Preparation and Characterization of Porous "*Baluko*" (Local Pen Shell)/Fly Ash/Titania Composite Geopolymer Sphere

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Abstract

In this study, the potential of utilizing "*Baluko*" shell, fly ash and nanotitania as material for the synthesis of porous geopolymer sphere was done. The alkaline activator was prepared by mixing 12 M NaOH to a sodium silicate solution in desired proportion. The prepared activator was added to the precursor along with the following: K12 solution (1.5% K12), H_2O_2, and distilled water. The foamy mixture was formed into a sphere by dropping it in PEG-600 with the help of a syringe. The composite spheres were characterized in terms of SEM-EDX, FTIR, XRD, bulk density, open porosity and water absorption capacity. It was identified via XRD and FTIR analysis that geopolymerization is apparent even with the "*Baluko*" shell replacement was done for fly ash. The addition of the "*Baluko*"shell as an accelerator shortens the initial setting time of the geopolymer sphere. Nevertheless, it had no significant effect in the geopolymer's bulk density, open porosity, water absorption, and extent of methylene blue degradation. Addition of nanotitania improved the methylene degradation from 53.45% to 85.54%.

Keywords: geopolymer sphere, "*Baluko*"shell, fly ash, nanotitania, methylene blue.

Introduction

Geopolymer, an amorphous alkali aluminosilicate, is considered to be a third generation cement due to its properties as concrete material [1]. Its application in cement-based structure has been widely accepted as a substitute for Portland cement [2, 3]. Its properties are high compressive strength, good chemical resistance and high temperature resistance due to its three-dimensional structure of aluminate and silicate tetrahedra joined by oxygen corners [4, 5]. Some recent studies shows that geopolymer can be utilized for pH adjustment, heavy metal adsorbent, and as catalyst in a form of porous sphere [6-9].

In making geopolymer, some waste materials such as fly ash, bottom ash, rice hull ash, red mud waste and others have been utilized to form such material for cement-based structure [10-12]. The presence of alumina and silica in these materials provide an environmental friendly source for geopolymer preparation due to waste valorization and carbon footprint reduction. Another critical element that can affect geopolymer properties is the presence of calcium. Some studies investigated the impact of addition of calcium in geopolymer formulation from various sources [13, 14]. In the Philippines, pen shells, locally known as "*Baluko*" shell, is very abundant in some parts of Philippines such Sorsogon in Luzon. The scallops of the "*Baluko*" are cooked and served as a local delicacy. The shells are commonly used as decorative material while majority of it has gone as waste in the landfill or in the ocean. This shell is a good source of calcium and could be utilized to make a composite geopolymer with fly ash. The use of such waste materials to produce valuable product to treat wastewater contributes not only in waste reduction but also to the realization of circular economy for energy and agricultural industries. Recently, geopolymer spheres with "*Baluko*" shell with photocatalytic activity and with antimicrobial property where been reported [15-16].

Several photocatalytic geopolymers for dye adsorption and degradation have been reported [17]. These geopolymers were evaluated for the removal of methylene blue (MB), methyl violet (MV), methyl orange (MO), and congo red (CR) from wastewater. Most of these geopolymer are synthesized as cube and powderized to evaluate its dye adsorption and degradation capability. One of the most studied photocatalyst is titanium oxide (TiO_2) also known as titania. However, the removal of this material from wastewater after treatment is the main obstacle for its utilization.

In order to utilize titania for wastewater treatment, this material was often incorporated in matrixes as support [18-21].

In this study, the potential of utilizing "*Baluko*" shell, fly ash and nanotitania as material for the synthesis of porous geopolymer sphere was investigated. The incorporation of titanium dioxide was done to utilize the material for dye degradation in wastewater. The composite spheres were characterized in terms of SEM-EDX, FTIR, XRD, bulk density, open porosity and water absorption capacity.

Experimental

Materials

The fly ash used in the study is an ASTM Class F provided by a coal-fired power plant in Central Luzon while the "*Baluko*" shells were obtained from Sorsogon bay. The following chemical were purchased from a local distributor: Titanium Oxide (TiO_2, >99.5% purity, Aldrich), technical grade sodium silicate, 12 M sodium hydroxide solution, sodium dodecyl sulfate (K12), hydrogen peroxide (50% wt/wt H_2O_2), polyethylene glycol (PEG-600, molecular weight of 600) and methylene blue (reagent grade, UNILAB).

Geopoylmer Sphere Synthesis

The "*Baluko*" shells were washed with bleach to remove the impurities prior utilization. The clean shells were grinded to powder form and sieve. The shells were calcined at 700°C for two hours. The calcined shells were further crushed and screened using a 75μm (mesh 200) sieve to achieve uniform and finer particle size. The geopolymer spheres were synthesis using a precursor composed of mixtures of fly ash, *"Baluko"* shells, and nanotitania at varying composition. The alkaline activator used in the study is prepared by adding 12 M NaOH into sodium silicate solution in appropriate proportion. The activator was added into the precursor followed by the addition of K12 solution (1.5% K12), H_2O_2, and distilled water. The foamy mixture was transferred to a syringe for sphere formation. The slurry was introduced in a PEG-600 bath at 90°C drop-by-drop. After hardening, the solid spheres were collected and washed with distilled water. Furthermore, the spheres were cured at 120°C for 24 hours. The setting time of the geopolymer was measured according to ASTM C191 using Vicat needle (CONTROLS).

Geopolymer Sphere Characterization

The porous spheres were characterized in terms of water absorption, bulk density and open porosity. The FTIR, SEM-EDX, and XRD analysis of the geopolymer samples were conducted at the Transdisciplinary Science and Engineering in Tokyo Institute of Technology and ADMATEL, DOST.

Methylene Blue Degradation

For photocatalytic degradation of dye, the geopolymer spheres were placed in flasks containing 200 mL of aqueous 3 ppm methylene blue dye solution. These flasks were placed on an orbital shaker at 120 rpm inside the fabricated photocatalytic degradation set up. These were subjected under a UV-lamp for 6 hours. Afterwards, the absorbance of aliquots was measured using spectrophotometry at 664 nm wavelength.

Results and Discussion

Porous Photocatalytic Geopolymer Sphere

Porous photocatalytic fly ash base geopolymers of varying "*Baluko*" shell (indicated as B) and nanotitania (indicated as T) concentration were prepared via mixing fly ash, "*Baluko*" shell and nanotitania with alkali activator together with pore- forming agent. The geopolymer sphere was formed by dropping the mixture in PEG-600 bath at 90°C and cured at 120°C. Figures 1 and 2 show the formed geopolymer sphere. The geopolymer spheres formed have a diameter ranging from 2 mm to 5 mm. It was observed that fly ash geopolymer are more spherical in shape compared to the one loaded with "*Baluko*" shell and nanotitania. Higher replacement of "*Baluko*" shells was observed to result to a more densed and viscous geopolymer slurry. As the geopolymer mix was dropped through the PEG solution and hit the bottom, the one with "*Baluko*" shells produced geopolymer beads with flatter sides. According to Tang et al. [9], the sphericity of the beads is due to the similarity of the densities between the geopolymer slurry and PEG-600. However, due to the addition of "*Baluko*" shells, whose density is higher than that

of fly ash, the resulting density of the slurry is heavier than PEG-600. This results to the decrease in sphericity of the geopolymer with the increase of "*Baluko*" shells content.

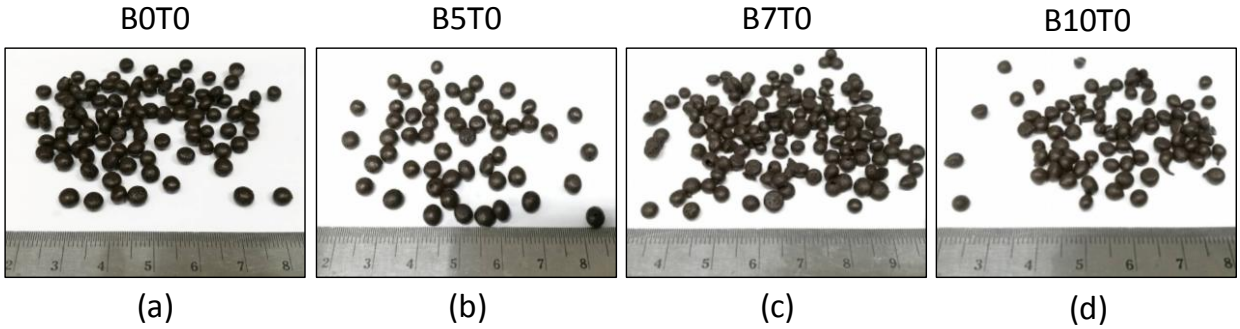

Figure 1. Geopolymer spheres with varying "*Baluko*" shell content: (a) 0% (b) 5% (c) 7% (d) 10% "*Baluko*" shell content.

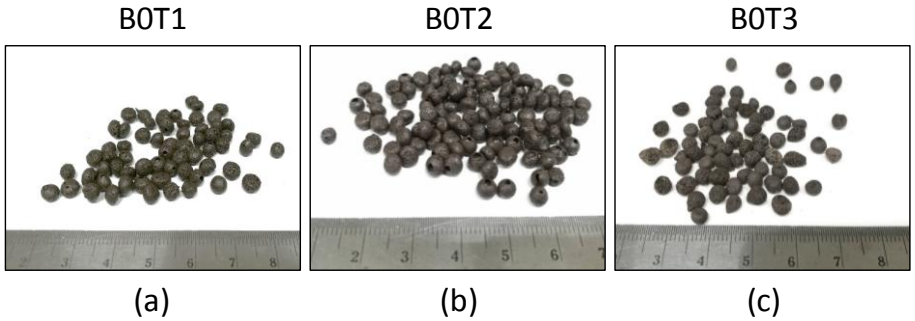

Figure 2. Geopolymer spheres with varying nanotitania content: (a) 1% (b) 2% (c) 3% nanotitania content.

Characterization of Geopolymer sphere

SEM images of some of geopolymer spheres are shown in Figures 3 and 4. It can be observed that the fly ash geopolymer (Figure 3a and 4a) has a heterogeneous matrix consisting of unreacted fly ash particle, geopolymer gel and residual alkaline precipitates. The fly ash particles in the figure are the large spherical images while the geopolymer are the gel-like coating. On the other hand, the presence of calcium carbonate in the geopolymer sphere containing "*Baluko*" shell (Figure 3b and 3c) provide a more consistent coating compare to the fly ash geopolymer. This phenomenon provides a better structure in the porous geopolymer. Moreover, Figure 4 shows that the synthesized geopolymer sphere are porous in nature as shown by the hollow internal structure in the image. The luminous coating in Figure 4b is an indication of the presence of nanotitania.

The FTIR spectrum of the synthesized fly ash-"*Baluko*" shell geopolymer sphere is shown in Figure 5. The presence of the peak at 1000-1100 cm^{-1} is attributed to the asymmetric Si-O and Al-O stretching observed in geopolymer material from aluminosilicate of the fly ash. The peak at 900-1000 cm^{-1} is due to asymmetric Si-O-Si and Al-O-Si stretching. Both bands signify that geopolymerization reaction occurred. Furthermore, a large broad band is seen at 3200-3800 cm^{-1} due to the O-H stretching of Si-O-H groups bonded to the geopolymer matrix. This is attributed to hydrogen bonds between adsorbed water and the Si-O- H group. The peak at 1600-1700 cm^{-1} is an indication of the presence of water molecules bonded to the geopolymer backbone. The peak at 1400-1450 cm^{-1} indicates the existence of O-C-O or carbonate bonds due to the sodium carbonate which came from the reaction between the excess sodium and atmospheric carbon dioxide. Furthermore, small bands seen at around 700-800 cm^{-1} is attributed to the unreacted fly ash.

Figure 6 shows the XRD pattern for fly ash geopolymer sphere (6a) and fly ash-"*Baluko*" shell-nanotitania geopolymer sphere. It can be observed that the XRD patterns of both geopolymers exhibited peaks identified as quartz at $2\theta = 20.75°$, 26.5°, and 36.4°. The main precursor used in the synthesis of the geopolymers is Class F fly ash which has high silica and alumina content. Thus, the expected peak of this type of fly ash is mainly due to the crystallinity of quartz (SiO_2) [22]. Geopolymers are said to be amorphous versions of zeolites due to the disorganized repeating aluminosilicate units [23]. This is reflected in the broad hump represented by the orange line

between 2θ = 15° and 40°. The geopolymerization of fly ash with alkaline solution resulted to an amorphous gel matrix. In addition, anatase, a crystalline form of TiO_2 was detected in the composite geopolymer sample, having peaks at 2θ = 25.3°, 37.9°, and 48.03°, similar to the peaks observed by Kim et al. [16] for the anatase crystallinity. The crystalline phase rutile was also observed at some peaks, since the TiO_2 used was a combination of the anatase and rutile crystals, predominantly anatase.

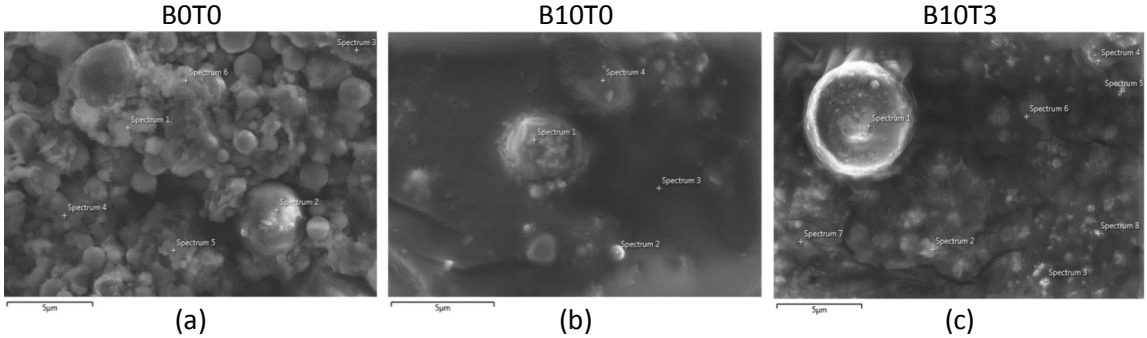

Figure 3. SEM images of synthesized geopolymer spheres at X100 magnification: (a) fly ash geopolymer sphere (b) 10% -"*Baluko*" shell fly ash geopolymer sphere (c) 10%-"*Baluko*" shell/3%-nanotitania fly ash geopolymer sphere.

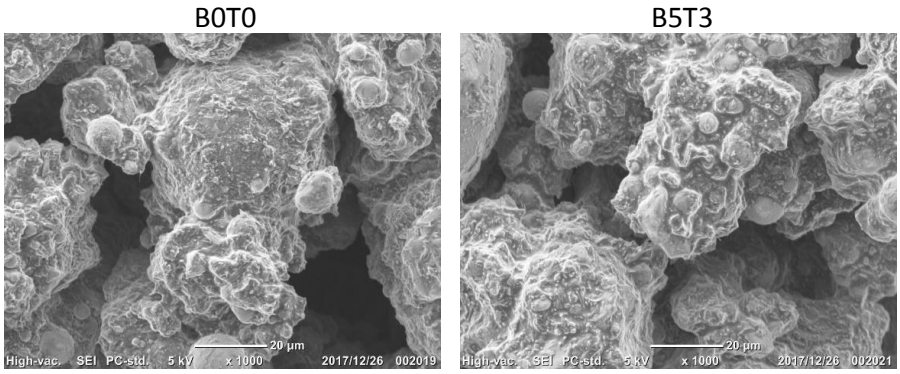

Figure 4. SEM images of synthesized geopolymer spheres at X1000 magnification: (a) fly ash geopolymer sphere (b) 5%-"*Baluko*" shell/3%-nanotitania fly ash geopolymer sphere.

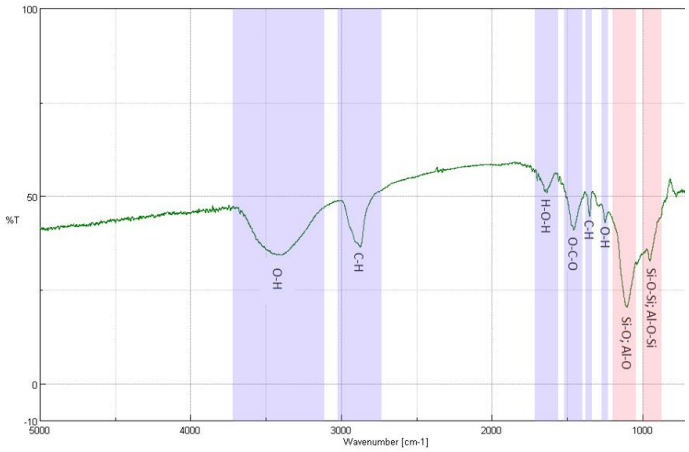

Figure 5. FTIR analysis of fly ash-"*Baluko*" shell geopolymer.

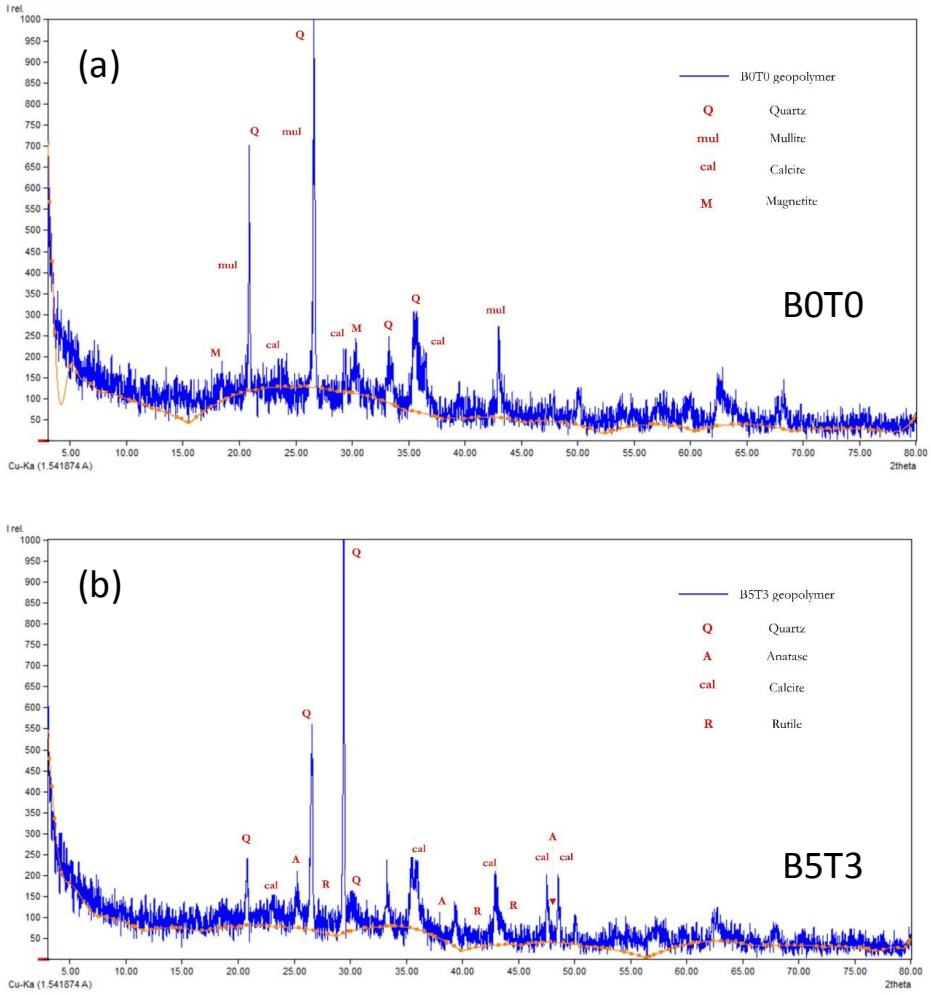

Figure 6. XRD pattern of (a) a fly ash geopolymer (B0T0) and (b) a 5% "*Baluko*" shell-3% TiO_2 fly ash geopolymer (B5T3).

Table 1 shows the different characterization of some selected composite geopolymer spheres. It can be observed that the setting time was shortened as the "*Baluko*" shell composition was increased. In the study by Wallah and Rangan [13], they observed that fly ash with low CaO content resulted to a longer setting time. Replacement of fly ash with calcined "*Baluko*" shells increases the CaO content of the geopolymer and tends to accelerate the setting time of the material. The bulk density of the geopolymer spheres ranges from 1.10-2.26 g/cm^3. The water adsorption and porosity of the geopolymer sphere varies significantly and is strongly due to the difficulty in the controlling pore forming method of the geopolymer sphere.

The efficiency of the geopolymer sphere to degrade methylene blue in solution was observed to decrease as the amount of "*Baluko*" shell increases. The reduction in methylene blue degradation could be attributed to the decrease in the adsorption capability of the porous sphere as the open porosity tend to decrease when calcined "*Baluko*" shells are added Furthermore, the presence of nanotitania improved the methylene blue degradation of the material from 53.45% to 85.54%. It is notable that samples with no added TiO_2 still exhibited a substantial amount of degradation, ranging from around 31-53%. This may be attributed to the adsorptive properties of the porous geopolymer spheres and also the trace amounts of TiO_2 present in the fly ash which was used as raw material.

Table 1. Characterization and performance of selected composite geopolymer sphere

Geopolymer Sphere (FA/BS + NT)*	Setting Time (min)	Water Absorption (g water/g solid)	Bulk Density (g/cm^3)	Open Porosity	Percent MB+ degradation
100/0 + 0	157.75	0.5185	1.91	0.0915	53.45
95/5 + 0	132.11	0.9028	1.10	0.0906	51.49
93/7 + 0	36.49	0.4712	2.04	0.0282	47.35
90/10 + 0	16.57	0.4456	2.26	0.0459	31.34
100/0 + 3	No data	0.7535	1.38	0.0269	85.54
95/5 + 3		0.4904	1.94	0.0416	63.54
93/7 + 3		0.9498	1.19	0.0280	75.25
90/10 + 3		0.4309	2.26	0.0499	65.38

* FA – percent Fly Ash, BS – percent calcined "*Baluko"* Shell, NT – percent nanotitania replacement
+ MB – methylene blue degradation

Conclusions

Coal fly ash and waste "*Baluko*" shell were utilized to produce a porous geopolymer sphere with nanotitania. It was identified via XRD and FTIR analysis that geopolymerization is still effective even with the Baluko shell replacement to fly ash. "*Baluko*" shell replacement has no statistically significant effect in bulk density, open porosity and water absorption of the geopolymer sphere. However, the addition of the shells affected its setting time, allowing the mixture to set at a faster rate with the increasing addition of "*Baluko*"shells. The methylene blue degradation decreases as the amount of "*Baluko*" shell replacement increases but improved significantly with the addition of nanotitania.

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