Photocatalytic Behaviour of TiO$_2$-geopolymer Paste under Sunlight

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Abstract. The photocatalytic degradation of methylene blue (MB) of the geopolymer paste with addition nanoparticles titanium dioxide (TiO$_2$) was investigated under illumination of sunlight radiation. In this work, TiO$_2$-based geopolymer paste was prepared by dry mixing of Class F fly ash (FA) and different amount of nano-TiO$_2$ (0, 2.5, 5.0, 10.0 & 15.0 wt%). Then, the alkali activator, which is combination of sodium hydroxide solution with sodium silicate was added to the dry mix FA-TiO$_2$ with ratio of 2.5. All the sample was cured at room temperature and aged for 28 days. The photocatalytic behaviour of nano-TiO$_2$ was evaluated and compared through photocatalytic testing and surface degradation testing by measuring the photodegradation of MB under sunlight rays. The experimental results revealed that the addition of nano-TiO$_2$ to the geopolymer paste shows excellent result on photocatalytic degradation of MB after exposure to sunlight up to 150 minutes.

1 Introduction

Recently, in highly polluted area, surface of the building faces the serious problem of tending to become dusty and dull in appearance. Thus, in order to maintain the surface cleaning of building, paint or high consumption of chemical detergents is used, consequently, a high cost was being issued [1]. The release of high amounts carbon dioxide (CO$_2$) and concrete dust during manufacturing process of Ordinary Portland cement (OPC) is a major contribution to the air pollution. Hence, air pollutions have becoming a hot topic has been attracted attention researcher and industries, which in turn geopolymer become an alternative material to OPC by replacing cements-based binder with industrial by-product such as fly ash (FA) [2-3].

In order to pursue the concept of green environment blending materials, the properties of geopolymer materials was expanded by adding a photocatalyst for self-cleaning purpose. The photocatalyst that most commonly used in cementitious materials is nanoparticles of titanium dioxide (TiO$_2$) due to its good photocatalytic behaviours. Properties of self-cleaning is developed by addition nanoparticles of photocatalytic material in the geopolymer structure.

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[3]. There is a researcher reported that nano-TiO$_2$ by playing a role of photocatalyst on the surface of cementitious materials, was activated due to the presence of ultraviolet (UV) radiation from the sunlight. In addition, there are two significant advantages by adding photocatalytic materials onto cementitious materials which is, reduce the air pollution and keep the surface of the concrete buildings free from dirt and preserves its colour, even in polluted conditions and industrial areas [4]. Thus, the building aesthetic appearance is maintained and also effectively reduces costs of maintenance in cleaning process.

Based on the literature, research work on the application of self-cleaning onto the geopolymer field are still lacking. This works aims to investigate the potential effect of nanoparticles titanium dioxide as a photocatalyst materials on the photocatalytic behaviour of self-cleaning based-geopolymer paste when directly subjected to sunlight rays.

2 Experimental Method

2.1 Materials and Chemicals

Fly ash as raw materials used in this study is supplied by Cement Industries of Malaysian Berhad (CIMA) in Perlis, Malaysia. The high purity (99.9%) of titanium dioxide (TiO$_2$) nanoparticles which has a particle size ranging from 30nm to 50nm were obtained from Hongwu Nanometer was used as photocatalyst. In this work, sodium hydroxide (NaOH) solution and sodium silicate (Na$_2$SiO$_3$) were purchased from Formosa Plastic Corp., and Taiwan South Pacific Chemical Industries Sdn. Bhd., Malaysia, respectively, and deionized water was used as alkali activator. Methylene blue (MB) used as dye was supplied from Sigma-Aldrich and ethanol (EtOH) solution with a 96% purity was obtained from Altia.

2.2 Mix Design and Sample Preparation

In the preparation of TiO$_2$-geopolymer paste, the class F fly ash was sieved at 150 μm. The 12M solution of sodium hydroxide (NaOH) was prepared by diluted the 480g of NaOH pellet in 1 litre deionized water, then was allowed to cool at room temperature for 24 hours. The alkali activator solution is a combination of NaOH and sodium silicate (Na$_2$SiO$_3$) at ratio 2.5 by mixing 71.43g of 12 M NaOH solution with 178.57g of Na$_2$SiO$_3$ solution. Fly ash was dry-mixed first with 2.5 wt% of nano-TiO$_2$ powder. Then, dry mixture was mixed with alkali activator at ratio of solid-to-liquid ratio of 2.0 that was conducted by mechanical mixer for 15 minutes until a homogeneous paste was obtained. Then, the slurry was casted into disc specimen with a diameter 90 mm and 10 mm thickness (European Standard ISO 679) under curing conditions of room temperature for 28 days. The sample was labelled as Sample T$_{2.5}$. The preparation of the TiO$_2$-geopolymer paste were repeated by varying the percentage by mass of nano-TiO$_2$, which are 5.0, 10.0 and 15.0 wt%. These samples were labelled as Sample T$_{5}$, T$_{10}$ and T$_{15}$, respectively. A geopolymer paste without the addition of nano-TiO$_2$ also was prepared and labelled as Sample T$_{0}$. The details about mix proportion of TiO$_2$-geopolymer paste is illustrated in Table 1.
Table 1. Mix design of TiO$_2$-geopolymer paste.

| Name of Sample | Mix Design | Alkali Activator | Mass Ratio |
|----------------|------------|-----------------|------------|
|                | TiO$_2$-nanoparticles (wt%) | Fly Ash (g) | NaOH 12M (g) | Na$_2$SiO$_3$ (g) | S/L | Na$_2$SiO$_3$/NaOH |
| T$_0$          | 0          | 500             | 71.43      | 178.57           | 2.0 | 2.5               |
| T$_{2.5}$      | 2.5        | 487.5           |            |                  |     |                  |
| T$_{5}$        | 5.0        | 475             | 71.43      | 178.57           | 2.0 | 2.5               |
| T$_{10}$       | 10.0       | 450             |            |                  |     |                  |
| T$_{15}$       | 15.0       | 425             |            |                  |     |                  |

2.3 Photocatalytic Testing

The ability of TiO$_2$-geopolymer paste to be functioned as self-cleaning was determined through photocatalytic test. A photocatalytic testing was carried to study the performance of the geopolymer paste with different wt% of nano-TiO$_2$. The test was conducted by immersed disc specimen with a diameter 90 mm and thickness of 10 mm in 150 ml of MB solution with concentration 10 mg/L. Then, the specimen is directly exposed under sunlight for 150 minutes as shown in Fig. 1.

In photocatalytic testing, an ultraviolet-visible spectrometer (Lambda 25, Perkin Elmer, USA) was used to measure the degree of degradation methylene blue (MB) solution. The degradation degree of the TiO$_2$-geopolymer paste was obtained using the Eq. 1:

$$A_t = \frac{I_t}{I_0} = \frac{I_0-I_t}{I_0}$$  

(1)

where,

$A_t$ is degradation ratio
$I_0$ is base absorbency
$I_t$ is absorbency after time $t$
2.4 Surface Degradation Testing

The decomposition of organic compound was evaluated through surface degradation testing. Experiment was carried out by applied directly dye the MB solution with the concentration of 30 mg/l on the surface of TiO$_2$-geopolymer paste disc specimens. Then, the specimens were exposed directly to the sunlight as a natural source for 150 minutes and visually observed in every 30 minutes.

3 RESULT AND DISCUSSIONS

3.1 Photocatalytic behaviour of TiO$_2$-geopolymer paste under sunlight

The ability of TiO$_2$-geopolymer paste as a photocatalyst material was evaluated through photocatalytic test. Fig. 2 shows the degradation of MB solution under natural source radiation as a function time of TiO$_2$-geopolymer paste.

The photocatalytic behavior of specimens was evaluated in terms of the efficiency of MB solution degradation. Fig. 2 shows the MB solution was degraded proportional with time. As can see, the colour gradually changed from blue to colourless from 30 min to 150 min. After 90 min exposed to sunlight, it was clearly seen that the MB solutions start to degrade. The role of nano-TiO$_2$ as a photocatalyst materials in the geopolymer paste was proved by level of MB degradation was increased as a function of time.
Fig. 2. Degradation MB solutions under sunlight as a function time of TiO$_2$-geopolymer paste
Fig. 3. The relationship between degradation rate of MB and time of exposure with different amount of nano-TiO$_2$ under sunlight.

The analysis of ultraviolet spectrophotometer was done for all specimen in order to confirm the photocatalytic behaviour of TiO$_2$-geopolymer paste. Fig. 3 shows the relationship between degradation rate of MB as a function of time with different amount nano-TiO$_2$ under sunlight. It is observed that there is a similar degradation trend for all sample which indicated that the degradation ratio is proportionally with the exposure time under sunlight. From Fig. 3, sample T$_{15}$ exhibit the highest photocatalytic performance with degradation ratio of MB dye of 0.99 % after 150 minutes. This is due to the nano-TiO$_2$ that was activated by sunlight and play its role as photocatalyst [5-6].

It also being observed from Fig. 3, after 150 min, sample T$_{0}$ which is geopolymer paste without addition photocatalyst nano-TiO$_2$ also showed the discoloration trend of MB solution. This is due to contents of fly ash, which consists of different amount of mineral oxides such as iron oxide (Fe$_2$O$_3$), zinc oxide (ZnO) and TiO$_2$, which is sensitizers to light [7-9]. In addition, the changes colour of MB was believed not only due to the photocatalytic activity but also due to the fly ash that contain in the geopolymar matrix, which act as an adsorbent for the dye [1,9].

3.2 Surface degradation of TiO$_2$-geopolymer paste under sunlight

The decomposition of organic compounds was examined through surface degradation test. The surface degradation testing was carried out for all specimen under direct exposing to the sunlight. Fig. 4 shows surface degradation of organic dye MB directly applied on the surface of TiO$_2$-geopolymer paste which exposed under sunlight for 150 min. It can be observed that colour degradation of MB was increased as the amount of nano-TiO$_2$ increased. This demonstrate that nano-TiO$_2$ nanoparticles act as catalyst on photocatalytic
degradation reaction on the MB as an organic compound [10]. Hence, it can be concluded that nano-TiO$_2$ nanoparticles have the potential as a photocatalyst to be applied in cementitious materials.

Fig. 4. Surface degradation of methylene blue applied on surface of TiO$_2$-geopolymer paste under sunlight.

4 Conclusion

The following conclusions were reached based on the result analysis as presented in this paper; the addition of TiO$_2$ nanoparticles as photocatalyst to geopolymer paste enhance the self-cleaning performance. The photocatalytic activity of geopolymer paste with different amount TiO$_2$ nanoparticles is effective in degrading methylene blue under the sunlight. By increasing the amount of addition TiO$_2$ nanoparticles, the degradation rate also increased. The TiO$_2$-geopolymer paste showed a photocatalytic performance compared to the sample without TiO$_2$ nanoparticles. However, without addition of nano-TiO$_2$, the geopolymer paste had indicated MB photocatalytic degradation due to some mineral oxide presence in the raw material when exposed directly to UV rays. Thus, TiO$_2$ nanoparticles have the potential as photocatalyst in order to be applied in building as surface finishing materials.

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References

1. J. Kumar, A. Srivastava, A. Bansal, Int. J. Innov. Res. Sci. Eng. Technol. 2(7), 2688–2693 (2013)
2. M.Z.N. Khan, Y. Hao, H. Hao, F.U.A. Shaikh, Cem. Concr. Compos. 104, 103343
(2019)
3. K. Carter, P. Ziehl, R. Anay, L. Assi, E. (Eddie) Deaver, J. Clean. Prod. 198, 1641–1651 (2018)
4. A. Kitab, M. Alam., H. Riaz, S. Rauf, Int. J. Adv. Life Sci. Technol. 1(4), 47–53 (2014)
5. W. Shen, C. Zhang, Q. Li, W. Zhang, L. Cao, J. Ye, J. Clean. Prod. 87(C), 762–765 (2015)
6. R. Khataee, V. Heydari, L. Moradkhannejhad, M. Safarpour, S.W. Joo, J. Nanosci. Nanotechnol. 13(7), 5109–5114 (2013)
7. P. Krishnan, M.H. Zhang, L. Yu, H. Feng, Constr. Build. Mater. 44, 309–316 (2013)
8. S.N. Zailan, N. Mahmed, M.M.A.B. Abdullah A. V. Sandu, IOP Conf. Ser. Mater. Sci. Eng. 133, 1-7 (2016)
9. M.M.A.B. Abdullah, K. Hussin, M. Bnhussain, A.R. Rafiza, Y. Zarina, ACI Mater. J. 109(5), 503–508 (2012)
10. K. Loh, C.C. Gaylarde, M.A. Shirakawa, Constr. Build. Mater. 167, 853–859 (2018)