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Formation of Photocatalytic, Antibacterial and Self Cleaning TiO_2 Film on Tiles

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Abstract
To ensure healthier environments in food industries, hospitals, swimming pools, pharmacies etc., we must clean the surfaces many times a day. Introduction of self-cleaning methods will, therefore, be very useful. This research focused on studying photocatalytic anti-bacterial properties of thin films of TiO_2 synthesized on ceramic tiles by both dip coating and spray coating methods. Antibacterial properties are influenced by a variety of factors, such as crystal structure, surface area, nanoparticle size distribution etc. The TiO_2 exist in three crystalline phases. Anatase is one of the most common and favorable phases used in the manufacturing industries due to its uniqueness of functional performance and favorability to humans and the environment. The anatase structure of TiO_2 was obtained after sintering at 450°C for 45 minutes. The microstructures were characterized by a scanning electron microscope (SEM). The study applied Energy Dispersive Spectrometry (EDS) to determine the chemical constituency of the coating. The study revealed that, dip coating the tile delivered a homogeneous and very thin film on the surface. Coated TiO_2 cannot destroy the bacteria but stops growth of bacteria by a considerable percentage.

Keywords
Photo-catalysis, Dip-coating, Anatase, Energy Dispersive Spectrometry (EDS/EDAX), SEM, E-Coli

1. Introduction

In recent years, growth of opportunistic bacteria in the environment has been responsible for a large number of disease outbreaks in a variety of settings. The demand for environmentally responsible construction and the ever more restrictive environmental requirements derived from legislation have increased the functional requirements of tiles (María *et al.* 2010). Substituting antimicrobial tiles for surfaces support healthier environments. Improving the ability to control and destroy microorganisms, is essential to many organizations and industries such as healthcare, food, water treatment and military (Archana *et al.* 2010).

In particular, to improve the surface cleanability properties the photocatalicity of titanium dioxide (TiO_2) nanoparticles has been used. TiO_2 is a photocatalyst and widely utilized as a self-cleaning and self-disinfecting material for surface coating in many applications. These properties have been applied in removing bacteria and harmful organic materials from water and air, as well as in self-cleaning or self-sterilizing surfaces for places such as medical centers (McCullagh *et al*. 2007). In the field of construction and building materials, it maybe the most widely used (Bondioli *et al.* 2013).

1.1 Objective of the Research

The objective of this research is to develop a TiO_2 coated photocatalyst antibacterial tile, and analyze the physical properties of the film and the antimicrobial activity.

1.2 Titanium Dioxide (TiO_2) Photocatalicity

TiO_2 exists in amorphous and crystalline forms. The amorphous form is photo-catalytically inactive. There are three natural crystalline forms of TiO_2; anatase, rutile and brookite. Anatase and rutile have a tetragonal structure, while the structure of brookite is orthorhombic. Brookite is less common than the former two crystal polymorphs and is far more difficult to obtain (Zeljko *et al.* 2011). Anatase and rutile are photocatalytically active, while brookite has never been tested for photocatalytic activity. Pure anatase is more active as a photocatalyst than rutile, probably because it has more negative potential on the edge of the conductive band, which means higher potential energy of photo generated electrons and also because of a larger number of –OH groups on its surface (Amy *et al.* 1995).

TiO_2 activity, however, is influenced by a variety of factors such as crystal structure, surface area, nanoparticle size distribution, porosity and the number and density of hydroxyl groups on the TiO_2 surface (Kwon *et al.* 2008).

2. Experimental Procedure

A nano scale thin TiO_2 film was synthesized on the tile surface in order to not to affect the aesthetic appearance. Two methods were employed to form the thin TiO_2 film on the surfaces of tiles and glass: (1) spray coating; (2) dip coating.

There were, however, difficulties in getting good SEM imagery of TiO_2 films on ceramic tiles. TiO_2 films were, hence developed on Fluorine doped Tin Oxide (FTO) coated glasses as well for improving SEM imagery.

2.1 TiO_2 Solution Preparation and Spray Coating

TiO_2 solution for spray coating was prepared by adding 15 g of TiO_2 powder, 5 ml of surfactant, and 30 ml of acetic acid into a beaker. The mixture was, then stirred in a magnetic stirrer for 20 min, and finally 60 ml of Ethanol was slowly added while stirring continuously for another 20 min.

After preparing the solution, tile samples were coated by using the spray coating method. Finally, all the prepared samples were placed in a furnace and sintered at 450°C for 45 minutes. Hence fabricated films were analyzed using Scanning Electron Microscopy (SEM).

2.2 Ethyl Cellulose Solution Preparation

Ethyl cellulose solution is needed to prepare TiO_2 solution for dip coating tiles (see Section 2.3). 2 g of ethyl cellulose powder and 40 ml of ethanol were put in a bottle and closed properly to prevent vaporization. Contents in the bottle were stirred using magnetic stirrer for 16 hours. Because it did not dissolve properly the following alternate formulas were tried:

- 1 g of Ethyl cellulose in 40 ml of Ethanol

- 1 g of Ethyl cellulose in 40 ml of Acetone

The temperature was, then, slightly increased while stirring. After allowing time for precipitation, the three samples were visually observed. All three appeared same in terms of quantities of precipitates. Therefore, Sample 1 was stirred further, left to precipitate and the solution was taken from the top by using a dropper.

2.3 TiO_2 Solution Preparation and Dip Coating Tiles.

The TiO_2 solution was prepared according to the formula given in Table 1.

Table 1: TiO_2 Solution Mixture Formula

Material	Weight
TiO_2 (P25)	1 g
Ethanol	20 g
Terpineol	4 g
Ethyl Cellulose Solution (Section 2.2)	10 g

All of above were measured and put into the bottle. It was stirred for 4 days at 8 hours per day. Powder particles, however, were not properly dissolved in the solution.

Small tile pieces were prepared by cleaning using ethanol. As described in Sections 2.4 and 2.5, two types of Samples, A and B, were made. They were labeled as given in Figure 1.

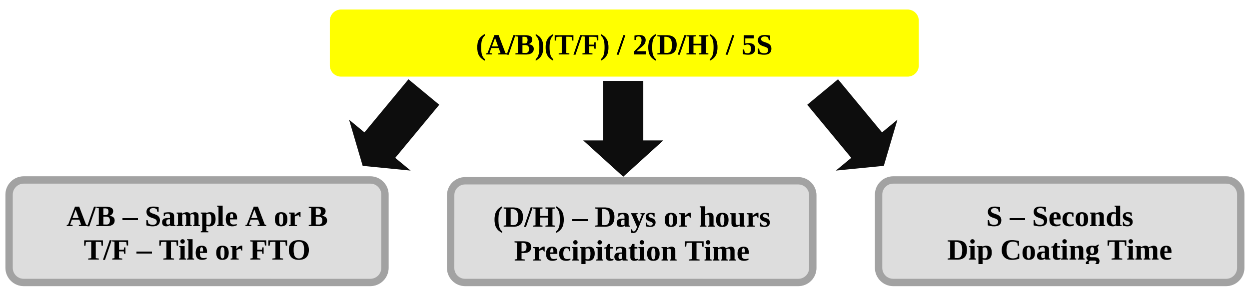

Figure 1: Sample Numbering Label

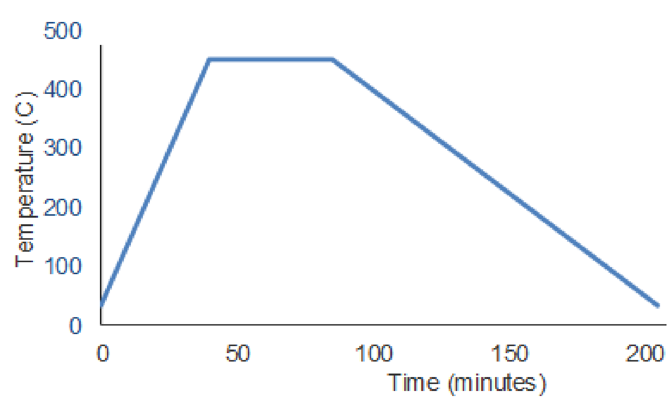

Figure 2: Firing Curve (Time vs. Temperature)

Before dip-coating, the solution was put inside the ultrasonic sonicater for 5 minutes. Samples were dip coated inside the ultrasonic sonicater, and sintered in the furnace following the temperature variations given in Figure 2.

2.4 Type A Samples

When dip coating Type A Samples, the TiO_2 solution was allowed to precipitate over relatively long periods; (a) one hour and (b) two days. Samples were dipped in the supernatant over specified periods as given in Table 2.

Table 2: Type A Samples TiO_2 Supernatant Preparation Condition and Dip Coating Time

Supernatant Condition \ Dipping Time	5 seconds	10 seconds	20 seconds
After one hour precipitation	AT/1H/5S	AT/1H/10S	AT/1H/20S
After two days precipitation	AT/2D/5S	AT/2D/10S	AT/2D/20S

2.5 Type B Samples

When dip coating Type B Samples, the TiO_2 solution was not allowed to precipitate over relatively long periods. All dipping happened with precipitation times of maximum 2 minutes as given in Table 3. Samples were dipped in the supernatant over very brief period of less than 5 seconds.

Table 3: Type B Samples TiO_2 Supernatant Preparation Condition and Dip Coating Times

Sample	Precipitation Time	Dip Coating Time
BT/00S	~ 0.5 seconds	Less than 5 seconds
BT/15S	15 seconds	
BF/60S	60 seconds	
BT/120S	120 seconds	

2.6 Application of TiO_2 Layer on FTO Glass

One piece of Fluorine doped Tin Oxide (FTO) coated glasses was used to prepare an additional sample to improve SEM imagery. The FTO glass piece was dip coated by using the solution given in Table 1. Again, the mixture was stirred for 15 minutes and left to precipitate.

2.7 Drying and Sintering of Samples

Tables 2 and 3 presents dip coating times for all samples; tile pieces as well as the glass.

All the samples were put inside the small closed vessel, dried by air for 15 minutes and dried by oven at 50 °C for 15 minutes. To enable placing the samples in oven such that impurities will not contaminate the surfaces, they were placed in a small container made of tiles. Then samples were sintered in the furnace following the temperature variations given in Figure 2. Samples were observed by the SEM.

2.8 Culture Medium Preparation and E.coli Growth

27 g of HiCrome Coliform Agar w/SLS (supplied by HiMedia[1]) was suspended in 1000 ml distilled water. The agar was heated up to boiling to dissolve the medium completely. Then the agar medium was sterilized by autoclaving at 15 psi pressure (121°C) for 15 minutes. As a precaution manufacturer advised to add 5 mg/l novobiocin before autoclaving the medium, when a high number of gram positive accompanying bacteria are expected.

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[1] HiMedia Laboratories, Mumbai, India, http://www.himedialabs.com

After cooling the prepared culture medium to 45-50°C, 10 ml of medium was mixed well and poured into petri plate. Then 1 ml of E.coli solution was distributed on the dried out culture medium. E.coli solution was extracted from a well grown E.coli sample, and ten times diluted before application. Then E.coli distributed samples were placed in an incubator at 44°C. To identify the shape, bacteria density and distribution of E.coli growth on the culture medium, Optical microscope images were taken (see Figure 3).

2.9 Investigation of Anti-Bacterial Activity of Synthesized Solution

To investigate the antibacterial activity in the solution given in Table 1, two methods were used.

1) Prepared bacteria samples placed on the coated surface (see Figure 4).
2) Prepared bacteria samples placed inside the solution (see Figure 5).

1 cm^2 bacteria samples were cut and number of bacteria were counted by using optical microscopic images. Then all samples were kept under sunlight and after one hour, number of bacteria were again counted. The image of immersed samples were not clear. But images of samples which were placed on the coated surfaces were clear. Then they were kept under sunlight for another hour and again counted.

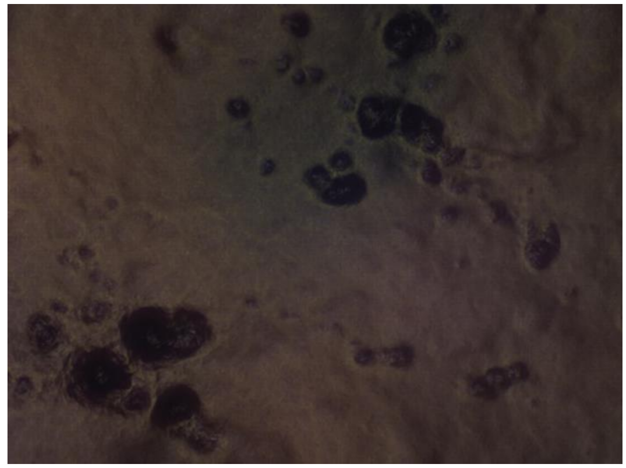

Figure 3: Optical Microscope Image of E-Coil Sample (X50

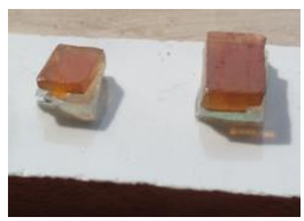

Figure 4: Bacteria Samples Placed on the Coated Surface

Figure 5: Bacteria Sample Immersed in the Solution

3. Results and Discussion

3.1 X-Ray Diffraction (XRD) Analysis of TiO_2

X-Ray Diffraction (XRD) pattern of the general purpose regent TiO_2 sample is shown in the Figure 6. In XRD patterns, powder particles show strong diffraction peaks with crystalline nature. The 2θ peaks lying at 2θ = 25.4 (101), 37.893 (004), 48.172 (200), 53.979 (105), 62.769 (204). When these peaks are compared with standard spectrum peaks, this sample includes TiO_2 anatase phase (Thamaphat *et al.* 2008). Small peaks correspond to the impurities present in the TiO_2 powder sample we used.

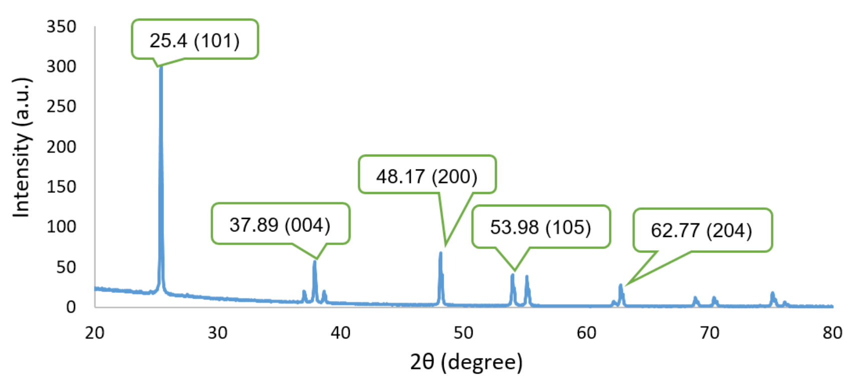

Figure 6: XRD Patterns of TiO_2 Sample

The preferred orientation is corresponding to the TiO_2 anatase phase. Some peaks are close to TiO_2 rutile phase and some of the small peaks which cannot be indexed can be attributed to the impurities contaminated with the TiO_2 powder sample.

3.2 SEM Analysis of TiO_2 Spray Coated Layer

Very simple equipment that was used for spray coating, was very easy to handle. There were, however, some disadvantages:

- irregularities of coated surface
- coating not being durable
- layer thickness being high causing surface to become white color

Solution properties and coating mechanism, hence, need to be further developed.

Figure 7 shows SEM micrograph of the TiO_2 coating prepared by the spray coating method and sintered at 450 °C for 45 minutes. Nano size TiO_2 particles were identified in the coating by observing the SEM image of TiO_2 coating. There were some irregularities of surface coating, and durability of the coating was low. Energy Dispersive Spectrometry (EDS) analysis was, hence, not carried out.

A clean tile sample was used to observe the pores by using SEM. But ceramic tiles are non-conductive. A result of that was the very dark image of the surface. Optical microscope was, therefore, used to observe the surface quality. Optical microscope revealed that there were lot of pores on the surface.

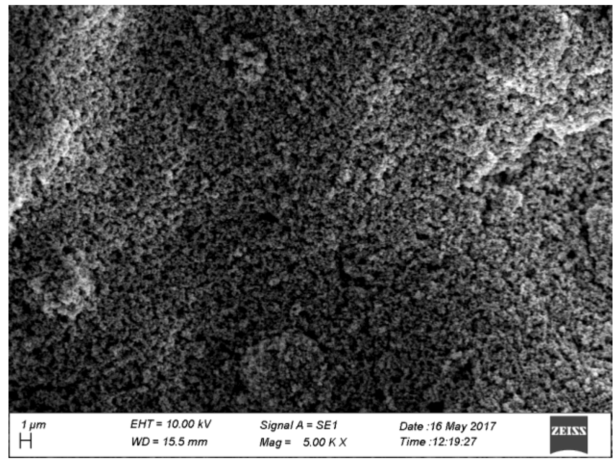

Figure 7: SEM Image of TiO_2 Spray Coated Tile Surface

3.3 Type A Samples: SEM and EDS Analysis of TiO_2 Layer

There was no TiO_2 coating observed on first five samples. A small percentage of area of TiO_2 was observed on the sample AT/1H/10S [TiO_2 dip coated tile surface (Coating time 10 seconds)] and sample AT/1H/20S [TiO_2 dip coated tile surface (Coating time 20 seconds) (see Figure 8)]. The latter did not have a uniform coating. Energy Dispersive Spectrometry (EDS) analysis of the dip coated TiO_2 film is given in Figure 9.

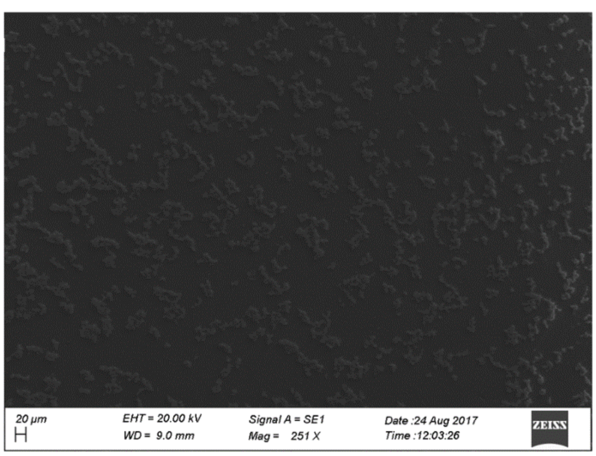

Figure 8: SEM Image of Sample AT/1H/20S

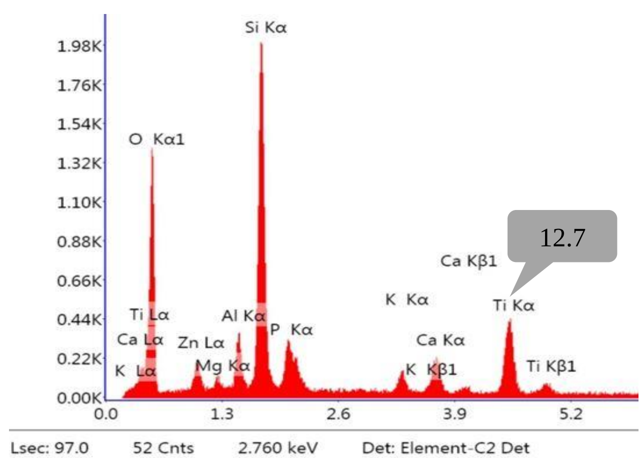

Figure 9: EDS Pattern of Sample AT/1H/20S

There are so many reasons for above results. Ethyl cellulose which we used is a commercial grade sample. Therefore we do not know whether it is pure Ethyl cellulose or not. Ethyl cellulose was not dissolved completely in ethanol and also TiO_2 nano particles were not dissolved in the coating. Having experienced the above results Type B Samples, where the TiO_2 solution was not allowed to precipitate, were tried.

3.4 Type B Samples: SEM and EDS Analysis of TiO_2 Layer

According to the SEM analysis only sample BT/00S (Figure 10) has complete coating layer and all of other samples have no regular layers. According to that we can deduce that there are some TiO_2 particles left in the solution when stirring but all of those particles did precipitate very quickly. That means particles are just mixed, not dissolved in solution.

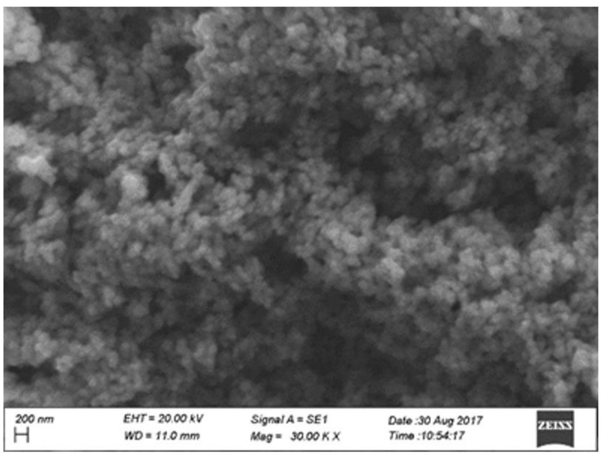

Figure 10: SEM Image of Sample BT/00S

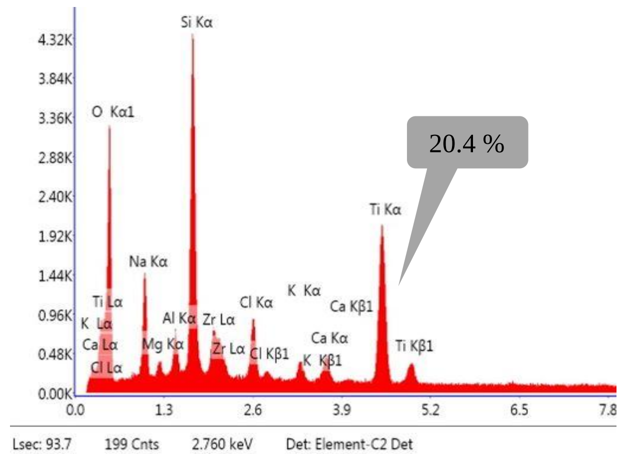

Figure 11: EDS Pattern of Sample BT/00S

Figure 11 shows EDS graph of the TiO_2 coating prepared by the dip coating method sintered according to firing curve given in Figure 2. According to the EDS analysis highest peak index is Silicon. Silicon is a material which is in the tile, but not in the coating. When considering other peaks they show Oxygen and Titanium in considerable percentages. EDS graph further indicated presence of other materials like Sodium, Calcium, Aluminum, Potassium, Magnesium etc. They can be considered as materials from impurities on the tile surface.

Figure 12 shows the SEM image of the thickness and homogeny of the layer. TiO_2 thickness obtained on the tiles by the dip coating method is around 900 nm. Micro TiO_2 particles were identified in the coating by observing the SEM image of TiO_2 coating. That means TiO_2 particles are agglomerated. So, there were some irregularity of surface coating and durability of the coating is low. The performance of the film is highly dependent on the homogeny and the thickness of the TiO_2 layer.

In the dip coating method material wastage is high and there were some irregularities of coated surface. So solution properties and coating mechanism are in need of development.

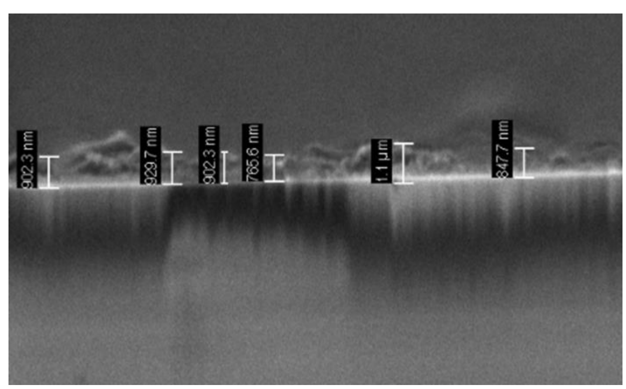

Figure 12: SEM Image of BT/00S Sample Film Thickness

3.5 Investigation of Anti-Bacterial Activity of Synthesized Solution

Optical microscope images of immersed samples were not clear, because TiO_2 fine particles were deposited on the bacteria sample. The bacteria samples which were placed on the coated surface were very clear as before. There was, however, no significant difference of number of bacteria that had grown. The reason, apparently, was bacteria growth is inside the agar media, and not the surface of the tile; therefore, bacteria were not in contact with the synthesized coating. It was, hence, observed that, TiO_2 coating on the tile cannot destroy bacteria but considerably retards the growth of bacteria on the surface of the tile.

4. Conclusions

This research focused on studying photocatalytic anti-bacterial properties of thin films of TiO_2 synthesized on ceramic tiles by both dip coating and spray coating methods. In that process, it was found that, the method of coating the tile surface, and the method of preparing the TiO_2 solution was significant.

To coat the tile surface with TiO_2 solution, two methods were used, viz; spray coating and dip coating. Spray coating the tile surface by the apparatus used was not successful, because the coating was not homogeneous and came off very easily. Dip coating the tile delivered a homogeneous and very thin film on the tile surface.

In preparing the TiO_2 solution, initially (in making Type A Samples), the TiO_2 solution was allowed to precipitate before coating the tiles. This did not yield a uniform TiO_2 coating. Subsequently (in making Type B Samples), no time was allowed for TiO_2 to precipitate, which yielded a complete TiO_2 coating layer. The reasons being that, TiO_2 particles did not dissolve properly in ethanol or particles were agglomerate together.

Observations by optical microscope showed that, TiO_2 coating on the tile cannot destroy bacteria but considerably retards the growth of bacteria on the surface of the tile.

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