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# FABRICATION OF SILICA-TITANIA AS CONSOLIDANT AND SELF CLEANING FOR THE CONSERVATION OF ANDESITE STONE

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***Abstract***

*The composites of silica-titania that have consolidant and self-cleaning property have been synthesized by mixing titania and colloidal silica. The coating of stone using silica-titania could improve the mechanical properties of andesite stone. In addition, the coating created the superhydrophilic properties and similar visual appearance with untreated andesite. The self-cleaning performance of treated andesite could remove the 92% of congo red and 67% of methylene blue as staining agents through photocatalysis process.*

***Keywords:*** *Colloidal silica; Titania; Consolidant; Self-cleaning; Andesite*

## Introduction

Indonesia has lots of heritage building all over the country such as the temples of Borobudur, Prambanan, and other temples, whereas mainly composed by andesite stone. Andesite is an extrusive igneous rock, has porous texture and contains 50-65% of silica. Organic pollutant, soiling, staining and cracking are serious problems that needed to solve. Cleaning is an action to remove the dirt, stain, polluting fluids, and living organism such as fungi algae, lichen, and bacteria. Photocatalysis is a widespread of cleaning technique thus allowing the degradation of pollutants and living organism. Titania has been widely used as photocatalyst because effective, inert, cheap, stable, and high activity. When photons are absorbed by titania, electrons will be promoted from valence band to conduction band, generates holes. In contact with water, holes produce hydroxyl radical. These radicals have ability to degradate the organic matter. Under UV exposure, titania becomes superhydrophilic (low water contact angle) therefore prevents the contact between surfaces and dirt. Quagliarni et al. reported that the two properties of titania (photacatalysis and superhydrophilicity) contribute to the easier of degradation process, since the formation of a water film over treated surfaces and the photocatalytic degradation of organic pollutant [1]. Because of that mechanism, it possible to obtain self-cleaning surface. In the last few years, titania have been used in the fields of conservation the travertine, limestone, white marble, and lecce stone [1-3].

Cracking is a form of stone decay that implies rupture of parts of the same one or loss of mater. Consolidation is one of action to restore some strength. Consolidants will penetrated to the stone, improve the pore structure, and increase the hardness of stone. Consolidants are

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usually applied to the surface stone by brush, spray, pipette, or by immersion [4]. The addition of silica nanoparticles with grain size less than 50 nm have been successfully increase the compressive strength values of sandstone through the ability to fill the big pores between grains. It also cover the grains of the sandstone with almost homogenous polymer networks [5]. Colloidal silica has often been used as consolidant whereas the adhesion can be controlled through silica dilution. It has a minimal effect on water vapor permeability, stable, compatible with silica stone, low toxicity, and ease of use. The previous research reported that colloidal silica easy to match when mixed with sand, crushed sandstone, and local earth. It also doesn't leave the color residues in the stone [6].

From these findings, our research has been to prepare a material that has both properties, self-cleaning and consolidant for the preservation of historical stone, especially andesite. Titania based self-cleaning able to acts as depolluting and biocidal treatment through its photocatalytic effect. Colloidal silica based consolidant can provides the uniform coating, high compatibility with andesite because silica is the main component of andesite, approximately 50-65%. From this phenomenon, silica consolidant easy to insert on the pore of andesite since the similar acidity. The combination of silica-titania for the preservation of limestone have been reported by *L. Pinho and M.J. Mosquera* [7]. Colloidal titania was added to the silica oligomer in the presence of n-octylamine as surfactant. The aims of adding surfactant are prevent cracking and enhance the photocatalyic activity by creating a mesoporous nanocomposite.

In this study, we have prepared a silica-titania composite from titania particles mixed with colloidal silica. Titania particle was synthesized using titanium tetraisopropxide as titanium source and ethylene glycol as a dispersant. Colloidal silica was observed from Ludox HS40. We evaluated the performance of silica-titania for the following: (1) hydrophilicity; (2) hardness properties; (3) self-cleaning properties using congo red and methylene blue as pollutant model.

## Experimental

### *Materials*

Titanium tetraisopropoxide, TTIP (by Sigma Aldrich) and colloidal silica, Ludox HS-40 (by Sigma Aldrich), were the main components in our research. The following reagents were used for this synthesis: ethylene glycol, ethanol, congo red, methylene blue, hydrochloric acid, and demineralized water. That chemicals were purchased from Merck, analytical grade, and used as received without further purification. The used instruments were infrared spectrophotometer (Shimadzu 8400), XRD (Philips X'PERT), SEM-EDX (Zeiss EVO MA 10), Vickers Hardness (Mirutoyo HM 211), UV-Vis spechtrophotometer (Shimadzu UV 1800).

### *Preparation of silica-titania composite*

Titania was prepared according to the previous literature [8]. TTIP was added to ethylene glycol with stirring at room temperature. After 30 min, water was added to the mixture. The acidity of mixture was kept at pH = 1.5 using HCl. Subsequently, the mixture was refluxed at 140°C for 16 h under vigorous stirring. The obtained solution was washed using ethanol and water till neutral. The solid titania was dried at 100°C and characterized using XRD. For application, titania was dispersed in water under ultrasonication. Composite silica-titania was prepared by mixing the suspension of titania with colloidal silica in each of the following ratios 3:7; 5:5: and 7:3. After the preparation of composite, the composite was analyzed using infrared spectrophotometer.

### *Coating of andesite stones*

Before being used for coating, andesite stones were cut into dimension 3x3x1cm. The composites were brushed onto the stone. After that, the treated stone was dried and measured the water contact angle. The hardness and morphology properties of treated stone were characterized using Vickers and SEM-EDX.

Finally, the self-cleaning effectiveness of treated stone was tested using congo red and methylene blue as staining agents. The stain was dropped onto the surface of treated stone, and was then irradiated under UV exposure. The concentration of stain after irradiation was measured using UV-Vis spectrophotometer UV-Vis [9-16]. The percent of stain discoloration was calculated from the following equation: stain discoloration (%) = $100\times(C_0-C_t)/C_0$, where $C_0$ represents the initial concentration of stain, $C_t$ represents the concentration of stain after irradiation. In this work, the composition of silica-titania and time of irradiation were investigated.

## Results and Discussions

The structure of synthesized titania were clearly confirmed by XRD analysis. The XRD pattern of synthesized titania was shown in Figure 1. The diffractogram showed the intensive peak at 2θ = 25.36°; 37.88°; and 48.2° which confirmed as anatase $TiO_2$. Furthermore, the synthesized titania was combined with colloidal silica to produce the silica-titania composite. FTIR spectra was used for further screening the interaction of silica and titania in the various composition (Fig. 2). All of materials exposed the bands about 478, 910, 1111, and 3425cm$^{-1}$. The band about 478cm$^{-1}$ was attributed to the Ti-O-Ti vibration [17]. The band at 910cm$^{-1}$, was consistent with Ti-O-Si vibration. The spectrum located at 1111cm$^{-1}$ was attributed to Si-O-Si bending [18]. The broad band at 3425cm$^{-1}$ verified the Si-OH groups [19]. Moreover, the large area of hydroxyl group able to increase the hydrophilicity and the rate of photocatalysis. The hydroxyl groups interact with holes, therefore they prevent the recombination of electron-holes [20]. The composite silica-titania with composition 7:3 displayed the larger area of hydroxyl group than others.

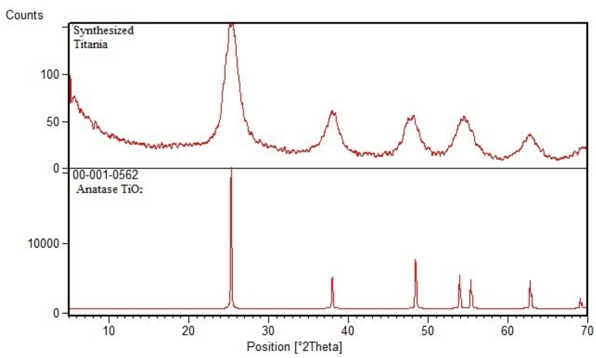


**Fig.1**. The diffractogram of synthesized titania

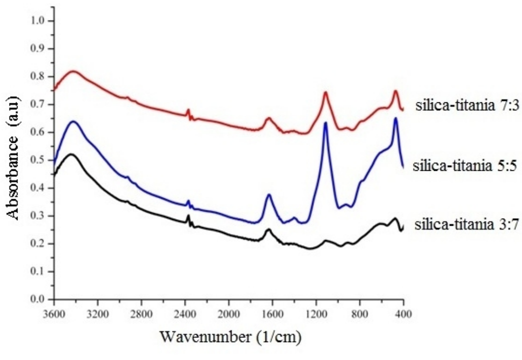


**Fig. 2**. The FTIR spectra of silica-titania composites with various compositions

The composites silica-titania was coated onto the surface of andesite. The result stated that treatment did not change the visual appearance of andesite, therefore we assume that composites silica-titania are promising of coating material (Fig. 3). The wettability of treated stone were assessed by measuring the water contact angle. The water contact angle of bare andesite, coated andesite using silica titania 3:7; 5:5; and 7:3 were 23.26°; 13.72°, 7.19°, and 0° (Fig. 3). In particular, the ratio of silica-titania amount greatly influenced the contact angle. The presence of silica able to enhance the surface acidity, whereas can adsorb the more of hydrophilic hydroxyl group [18].

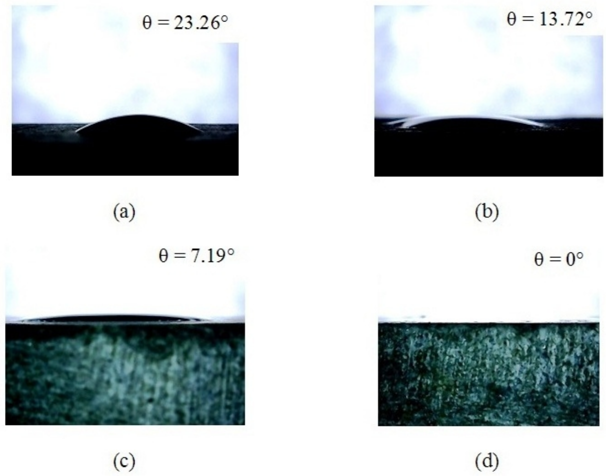


**Fig. 3**. The visual appearance of contact angle of investigated andesite areas:
a. treated with composition of silica-titania composite 3:7;
b. treated with composition of silica-titania composite 5:5;
c. treated with composition of silica-titania composite 7:3;
d. untreated andesite stone

The consolidation effectiveness of silica-titania were determined using Vickers hardness. The hardness of bare andesite, coated andesite using silica-titania 3:7; 5:5; and 7:3 were 141.68; 163.8; 177.84; and 285.4 VH. The greater the concentration of silica, the higher of obtained the hardness value. This behavior is due to many silica penetrates into the pore of andesite and builds the linkage whereas generates the rigid structure.

The presences of silica-titania over stone surface were clearly confirmed by SEM-EDX analysis. Figure 4 showed the micrographs of bare and coated andesite. From this result, we assumed that the andesite was successfully coated where there was an increasing amount of silica and titania in the coated andesite. The coating was also homogeneously spread over stone.

The self-cleaning property was assessed by photo discoloration of staining agents (congo red and methylene blue test). The influence of composition silica-titania toward the loss discoloration ability was shown in Figure 5. In this study, there was an interesting perspective where composition of silica-titania 7:3 exhibited the higher degradation than composition of 3:7. From this result, we assumed that discoloration process was influenced not only the amount of titania, but also the amount of silica. In other words, there was synergism effect between silica and titania. Silica can increase the surface area of titania because silica acts as support. The large surface area results the improvement of site active interaction in the photocatalysis process [18]. Moreover, silica also acts as a dopant that can reduces the gap energy of titania, therefore it promotes the easier electron excitation from valence band to the conduction band [21]. The effect of time irradiation towards the self-cleaning ability was displayed in Figure 6.

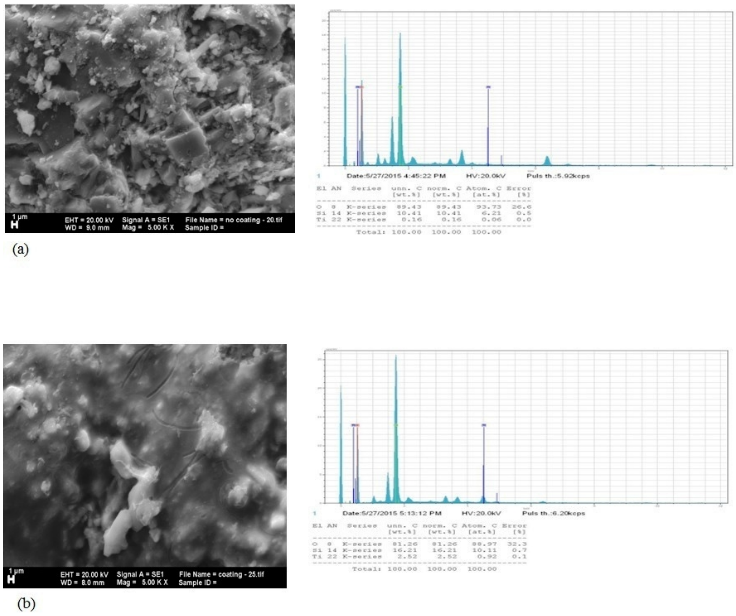

**Fig. 4**. The SEM-EDX analysis of untreated (a) and treated (b) andesite stone

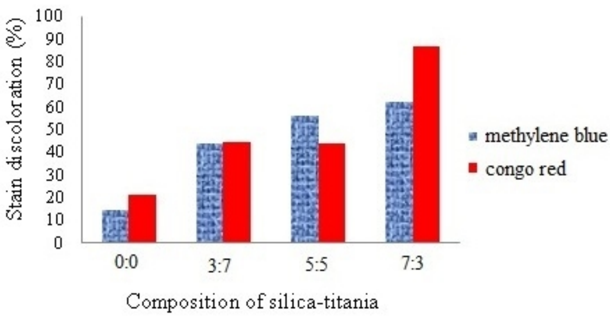


**Fig. 5**. Percentage of the stain discoloration with different composition of silica-titania

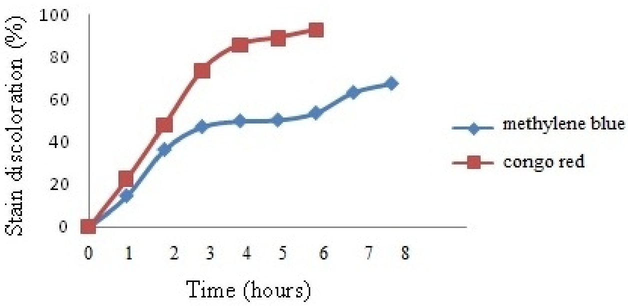


**Fig. 6**. The influence of irradiation time towards the percentage of the stain discoloration using silica-titania composites 7:3

The results indicated that the longer of irradiation time, the higher of degradation percent of staining agent. Silica-titania able to remove the congo red about 92% at 6 hours and methylene blue about 67% at 8 hours.

## Conclusions

The composite of silica-titania as consolidant and self-cleaning coating for andesite stone, the main component of heritage building in Indonesia was reported. The application of silica-titania have required the basic criteria of preservation that it did not impact the visual appearance the stone. Furthermore, the composite increased the hardness properties of andesite. It also efficient to remove the staining agents on treated surface. In other word, the promising material have successfully synthesized. Further study are necessary to better assess suitability and durability of silica-titania coating for long term. The depth investigation also necessary to analyze the self-cleaning properties against biocidal agents.

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