Photocatalytic Activity of ZnO-doped Geopolymer Paste

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Abstract. This study aims to investigate the photocatalytic activity of ZnO nanoparticles as photocatalyst material which was doped onto a geopolymer paste. ZnO-doped geopolymer paste were prepared by mixing Class F fly ash and various amount of ZnO nanoparticles with alkali activator, which is combination of sodium hydroxide solution with sodium silicate. Meanwhile, geopolymer paste without ZnO was produced by mixing Class F fly ash and alkali activator. Then, both samples were cured in room temperature and aged for 28 days. The photocatalytic activity for geopolymer paste with and without ZnO nanoparticles were evaluated and compared through photocatalytic testing and discolouration testing. The experimental results revealed that, as increasing the amount of addition ZnO nanoparticles, the degradation of methylene blue also was increased. However, mineralogical determination of ZnO-doped geopolymer paste were characterized using X-ray Diffraction (XRD).

1. Introduction
Nowadays, a building always faces the problem of tending to become dirty especially in highly polluted area for a long-time exposure. Besides that, the demolition of old buildings and natural disasters also contribute to the release of the concrete dust and also give the dusty and dull appearances to the surface of the building. Hence, air pollutions have becoming a main issue in environment. This case was pressured the industries to develop an alternative material by replacing cements in the construction materials with waste materials such as fly ash, so-called geopolymer [1-3]. The properties of geopolymer materials can be expanded by adding a self-cleaning material, i.e. photocatalyst are doped during the preparation process. The photocatalytic nanoparticles that most commonly used in cementitious materials is zinc oxide nanoparticles, which has a high potential to be used as a self-cleaning material due to its good photocatalytic behaviour [4]. Self-cleaning behaviour are developed by addition nanoparticles of photocatalytic material in the geopolymer structure [5]. The development of geopolymer construction materials with self-cleaning properties will not only reduce the air pollution, but keep the surface of the concrete buildings free from dirt [6]. Thus, the aesthetical appearance can be maintained especially in the highly polluted area [5]. The development of ZnO-doped geopolymer paste is an innovative construction material which are environmentally friendly that contribute towards green environment. This paper discussed about current studies photocatalytic activity of the addition ZnO nanoparticles as photocatalyst materials onto geopolymer paste.
2. Experimental Method

2.1. Materials and Chemicals
Fly ash used in this study were supplied by Cement Industries of Malaysian Berhad (CIMA) in Perlis, Malaysia as source materials. The high purity (99.8%) of commercial zinc oxide (ZnO) nanoparticles which has a particle size ranging from 30nm to 50nm were obtained from Hongwu Nanometer was used as photocatalyst. The chemicals that were applied during the experiment are 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, which was used as alkali activator.

2.2. Mix proportion and Sample Preparation
In the preparation of ZnO-doped geopolymer paste, the fly ash was sieved at 150 μm. The solution of sodium hydroxide (NaOH) was prepared by diluted the NaOH pellet at 12M and was allowed to cool down at room temperature. The alkali activator solution was formed by mixing NaOH and sodium silicate (Na$_2$SiO$_3$), which prepared at ratio 2.5 by mixing 71.43g of 12 M NaOH solution with 178.57g of Na$_2$SiO$_3$ solution. The solution of alkali activator was prepared for minimum 24 h in order to ensure the solution was mixed completely. Fly ash was dry-mixed first with 2.5 wt% of ZnO nanoparticles powder. Then, fly ash-ZnO nanoparticles powder was mixed with alkali activator at 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 90 x 10 mm (European Standard ISO 679) which was cured for 28 days at room temperature. The sample was labelled as Sample Z2.5. The preparation of the ZnO-geopolymer paste were repeated by varying the amount of ZnO nanoparticles powder used, which are 5.0, 10.0 and 15.0 wt%. These samples were labelled as Sample Z5, Z10 and Z15, respectively. A geopolymer paste was also prepared without the addition of ZnO nanoparticles powder and labelled as Sample Z0. The details about mix proportion of ZnO-doped geopolymer paste is illustrated in table 1.

Table 1. Mix proportions of ZnO-doped geopolymer paste.

| Name of sample | ZnO nanoparticles (wt%) | Fly ash (g) | NaOH 12M (g) | Na$_2$SiO$_3$ (g) | S/L | Na$_2$SiO$_3$/NaOH |
|----------------|-------------------------|-------------|--------------|-------------------|-----|-------------------|
| Z0             | 0                       | 500         |              |                   |     |                   |
| Z2.5           | 2.5                     | 487.5       | 71.43        | 178.57            | 2.0 | 2.5               |
| Z5             | 5                       | 475         |              |                   |     |                   |
| Z10            | 10                      | 450         |              |                   |     |                   |
| Z15            | 15                      | 425         |              |                   |     |                   |

3. Results and Discussions

3.1. Mineralogical Determination
The mineralogical composition of fly ash, ZnO nanoparticles and ZnO-doped geopolymer paste were accessed via X-ray diffraction (XRD D8-Advance, Bruker, Germany) over a 2θ range 10° – 90° using CuKα ($\lambda=1.5046\text{nm}$) at 0.02 steps per second in powder form. The pattern of XRD was analyzed by X’pert Highscore Plus software with ICDD PDF-2 database. Fig. 1a shows XRD pattern of fly ash. As observed in Fig. 1a., there is a numerous peak of mullite (3Al$_2$O$_3$SiO$_3$), quartz (SiO$_2$) and hematite (Fe$_2$O$_3$) that is the main phases in fly ash which contains high silica and alumina. Fig. 1b shows XRD pattern of zinc oxide (ZnO) where zinc oxide is the dominant peaks.
Meanwhile in Fig. 2 shows XRD pattern of ZnO-doped geopolymer paste. As shown in Fig. 2, sample $Z_0$ contains main peaks of crystalline phase which are mullite and quartz. The broad peak between the 25° to 35° contributed to the formation of alumina silicate gel in the geopolymer structure due to the reaction between fly ash and the alkali activator [4,8]. As shown in the XRD patterns, the sample with doping of ZnO nanoparticles shows the phase of the geopolymer paste remains unchanged, except the appearance peak of zinc oxide (ZnO) that exist between 40° to 60°. Interestingly, other than detected typical peak of geopolymerization product e.g. quartz, mullite and hematite phases [9, 10], there is a new peak formed between 30° to 70° in sample $Z_{10}$ and $Z_{15}$ which is zinc hydroxide (Zn(OH)$_2$). This indicated that phase of ZnO are also appears in another form which in Zn(OH)$_2$ after undergoes geopolymerization. After the addition of ZnO nanoparticles to the system, the crystalline phases of ZnO and Zn(OH)$_2$ appeared. Thus, it can be concluded that the addition of nano-ZnO did not change the phase of the geopolymer paste. It was indicated that the addition of photocatalyst to a cementitious material has no effect on the crystallinity phases of the material, but contributes in the formation of new crystalline phases [7,11,12]. This result was justified by previous research which has found that XRD pattern measured the presence of additional peaks when photocatalyst was added to the raw cement and no impact on the phase composition for raw cement [7].
3.2. Photocatalytic Activity of ZnO-doped Geopolymer Paste

The ability of ZnO-doped geopolymer paste as a photocatalyst material was evaluated through photocatalytic test. A photocatalytic testing was conducted to study the performance of the geopolymer paste with different wt% of ZnO nanoparticles to be functioned as a self-cleaning. In photocatalytic testing, the disc specimen with a diameter 90 mm and thickness of 10 mm was immersed in 150 ml of MB solution of 10 mg/L of concentration, and exposed under direct sunlight for 150 minutes. The ability of photocatalytic is evaluated by measure the degradation degree of methylene blue (MB) solution that was conducted by using a UV-visible spectrometer (Lambda 25, Perkin Elmer, USA). The degradation ratio of the photocatalytic properties of the ZnO-doped geopolymer paste can be obtained from the Eq. 1:

$$A_t = \frac{l_b}{l_a} = \frac{l_o}{l_t}$$

where,
- $A_t$ is degradation ratio
- $l_o$ is base absorbency
- $l_t$ is absorbency after time $t$

Figure 4 shows degradation MB solutions under UV radiation as a function time of ZnO-doped geopolymer paste. From Figure 4, it can be clearly seen that the MB solution was degraded under UV radiation of sunlight as a function of time for sample with and without ZnO-doped geopolymer paste. The colour was changed from blue to colourless from 30 min to 150 min, respectively. The MB solutions start to degrade after 90 minutes being exposed to sunlight. This situation indicates that the ZnO nanoparticles did act as a photocatalyst materials in the geopolymer paste.

The ultraviolet spectrophotometer analysis proved that the photocatalytic activity of ZnO-doped geopolymer paste. Figure 3 displays the relationship between degradation efficiency of MB as a function of time with different ZnO nanoparticles amounts under sunlight. It is observed that the value of the degradation ratio proportionally with the exposure time under sunlight. Sample Z10 exhibit the highest photocatalytic performance by degrading the MB dye with a degradation ratio of MB dye of 0.98 % after 150 minutes. This is due to the chemical reaction of ZnO nanoparticles which play a role as photocatalyst in photoreactivity which was activated by sunlight [13].

![Figure 3](image_url)

**Figure 3.** The relationship between degradation efficiency of MB and time of exposure with different ZnO nanoparticles amount under sunlight.
Figure 4. Degradation MB solutions under UV radiation as a function time of ZnO-doped geopolymer paste

It can be observed from the same figure 4, sample Z₀ (ZnO-free geopolymer paste) showed the discoloration trend of MB with about 0.93 % after 150 min. This was believed due to contents of fly ash, which consists of Fe₂O₃, TiO₂ and ZnO with different amounts, those mineral oxides are considered as semiconductors, which can act as sensitizers for light [14-16]. In addition, the changes of the MB were believed not due to the photocatalytic activity but due to the fly ash that contain in the geopolymer matrix, which act as an adsorbent for the dye [16,17].

Other than that, the decomposition of organic compounds was examined through discolouration test. Experiment was carried out by applied dye of MB solution of 30 mg/l concentration on the surface of ZnO-doped geopolymer paste and subjected to a direct sunlight for 150 minutes and visually observed in every 30 minutes. Discolouration testing were carried out for all specimens with and without ZnO-photocatalyst by a direct exposing to an ultraviolet (UV) radiation from the sunlight.
Figure 5 shows a discolouration test of organic dye MB directly applied on the surface of ZnO-doped geopolymer paste and ZnO-free geopolymer paste which subjected to illuminate UV rays for 150 min. It can be observed that colour degradation of MB was increased as ZnO nanoparticles amounts increased and also not much change of the MB colour for the sample of ZnO-free geopolymer paste. This demonstrate that ZnO nanoparticles as catalyst was play a part on photocatalytic degradation reaction on the MB as an organic compound. Hence, it can be concluded that ZnO nanoparticles have the potential as a photocatalyst for building materials.

![Figure 5. Discolouration of methylene blue applied on ZnO-doped geopolymer paste surfaces under sunlight.](image)

4. Conclusions
The following conclusions were reached based on the result analysis as presented in this paper which is, addition of ZnO nanoparticles as photocatalyst to a cementitious material has no effect on the crystallinity phases of the material and did not change the structure of the geopolymer paste, however contributes to the formation of new crystalline phases. Meanwhile in photocatalytic activity, geopolymer paste with different amount ZnO nanoparticles is effectively degraded methylene blue under ultraviolet (UV) irradiation, by increasing the amount of addition ZnO nanoparticles, the degradation rate also increased. The ZnO-doped geopolymer paste showed a photocatalytic performance compared to the sample without ZnO nanoparticles. However, without any addition of ZnO nanoparticles, the geopolymer paste showed a photocatalytic degradation of methylene blue, due to the presence of some mineral oxides in the raw material when subjected to an illuminate UV light. Thus, ZnO nanoparticles have the potential as a photocatalyst for applied in building materials.

References
[1] Aziz I H, M Abdullah, H Yong, L Ming, D Panias and K Sakkas 2017 IOP Conference Series: Materials Science and Engineering IOP Publishing pp. 012040
[2] Wan Mastura W I, Kamarudin H, Khairul Nizar I, Al Bakri Abdullah M M and Mohammed H 2013 Adv. Mater. Res. 626 937-941.
[3] E Azimi, M Abdullah, L Ming, H Yong, K Hussin and Aziz I H 2016 MATEC Web of Conferences EDP Sciences pp. 01090
[4] Nochaiya T, Sekine Y, Choopun S and Chaipanich A 2015 J. Alloys Compd. 630 p 1–10
[5] Zailan S N, Mahmed N, Abdullah M M A B and Sandu A V 2016 IOP Conf. Ser. Mater. Sci. Eng. p 1-7
[6] Azani A, Halin D S C, Razak K A, Abdullah M M A B, Salleh M A A M, Mahmed N, Ramli M M, Sepeai S, Sharin M F, Chobpattana V 2019 AIP Conf. Proceedings 2129 020062
[7] Janus M, Zatorska J, Czyzewski A, Bubacz K, Nejman E K and Morawski A W 2015 Appl. Surf.
[8] Aziz I H, M M Al Bakri Abdullah, H C Yong, L Y Ming, K Hussin, A Surleva and E A Azimi 2019 P. I. Mech. Eng. L-J Mat. 233 721-733

[9] Aziz I H, M M A B Abdullah, M M Salleh, E A Azimi, J Chaiprapa and A V Sandu 2020 Constr. Build Mater. 250 118720

[10] Ibrahim W M W, Hussin K, Abdullah M M A B and Kadir A A 2017 AIP Conf. Proc. 1835(1) 020048

[11] E A Azimi, M M Al Bakri Abdullah, L Y Ming, H C Yong, K Hussin and Aziz I H 2016 Rev. Adv. Mater. Sci. 44

[12] Aziz I H, M M A B Abdullah, C-Y Heah and Y-M Liew 2019 Adv. Cem. Res. 1-11

[13] Jang Y J, Simer C and Ohm T 2006 Mater. Res. Bull. 41 p 67–77

[14] Chen J and Poon C S 2009 Build. Environ. 44 p 1899–1906

[15] Maleki A, Mohammad M, Emdadi Z, Asim N, Azizi M and Safaei J 2018 Arab. J. Chem.

[16] Ariffin N, Abdullah M M A B, Zainol R R M A and Murshed M F 2017 AIP Conf. Proc. p 1-6

[17] Khan T A, Ali I, Singh V V and Sharma S 2009 J. Environ. Prot. Sci. 3 p 11–22