Using Self Cleaning TiO_2 Photocatalyst in the Making of Ceramic Tiles to Decrease Ammonium Concentration and Bacterium Growth

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Abstract :

The purpose of this research is using self-cleaning TiO_2 photo catalyst in the making of ceramic tiles to decrease ammonium concentration and bacterium by determining the most appropriate percentage of TiO_2 towards the density, hardness, and bending strength on ceramic tiles, degrading ammonium concentration and bacterium on the tiles on sintering temperature with the optimum percentage of catalyst volume variation. Result of the research shows that the best condition in making ceramic tiles is when the sintering temperature is 1100°C, the best density is 15% TiO_2 that is (2.697 ± 0.049) gram/cm^3, the best hardness and bending strength by adding 10% TiO_2 (592.594 ± 22.518) Mpa and (1929.696 ± 411.54) Mpa, therefore the making of ceramic is using 1100°C sintering temperature and adding 10% TiO_2. The decreasing of the ammonium concentration on ceramic tiles by adding 10% TiO_2 on sintering temperature of 1100°C with 2 hours ray time is 65.23%. On glasured ceramic tiles, degradation of *E. Coli* is 100% with 3 hours ray time, while *P. Aeruginosa* and *S. aureus* are only degraded 9.99%. On non glasured ceramic tiles, degradation of *P. Aeruginosa* is 100% with 2 hours ray time, while *E. coli* dan *S. aureus* are only degraded 9.99% with 3 hours ray time. Ceramic tiles with 10% added TiO_2 is very suitable for bathrooms or places with water that have the possibility of *E. coli* or *P. aeruginosa* contamination.

Keywords: Ammonium, Bacterium, Ceramic tiles, Self-cleaning, TiO_2 catalyst

1. Introduction

TiO_2 catalyst is a self-cleaning substance which has the ability to omit strong odor like ammonia. Ammonia comes from the decomposition of urea as a component of urine and is converted into energy and NH_3 by microorganism. Ammonia (NH_3) interferes breathing system, irritates the mucous membranes of nose and throat. The concentration of ammonia at 5000 ppm can cause laryngeal and lung edema, death, eye irritation (red and watery eye), total blindness, skin rash, and is teratogenic in the chronic exposure **[1]**.

Besides that, the self-sterilizing TiO_2 catalyst has the ability to kills the germs (anti-bacterial substance) such as the germs that can be found in the toilet **[2]**. According to the Provincial Regulation of Central Java No 10 year 2004 on Sewage Water Standard, the maximum level of ammonia is 0.5 ppm as nitrogen, and the hospital surgery rooms must not contain any bacteria so that a research to reduce or eliminate the ammonia and bacteria is needed **[3]**. The amount of ammonia concentration and the speed of bacterial growth can be reduced by the presence of ultraviolet rays from sunlight or ultraviolet light. Unfortunately the bacteria grow faster than the reduction process. Reducing the amount of ammonia can be done effectively by using transition metal oxides such as TiO_2. Combined with the presence of ultraviolet light, the substance can produce OH radicals to lower ammonia concentration and bacteria growth. TiO_2 photo catalysis is capable of absorbing radiation and produces OH radicals which are powerful oxidants for water and air purification, anti-bacterial, anti-cancer, anti-oil, and anti-fogging. Active radical species (ROH) which consists of OH and O_2 is an oxidized solid substance to degrade organic matters of the bacteria's cell wall and cell membrane.

The ceramic tiles were made from clay and kaolin based on 40:60 ratio, then TiO_2 (varied between 5, 10, and 15 % of the volume) was added. Next, the tiles were formed using hydraulic press machine and heated between sintering temperature 900˚ – 1100˚C, some of them were glazed and others were not. After that, those ceramics tiles were tested for their density, hardness, and fracture toughness to determine the quality. Compacting pressure, un-axial pressing, and sintering temperature are the factors that determine the quality of ceramic tiles **[4]**. The research objective is making ceramics with variations on sintering temperatures and TiO_2 amount as the catalyst on glazed and unglazed ceramics, determining the optimum sintering temperature and TiO_2 amount based on density test, hardness, fracture toughness, and bending test, reducing the ammonia and bacteria concentration on glazed and unglazed ceramic tiles with optimized sintering temperature and TiO_2 catalyst amount.

2. Research Methodology

2.1. Making the Ceramic Tiles

Clay taken from Pagerbelah, Karangkobar, Banjarnegara was soaked for one night and mixed to make a porridge-like material. After that, the material was formed into small pieces, put under the sun, and crushed the pieces to get 100 mesh in size.

2.2. Making the Glaze for the Tiles

The material containing 250 g PbO, 1000 g TSG, and 100 g Zirconium was mixed and soaked in 40% water. After that, the glaze was added with 5.10, and 15% TiO_2, applied on ceramic tiles, and heated at sintering temperature 900˚C - 1100˚C.

2.3. The decrease of ammonia and bacteria concentrate on glazed and unglazed ceramic tiles with optimum sentering temperature along with increase % volume of optimum TiO_2 catalyst.

80 µl of ammonia or 100 µl of bacteria was added into TiO_2 10 % ceramic tiles of (3×1×0.5) cm^3. Then the tiles were put into the reactor equipped with a 40 watt UV lamp and lighted in certain amount of time. Content of ammonia left was established by spectrophotometer and the living bacteria is put into 10 mL of appropriate media of certain concentrate, poured into the cell culture dish and incubated for 24 hours, in 37^0C temp and left in the incubator for 1-4 hours. Next, the number of surviving bacteria was counted and the action was repeated 3 times each.

2.4. Ammonia Degradation Procedure on Ceramic Tiles containing 10% TiO_2 with varied Irradiation Length

80 ml solution of ammonia 100 ppm was pippeted and dropped on ceramic tiles containing 10% TiO_2 with size (3 × 1 × 0.5) cm^3. Then, the ceramic tiles were inserted into the reactor which is equipped with 40 watt UV lamp. The remaining ammonium level on the tiles was checked after 30, 60, 90, and 120 minutes irradiation and five repetitions of the test were performed.

2.5. Ammonia Level Measurement on Ceramic Tiles

Remaining ammonia on the ceramic tiles was washed with 5 ml of distilled water and then put into a 10.0 mL volumetric flask. Then 0.40 ml Nessler reagent, 0.25 ml KNa Tatrat, and distilled water were added to fulfill the volume, after that, it was homogenized. The absorbance was read with a spectrophotometer at a wavelength of 415nm.

2.6. Degradation Procedure using S. aureus, E.coli dan P. aeruginosa on ceramic tiles which are catalyzed by TiO_2 5, 10, dan 15 % (glazed and unglazed)

A drop of 100 µl bacteria was put on ceramic tiles of (3×1×0.5) cm^3 containing 10 % TiO_2. Then the tiles were put into the reactor equipped with a 40 watt UV lamp and lighted for 0-4 hours. The living bacteria is put into 10 mL of appropriate media of certain concentrate, poured into the cell culture dish and incubated for 24 hours, in 37ºC temp and left in the incubator for 1-4 hours. Next, the degradation percentage of *S. aureus, E.coli* and *P. aeruginosa* was calculated by dividing the surviving bacteria with the number of bacteria, times 100%.

3. Results and Discussions

3.1. Glazed and non Glazed Ceramics Test with Varied Volume of TiO_2 as the Catalyst

The best conditions in the manufacture of ceramic tiles is the sintering temperature of 1100^oC, the best density by 15% of the TiO_2 (2.697 ± 0.049) gram/cm^3, the violence and the best bending strength with the constant

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addition of 10% TiO_2 is (592.594 ± 22.518) MPa and (1929, 696 ± 411.54) MPa, so that the manufacture of ceramics using sintering temperature of 1100^{o}C and the addition of 10% TiO_2.

3.2. The Ammonia Declined Percentage on Several TiO_2 at 100 ppm Ammonia

The calculation Ammonia of declined percentage in ceramic tiles in several amount of photocatalyst TiO_2 0%, 5%, 10%, and 15% on Table 1.

Table 1. Ammonia Declined Percentage in Several TiO_2 at 100 ppm Ammonia Solution

Amount of photocatalyst TiO_2	Initial Ammonia Level (ppm)	Final Ammonia Level (ppm)	Declined ammonia level (%)	Ammonia Level Decline with photocatalyst TiO_2 0% (%)
0%	100	73.84	26.16	-
5%	100	59.98	40.02	18.77
10%	100	35.06	64.94	52.52
15%	100	25.57	74.43	65.37

Table 1 shows the addition of TiO_2 photocatalyst on ceramic tiles after irradiation for 60 minutes can reduce levels of ammonia. This is because the TiO_2 photocatalysts have self-cleaning properties which function to eliminate the urine odor. TiO_2 photocatalysts in the presence of ultraviolet light can produce OH radicals to reduce levels of ammonia. However, the addition of TiO2 photocatalysts is not the only factor that can reduce levels of ammonia, but also due to the volatile nature of ammonia and ceramic tiles with a number of 0% TiO_2 photocatalyst were used as a scale or control. Table 1 can be seen too that the greater the amount of photocatalyst TiO_2 was reduced, the more levels of ammonia were produced, but this can not be concluded that the decrease in ammonia levels in the ceramic tile is optimal with the addition of 15% TiO_2 photocatalysts. It is because the increase which occurs is not comparable with the addition of TiO_2 photocatalysts. Increasing the number of photocatalyst TiO_2 (0% - 5%) decreased the levels of ammonia 18.77%, TiO_2 (5%-10%) decreased the ammonia levels by 33.75%, and TiO_2 (10%-15%) decreased the levels of ammonia 12.85%, so it can be concluded that the optimal reduction in ammonia levels in the ceramic tile is with the addition of TiO_2 photocatalysts as much as 10%. The percentage decrease in ammonia levels in the ceramic tile containing 10% TiO_2 can be seen in Table 2.

Table 2. Decreased levels of ammonia on ceramic tiles containing TiO_2 10%

Duration (minutes)	Decreased levels of ammonia (%)
30	12.23
45	26.61
60	37.31
90	65.23

From Table 3 that the results in decreased levels of ammonia-containing TiO_2 ceramic tiles on the variation of radiation (0-30) hours is 12.23%, irradiation (30-60) hours is 14.38%, irradiation (60-90) minutes is 10.70%, and irradiation (90-120) minutes is 27.92%, which can be obtained that the ceramic tiles with% catalyst volume TiO_2 10% and irradiation time of 120 minutes can reduce ammonia levels by 65.23%.

3.3. Reduction in Escherichia coli, Staphylococcus aureus, and Pseudomonas aeruginosa bacteria without the glaze on ceramic tiles and with glaze over the incubation for 0-4 hours

Culture of the bacterium E. coli, Staphylococcus aureus and Pseudomonas aeruginosa in BHI media were incubated in the photocatalic reactor, by irradiation with light UV for 1, 2.3, and 4 hours, then calculated the amount of reduction in bacterial counts for each species on Table 3.

Table 3. The number of bacteria without and with glaze on ceramic tiles

Type of the bacteria	Number of cells (cells/ml)	Number of cells per ml				
		Ceramic tiles	Inc. 1 hour	Inc. 2 hours	Inc. 3 hours	Inc. 4 hours
E.Coli	1.9×10^{9}	Glazed	190	20	0	0
		Not glazed	110	23	15	11
P. aeroginosa	3.4×10^{8}	Glazed	1466	120	12	0
		Not glazed	15	0	0	0
S.aureus	2.7×10^{9}	Glazed	207	80	60	22

Table 3 shows that the number of bacteria of all three types of bacteria in a glazed ceramic tile and non-glazed one shows a decrease in the number of bacteria. This happens because the TiO_2 has self-cleaning properties and self-sterilizing **[2]**. Mechanism of inhibition of bacterial growth due to TiO_2 photocatalysts can inhibit protein synthesis (DNA synthesis), which causes damage to cell walls of bacteria and damage enzymes, thus, they can kill bacteria. Degradation percentages of bacterial growth on glazed and non-glazed ceramic tiles are listed on Table 4.

Table 4. Bacteria Growth Degradation Percentage in Glazed and Non-Glazed Ceramic Tile during 0-4 Hours Incubation

Type of Bacteria	% Initial Degradation	Degradation Percentage (%)				
		Ceramic Tiles	Inc. 1 Hour	Inc. 2 Hours	Inc. 3 Hours	Inc. 4 Hours
E.Coli	0	Glazed	9.99	9.99	100	100
		Non-Glazed	9.99	9.99	9.99	9.99
P. aeroginosa	0	Glazed	9.99	9.99	9.99	100
		Non-Glazed	9.99	100	100	100
S.aureus	0	Glazed	9.99	9.99	9.99	9.99
		Non-Glazed	9.99	9.99	9.99	9.99

Based on Table 4, the ceramic tiles are glazed with the addition of the catalyst TiO_2 10%, *E. coli* bacteria degraded 100% by the incubation time of 3 hours, and *P. aeruginosa* degraded 100% by the incubation time of 4 hours, while *S.aureus* degraded only 9.99% by an incubation time of 1-4 hours. On non-glazed ceramic tiles, the bacteria *P. aeruginosa* and *E. coli* can be degraded 100% with a constant incubation time of 2 hours and 3 hours, while *S. aureus* are degraded only 9.99% with an incubation time of 4 hours. It is because *S. aureus* bacteria is a gram-positive bacteria that have cell walls thicker than the cell wall of *E. coli* and *P. aeruginosa* which are included as gram-negative bacteria. The *S.aureus* bacterial cell wall thickness makes it is more difficult for the bacteria to enter OH radicals generated by TiO_2 photocatalyst so that it affects on the degradation of small bacterial growth. This indicates that the ceramic tiles which are glazed with the addition of a catalyst $TiO_2$10%, and non-glazed ones are highly appropriate to be used in the bathroom, because *E. coli* is a normal bacterial flora of human large intestine, so often found in human faeces and contaminate the bathroom. In addition, *P. aeruginosa* were also encountered in the bathroom, because these bacteria are obligate aerobes and able to live in an unfavorable environment.

4. Conclusions

The best condition in the manufacture of ceramic tiles is the sintering temperature of 1100^{o}C, and the addition of 10% TiO_2. Decrease in ammonia concentration in the best conditions ceramic tiles for 2 hours was 65.23%. Ceramic tiles with photocatalyst TiO_2 is very appropriate to be used in a bathroom or places associated with the possibility of water contamination by *Escherichia coli* and *Pseudomonas aeruginosa.*

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