3$ as Fe source. Subsequently, the antimicrobial test (*Escherichia coli*, *Staphylococcus aureus* and *Candida albicans*) was carried out under photocatalysis system. The FeTiO_3 was formed on 20 of 20°, 24°, 36°, 48°, 53° and 62° having crystal size 53.75 nm. Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) was investigated that the particle sized was under 100 nm and Fe element peak was on 6.398 keV. The antimicrobial test showed that the efficiency of 15 % FeTiO_3 was active under visible light irradiation to inhibit of *E. coli*, *S. aureus* and *C. albicans* with diameter zone were 18.778, 19.889 and 20.22 mm, respectively.

Keywords: Ilmenite, Antimicrobial activity, Photocatalyst.

INTRODUCTION

Currently, nanoparticle materials are becoming the interest of researchers for development in science and technology [1,2]. The development of preparation methods and applications of nano-sized materials has many advantages namely having large surface contact areas and their efficient use because of their small size [3,4]. According to Khan *et al.* [5] and Maulidiyah *et al.* [6], the characteristics of nanoparticles depend on their size, distribution, morphology and phase. Nanoparticles have many uses such as detectors, catalysts, surface coating agents and antibacterials [7,8]. Materials with nanometer-scale particle size commonly used in commercial products range from 1 to 100 nm [9].

One of the nanoparticle types that is currently being developed based on titanium dioxide (TiO_2) and has superiorities of being environmentally friendly, non-toxic and several other benefits [10,11]. However, the reactivity of TiO_2 is only active in ultraviolet (UV) light which affects its performance so that the modification of TiO_2 material is needed to improve the performance under visible light which expected to be able to utilize sunlight as abundance source in nature [12-14].

The most popular dopant elements which is easily made and found is ilmenite material (FeTiO_3). Its existence can be found in nature from the extraction process of iron sand

leaching [15,16]. Based on various studies indicating that the extraction of iron sand produces very little involvement so that the utilization of FeTiO_3 is currently less optimized. In addition, it takes long time to obtain FeTiO_3 from iron sand. Therefore, an appropriate method for obtaining FeTiO_3 as a model of natural ilmenite is to synthesize FeTiO_3 using sol-gel method. The sol-gel method is one of the most effective methods to modify materials so it will produce new materials and new properties with size under 100 nm [17].

Chen [18] has synthesized FeTiO_3 using sol gel method with particle size of 20 to 60 nm that potentially as photocatalyst material for methylene blue dye adsorption. The addition of $\text{Fe}(\text{NO}_3)_3$ compound can decrease band gap value of TiO_2 by 2.03 eV. Raghavender *et al.* [19] succeeded in synthesizing FeTiO_3 by adding $\text{Fe}(\text{NO}_3)_3$ and TiCl_4 using sol-gel method which has been applied as dye adsorption agent. FeTiO_3 containing ferro(II) oxide (FeO) and TiO_2 are classified in semiconductor materials as smart materials because they have photoactive properties and respond to visible light. The function of adding material elements to the TiO_2 crystal lattice has been extensively studied by various researchers to improve the physical and chemical properties with expectations of providing optimal benefits for human use and utilized as an antimicrobial ingredient [20,21].

According to Manjunath *et al.* [22] the addition of TiO_2 catalyst with UV light irradiation to inactivate *E. coli* bacteria showed that it has very good performance, while the use of visible light irradiation takes a very long time. TiO_2 acts as photocatalyst suppresses the growth of microorganisms by producing hydroxyl radicals ($\cdot\text{OH}$) and reactive oxygen species (ROS) produced during UV light irradiation [23]. The role of hydroxyl radicals an important in inactivating microorganisms by oxidizing phospholipids contained in cell membranes [24]. Kalantari and Emtiazi [25] reported that when $\cdot\text{OH}$ reacts with H_2O_2 produced from TiO_2 and Fe ions, it can damage the protein structure. The combination of Fe ions in nanoparticle-sized TiO_2 crystal lattice is expected to inactivate pathogenic microbial. Microbes pathogenic are one of the causes of many infections of diseases found. Humid environmental conditions allow the development of bacteria and fungi [26].

Microbes pathogens can be found in several places such as in hospital, bathroom, kitchen, children's playground and other rooms in a house. Several types of harmful bacteria *e.g.*, *E. coli* and *S. aureus*. *S. aureus* can cause skin diseases, infection of surgical wounds and pneumonia and *E. coli* bacteria can cause diarrhea, stomach cramps and kidney failure [27,28]. In addition, *C. albicans* is one of fungus types that causes candidiasis disease, namely diseases on mouth, mucous membranes, digestive tract and respiratory tract [29]. Candidiasis is an infection of the *Candida* genus especially *C. albicans*. More than 150 species of *Candida* have been identified and seventy percent of candidiasis is caused by *Candida albicans* [30]. So, this study aims to develop FeTiO_3 material synthesized using sol-gel method and can be utilized in the industrial field as an antimicrobial desifectant (*E. coli*, *S. aureus* and *C. albicans*).

EXPERIMENTAL

Synthesis of ilmenite (FeTiO_3): FeTiO_3 precursor was prepared from solution 1 in the form of colloidal solution of TiO_2 prepared by 4 mL titanium tetra-isopropoxide (TTIP) of controlled hydrolysis, 0.5 mL of acetyl acetone and 15 mL of ethanol (99 %). Solution 2 was 15 mL of 99 % EtOH and 2 mL of distilled water with addition of 1 mL of 0.1 M acetic acid and added with 0.5 M of $\text{Fe}(\text{NO}_3)_3$. The solution mixture was refluxed for 3 h at 50 °C. Then, FeTiO_3 sol was calcined at 450 °C to obtain FeTiO_3 nanocrystal.

Characterizations: The morphology of the synthesized FeTiO_3 nanocrystal was observed by using SEM (JEOL, Model 5900LV) which supported by EDX analyze (Oxford) to obtain the composition of elements. The X-Ray Diffraction (XRD) (Shimadzu PC. 6000) to obtain the crystal type and crystal size of FeTiO_3 . To provide the existence of Fe and TiO_2 by using X-ray fluorescence (XRF) type Epsilon3.

Antimicrobial activity

Preparation of 15 %, 10 % and 5 % FeTiO_3 sol gel:

The 15 % FeTiO_3 solution test was prepared by weighing 7.5 g of FeTiO_3 into a 50 mL flask then diluted and sterilized in an autoclave at 1 atm pressure at 121 °C for 15 min and diluted in concentrations of 10 % and 5 %. The positive control solution used was 4 % phenol solution whereas the negative control used in this research was aquadest.

Antibacterial activity test: The antibacterial activity was performed by well-diffusion method. The well method was performed by using 2 median layers, namely solid NA media and semi solid NA. The solid NA was poured into petri dish as base layer and made a well placed on top of the base media. Semi-solid NA was added into the tested bacteria (*E. coli* and *S. aureus*) of 1 mL and homogenized using vortex at ± 45 -50 °C. Then semi solid NA was poured over the base layer (solid NA) where tips hole had been made and filled with 50 μL of FeTiO_3 and sterile aquadest as negative control and phenol as positive control. Then, it was incubated in an incubator for 24 h at 37 °C. After the incubation period, measurements of the formed inhibit zone were performed using vernier caliper.

Antifungal activity test: The antifungal activity was performed by the well-diffusion method. This method was performed by using 2 layers namely the solid PDA media and semi-solid PDA. Solid PDA was poured into petri dishes as the base layer and semi solid PDA was poured over solid PDA containing 1 mL of *C. albicans*. Then, it was discharged with 50 μL of FeTiO_3 solution and sterile aquadest as negative control and phenol as positive control. Then incubated in incubator for 24 h at 37 °C and measurement of inhibition zone using vernier caliper.

RESULTS AND DISCUSSION

Synthesis of ilmenite by using sol gel method: FeTiO_3 nanoparticles were synthesized using the sol-gel method which has advantage namely easy to control the reaction conditions such as pH, temperature and rate of precursor hydrolysis [31]. In this study, FeTiO_3 sol was made with TTIP which firstly reacted within acetyl acetone and ethanol. TTIP is the source of nano-sized TiO_2 formation by hydrolysis technique. The addition of acetyl acetone served as a ligand for titanium-chelating in order not to produce TiO_2 precipitate which characterized by the change of sol to yellow colour. Ethanol served as controlling the rate of hydrolysis because TTIP is easily transformed into $\text{Ti}(\text{OH})_4$ when it directly reacts with water [3]. The process of FeTiO_3 sol formation with sol-gel method can be seen in Fig. 1A.

$\text{Fe}(\text{NO}_3)_3$ was used as Fe(II) source to form FeTiO_3 structure. Based on Chen [18] and Raghavander *et al.* [19] were used of $\text{Fe}(\text{NO}_3)_3$ very effective to serve as Fe source to form FeTiO_3 and decrease the band gap value of TiO_2 . The composites obtained were then recalcined at 450 °C for 1.5 h to remove solvents such as water and ethanol. Besides, the calcination process aims to decompose $\text{Fe}(\text{NO}_3)_3$ into Fe(II) to be inserted in TiO_2 crystal [3]. The calcination process will generate FeTiO_3 powder which can be seen in Fig. 1B.

Fig. 1. Synthesized FeTiO_3 , (A) sol FeTiO_3 and (B) Powder of FeTiO_3

The addition of Fe ions can increase TiO_2 activity in the visible region to inactivate microbes [20]. Increased activity of the material is determined by the value of the band gap energy that affects the movement of electrons in the semiconductor to form hydroxyl radical species. The decrease in the band gap value of FeTiO_3 has been reported by several researchers like Raghavender *et al.* [19] have successfully synthesized FeTiO_3 with a band value gap of 2.80 eV and Chen [18] who reports that FeTiO_3 has a band gap value of 2.03 eV. From these results, it proved that FeTiO_3 is formed between 2.8-2.03 eV so can be applied under visible light.

Characterization of FeTiO_3 composite

Scanning electron microscopy (SEM): The surface characteristics of FeTiO_3 prepared by the sol-gel method containing TiO_2 and FeO are shown in Fig. 2. According to Nurdin *et al.* [7] nanoparticles are particles having size less than 100 nm. Fig. 2 shows FeTiO_3 with magnification of 10,000 with the formation of white clots showing the TiO_2 compound while the gray clots showing TiO_2 covered by Fe(II).

Emission dispersive X-ray (EDX): The elements content in the natural and synthesized FeTiO_3 can be known by using EDX characterization. The characterization results using EDX can be seen in Fig. 3.

Fig. 3 shows the different of elements types the natural ilmenite (Fig. 3A) and synthesized FeTiO_3 (Fig. 3B). Fig. 3A explained that the natural ilmenite containing many of elements such as Ti, O, Fe, Na, Al and Si. Whereas, the Fig. 3B shows that the composite contains the three expected elements of Ti, O and Fe. The peaks indicating the presence of iron at the energy levels of 0.5, 6.3 and 7.1 keV, whereas the presence of titanium element at the energy levels of 0.5, 4.3 and 5.0 keV. This is in accordance with research performed by Rasidhar *et al.* [32] and Raghavender *et al.* [19]. Fig. 3B shows fewer titanium and iron levels than ilmenite synthesis. EDX results show that natural FeTiO_3 still contains many other compounds (Table-1).

X-ray diffraction (XRD): The aim of XRD analysis is to know the structure of FeTiO_3 crystal from the synthesis result. Fig. 4 is an XRD comparison between natural and synthesized FeTiO_3 composites indicating the presence of FeTiO_3 .

Fig. 4A shows the presence of 5 specific peaks that the presence of natural FeTiO_3 *i.e.* in 2θ were 20° , 24° , 36° , 48° ,

Fig. 2. Morphology of natural ilmenite powder with magnification of 10,000 (a) and synthesized of FeTiO_3 powder with magnification of 10,000 (b)

TABLE-1
ELEMENTS COMPOSITION OF
NATURAL FeTiO_3 AND SYNTHESIZED FeTiO_3

Elements	Mass (%) ^a	
	Natural	Synthesis
C	8.50	—
O	46.50	50.59
Na	0.33	—
Mg	0.37	—
Al	18.38	—
Si	16.04	—
Ti	16.04	47.98
Fe	9.07	1.43

Fig. 3. EDX spectra of FeTiO_3 ; (A) natural ilmenite and (B) synthesized FeTiO_3

Fig. 4. XRD pattern of FeTiO₃; (A) natural FeTiO₃ and (B) synthesized FeTiO₃

53° and 62°. It has a rutile crystal form with a crystal size of 53.75 nm. In addition, Fig. 4B the results of XRD diffractogram analysis of synthesized FeTiO₃ show the presence of 3 peaks in 2θ of 24°, 36° 48° and 53° with the crystal size of 54.3362 nm. Raghvander *et al.* [19] reported that FeTiO₃ has particle size below 100 nm. In addition, Chen [18] successfully synthesizes FeTiO₃ with particle size of 60 nm.

These results have been adjusted based on JCPDS data No. 291-0773. Chen [18] reported that there are six peaks in the region of 2θ = 24°, 32°, 36°, 40°, 48° and 56° with (012), (104), (110) (113) (024) and (116) Miller index which are typical peaks of ilmenite crystals.

X-ray fluorescence (XRF): The synthesis results of FeTiO₃ composite were confirmed with XRF data to identify the chemical components in the sample and how great the percentage was and to know the compounds produced from the sol-gel method. The results of XRF characterization can be seen in Fig. 5.

Fig. 5. XRF characterization of synthesized FeTiO₃

Fig. 5 shows the results of XRF analysis on FeTiO₃ composite, there are 4 compounds with different percentages. There are 2 compounds that have the largest percentage namely TiO₂

of 95.21 % and Fe of 3.20 %. The results show that Fe element is inserted in TiO₂ crystals to form FeTiO₃ compounds. Samal [33] reported that the highest contents of FeTiO₃ from iron sand are TiO₂ (50 %), FeO (34.20 %), and Fe₂O₃ (12.20 %).

Antimicrobial activity test: The FeTiO₃ composite antimicrobial was conducted against *E. coli*, *S. aureus* and *C. albicans* under visible light. Microbial test was conducted qualitatively based on the clear zone width of microbial media [26,27]. Therefore, a material can inhibit the growth of these microbes in the environment is needed.

This study, antimicrobial activity test used negative and positive control. Negative control used aquadest solvent, while the positive control used phenol with 4 % concentration. Phenol solution with 2-4 % concentration is standard for comparison with other disinfectants in inhibiting microorganism. The purpose using positive control to obtain of FeTiO₃ compound activity tested. If the clear zone diameter of the FeTiO₃ compound is greater than the control zone, it indicates that the FeTiO₃ composite material is very effective as an antimicrobial, whereas if the clear zone formed by the FeTiO₃ composite material is smaller or even absent, then FeTiO₃ is less effective or unusable as antimicrobials.

The composite test of FeTiO₃ nanoparticles was performed with two treatments, under visible and UV lights. This was performed to determine the effect of Fe(NO₃)₃ which is expected to improve the FeTiO₃ composite performance under visible light. The inhibitory activity of FeTiO₃ compound against pathogenic microbes by the diameter of clear zone. The diameter of clear zone produced from each microbe by using visible light can be seen in Table-2 and for the treatment under UV light can be seen in Table-3.

TABLE-2
ANTIBACTERIAL ACTIVITY TEST OF
FeTiO₃ COMPOSITE UNDER VISIBLE LIGHT

Microorganism	15 %	10 %	5 %	(+)	(-)
<i>E. coli</i>	18.778	14.111	9.666	6.22	—
<i>S. aureus</i>	19.889	15.444	12.888	6.77	—
<i>C. albicans</i>	20.222	15.777	13.000	10.33	—

TABLE-3
ANTIBACTERIAL ACTIVITY TEST OF
FeTiO₃ COMPOSITE UNDER UV LIGHT

Microorganism	15 %	10 %	5 %	(+)	(-)
<i>E. coli</i>	3.667	3.444	2.889	6.220	—
<i>S. aureus</i>	5.556	5.333	3.111	6.660	—
<i>C. albicans</i>	17.556	14.110	11.333	10.667	—

Tables 2 and 3 show the increased concentrations that affect TiO₂ performance under visible light. FeTiO₃ performance is further increased in activating *E. coli*, *S. aureus* and *C. albicans* under visible light than UV light. Based on data, it showed that the FeTiO₃ composite can inactivate microbes under visible light. This is in accordance with Kalantari and Emtiazzi [25] report that the FeTiO₃ was able to inactivate the growth of *Bacillus* sp. by 50-87 % under visible light. The FeTiO₃ composite can inactivate microbes by damaging the cell walls of each microbe. FeTiO₃ compounds will react with water and form •OH and O₂^{•-} radicals which will damage bacterial cell walls [34].

Fig. 6 explain that the *E. coli*, *S. aureus* and *C. albicans* were interact with FeTiO_3 composite compound. The three microbes secrete enzymes to protect cells from oxidation reactions, but when $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ concentrations are higher than the number of enzymes secreted by *E. coli*, *S. aureus* and *C. albicans* will cause the third cell of the microbe to oxidize which will have an impact on death. Deaths of microbial can also be caused by the activity of $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ compounds which damage the cell wall, so that cells will leak and the cytoplasm of cells will out and will experience dryness results in death [34].

Fig. 6. Purpose of mechanism inactivation of microbials

The FeTiO_3 composite is the most active against *C. albicans* than bacteria. This is due to the interaction between ergosterol and radical compounds ($\cdot\text{OH}$ $\text{O}_2^{\cdot-}$) will damage *C. albicans* cell membrane. Antifungal activity depends on the interaction between antifungal compounds with sterols in fungi cell membranes, especially ergosterol. It will experience dryness, due to the formation of interactions between sterols and antibacterials [30].

Tables 2 and 3 data shows that the FeTiO_3 composite is more susceptible to damage Gram-positive bacterial cell walls than Gram-negative bacteria. This is due to differences in cell wall structures of both types of bacteria. The cell walls of Gram-positive bacteria consists of peptidoglycan layers that form thick and rigid structures to maintain the integrity of the cell, whereas the cell walls of Gram-negative consist of thin peptidoglycan layers and have layer of wall outside the peptidoglycan layer that makes it difficult for antibacterial compounds to destroy Gram-negative bacteria [35].

The results of this study prove that FeTiO_3 composites are more effective in inactivating microbes under visible light compared with UV light. This proves that the change of TiO_2 crystal structure by Fe ions effects the change of opto-photonic properties of a material.

Conclusion

The FeTiO_3 successfully synthesized by using the sol-gel method. The SEM indicated that the FeTiO_3 nanoparticle has formed under 100 nm. Supported by using EDX to analyze of elements composition on Ti, O and Fe were 47.98 %, 50.59 % and 1.43 %, respectively. The XRD result showed the rutile

polymorph formed with crystal size 53.75 nm in 2 θ were 20°, 24°, 36°, 48°, 53° and 62°. Antimicrobial activity test (*E. coli*, *S. aureus* and *C. albicans*) under visible light was a better activity than UV light. The 15 % sol-gel FeTiO_3 showed the high-inhibited zone of *E. coli*, *S. aureus* and *C. albicans* were 18.778, 19.889 and 20.222 mm, respectively.

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