Geopolymerization of Coal Fly Ash, Ceramic Tile Waste and Spent Bleaching Earth for the Production of Sodium Aluminosilicate Monolith

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Abstract In this study, compressive strength, density, porosity, and methylene blue adsorptive intensity of sodium aluminosilicate monolith produced from coal fly ash (CFA), ceramic tile waste (CTW), and spent bleaching earth (SBE) were evaluated. Using simple lattice mixture design, CFA-CTW-SBE blend with mass ratio of 55.95% CFA, 38.73% CTW, and 5.31% SBE, and an alkalai solution containing 80% 8M NaOH and 20% sodium silicate, resulted to a maximum desirability of 12.4MPa compressive strength, 1310 kg/m³ density, 17.03% porosity, and 1.63% methylene blue adsorption intensity. The properties of the product conform to the specifications of ASTM C90-14 for lightweight load-bearing concrete.

1 Introduction

Geopolymerization is an innovative technology that can utilize raw materials rich in alumina and silica to produce new materials characterized by three-dimensional polymeric structures called geopolymers. Sodium aluminosilicate monolith is a geopolymer that can be used as concrete in building and construction materials (Provis and van Deventer, 2014; Malenab et al., 2017). Moreover, it has the greatest potential to replace zeolite adsorbent in removing heavy metal from wastewater since they have similar amorphous structure constituted by SiO₂ and Al₂O₃ tetrahedra (Novais et al., 2018; Arrifin et al., 2017; Lee et al., 1997). Furthermore, this can be applied in high temperature applications such as furnace linings, fire resistant coatings, thermal insulation and wall panels (Provis and Bernal, 2014).

In the production of sodium aluminosilicate monolith, materials rich in alumina and silica are reacted and formed by alkaline activation at slightly higher than room temperature (Nguyen et al., 2017; Sanjayan et al., 2015; Sumabat et al., 2015). Industrial by-products such as coal fly ash (CFA), ceramic tile wastes (CTW), and spent bleaching earth (SBE) shows great potential for silica and alumina sources (Tigue et al., 2018; Oladosu et al., 2017; Aly et al., 2018). CFA is an industrial by-product derived from coal combustion in thermal power plants. According to Department of Energy (DOE, 2018a), coal-fired power plants has remained the dominant energy source in the Philippines with a share of 35.4% or 8,049 megawatts (MW), and it will continue to increase to over 55% by 2027. In addition, the total generation of CFA amounted to 168,650.20 metric tons for year 2017 (DOE, 2018b). This by-product has been minimally utilized as an additive in cement (Sumabat et al., 2015) and largely being disposed in the landfills near the power plant. In addition to the issue of increasing need for landfill area, coal ash disposal poses the threat of the contamination of surface waters and groundwater from its heavy metal and mineral contents and poses harmful effects on the residents living near the power plant (Kalaw et al., 2018; Ho and Orbecido, 2018).

Another raw material used is SBE which is a solid waste generated in vegetable oil industry. During the refining process, bleaching earth is used to remove color, phospholipids, residue gums, oxidized products and any trace metals from the oil. These colored pigments are trapped and adsorbed in the bleaching earth, thus transforming the originally whitish earth to dark grey, which is the generated SBE. The amount of SBE generated is 0.5 to 1% of the total production of vegetable oil (Huang and Chang, 2010). In the Philippines, 1,781,000 tons of vegetable oil is produced in 2017, generating 13,357.50 tons of SBE at an average (Organisation for Economic Co-operation and Development and Food and Agriculture Organization, 2017). It is considered an industrial by-product as there is hardly any practical application for it (Oladosu et al., 2017). Moreover, SBE is highly susceptible to spontaneous combustion due to the 20% to 40% by weight of oil entrained in it. SBE is usually disposed in landfills or waste dumps which can cause environmental hazards, since it is prone to catching fire, besides polluting the ground water (Wangrakdiskul et al., 2015). Handling and disposing of SBE is a fire risk, an operating expense, and a source of environmental...
regulatory concerns (Oladosu et al., 2017; Huang and Chang, 2010).

The third raw material is CTW which is a solid waste generated from ceramic industry, which was used because of its high generation and good alumina and silica content. According to Reig et al. (2013), CTW is a non-hazardous material, but its non-biodegradability poses a problem because only 65% of this waste is recycled leaving a large amount of solid waste from the ceramic tile industry.

In this study, the proponents aimed to produce sodium aluminosilicate monolith from the ternary mixture of CFA, CTW, and SBE that conforms to the properties of lightweight concrete panels. The raw materials were characterized using X-ray fluorescence (XRF) spectroscopy. In addition, geopolymerization is highly dependent on the reactivity of the materials used. To determine the reactivity of the raw materials, dissolution tests were conducted at room temperature adapting the procedure outlined in the study of Kalaw et al. (2018). A simple lattice mixture design generated from Design Expert 11 software was used to determine the mix proportions and to obtain the optimum mix conditions of a CFA-CTW-SBE ternary mix geopolymer to obtain the properties for lightweight and medium strength structural material. The mechanical properties of the geopolymer samples formed were evaluated using compressive strength tests. Lastly, to assess its suitability as adsorbents for wastewater treatment, the optimum ternary mix geopolymer obtained were used for adsorption of methylene blue and its mechanism were fitted using Langmuir and Freundlich isotherm models.

2 Materials and Methodology

2.1 Sources of raw materials

CFA was obtained from a coal fired power plant located in Batangas, Philippines and was used as received. On the other hand, SBE samples were obtained from a palm oil manufacturing facility in coordination with Department of Environment and Natural Resources (DENR). Lastly, CTW was obtained from a ceramic tile manufacturing plant in Batangas, Philippines. Alkali activator used in the study was prepared using analytical reagents purchased from a local company at an 80-20 mass ratio of 8M NaOH (sodium hydroxide) solution and Na₂SiO₃ (sodium silicate) solution. In addition, the blowing agent used is 3% hydrogen peroxide solution.

2.2 Characterization of raw materials

X-ray Fluorescence analysis was conducted to determine the elemental composition of raw materials. For CFA, the analysis was provided by the power plant company in Batangas. On the other hand, the other raw materials were tested at InterTek Minerals Testing Philippines.

2.3 Dissolution tests

To determine the reactivity of the raw materials, dissolution experiments were conducted at room temperature. First, dissolve 2.5 g of the sample (CFA, CTW, SBE) in three separate beakers containing 50 mL of 80% 8M NaOH solution and 20% sodium silicate. Next, stir the solution continuously for two hours and filter the solid residues. Then, dry the filtered solid residues at 105°C until the weight is constant. Finally, calculate the percent dissolution using the formula:

\[
\% \text{ dissolved} = \frac{\text{mass of sample (g)} - \text{solid residue (g)}}{\text{mass of sample (g)}} \times 100 \tag{1}
\]

2.4 Pre-Treatment of raw materials and geopolymer production

2.4.1 Preparation of raw materials

The average particle size of CFA and SBE used is 425 μm (mesh 40). On the other hand, CTW was ground for 30 minutes and sieved using Tyler Mesh 40 (425μm). Also, residual oil in SBE was removed using isopropanol with 1:1.5 (w/w) ratio through leaching at 70°C for 60 minutes, then the resulting mixture was filtered and the recovered SBE cake was dried at 90°C for 1 hour.

2.4.2 Geopolymer production

CFA, ground CTW, and pretreated SBE were mixed according to different mix ratios obtained using simple lattice design for mixtures from Design Expert 11 as shown in Figure 1 and Table 1 and reacted with alkali solution at 70-30 mass ratio at ambient temperature for 30 minutes to facilitate breakdown of aluminosilicates releasing reactive silicate and aluminate monomers, which then reforms and rearranges to a 3D structure geopolymer. Afterwards, 3%(w/v) hydrogen peroxide is reacted with the geopolymer slurry at ambient temperature for 30 minutes, then the mixture is poured in 50mm cubical mold and is cured at 50°C for 2 hours. Afterwards, the monolith is allowed to cure again for 7 days at ambient room temperature. The compressive strength of the samples were tested using UTM Digimax C0019/Y.

| Mix Ratio | CFA (A) (g) | CTW (B) (g) | SBE (C) (g) |
|-----------|-------------|-------------|-------------|
| R1        | 500         | 0           | 0           |
| R2        | 0           | 500         | 0           |
| R3        | 0           | 0           | 500         |
| R4        | 250         | 250         | 0           |
| R5        | 250         | 0           | 250         |
| R6        | 0           | 250         | 250         |
| R7        | 333.33      | 83.33       | 83.33       |
| R8        | 83.33       | 333.33      | 83.33       |
| R9        | 83.33       | 83.33       | 333.33      |
| R10       | 166.67      | 166.67      | 166.67      |
In determining the optimal mix ratio of the ternary blend CFA, CTW, and SBE, multiple response surface optimization via desirability functions was used, having compressive strength and density as the output response.

2.5 Methylene blue (MB) adsorption determination

For adsorption, the monoliths were immersed in 200 mL of a solution containing 10 ppm MB concentration and stirred occasionally during a predetermined period of time (30 h) at room temperature. Aliquots from the solution were taken from the liquid, and its MB concentration was evaluated by determining the absorbance in a UV-vis spectrometer (PerkinElmer λ 365 (664 nm)). To determine the adsorption mechanism, the data were fitted using both the Langmuir and Freundlich models.

2.5.1 Langmuir model

The Langmuir model assumes homogeneous binding sites and equivalent sorption energies in the surface, and that there is no interaction between the sorbed species (Kim et al., 2015). It is described by the equation:

\[ q_e = \frac{C_0 - C_e}{m} \times V \quad (2) \]

Where \( q_e \) is the quantity of MB uptake by the monolith (mg/g), \( C_0 \) is the initial concentration of MB (mg/L), \( C_e \) is the remaining equilibrium MB concentration (mg/L), \( V \) is the volume (L) and \( m \) is the mass of the monolith (g).

2.5.2 Freundlich model

The Freundlich isotherm model, on the other hand, has been interpreted as sorption onto a heterogeneous surface, having sites with different affinity. In that model, one presumes that the stronger binding sites are occupied first, and that the binding strength decreases with the increasing degree of occupation (Kim et al., 2015). The model has the form:

\[ q_e = K_F C_e^n \quad (3) \]

where \( K_F \) is the Freundlich constant, and \( n \) is a parameter which represents the absence of linearity of the adsorbed quantity in function of \( C_e \). If the value of \( 1/n \) is between 1 and 10, then there is favourable adsorption. Larger values of \( n \) suggests, on the contrary, a stronger interaction between the surface of the adsorbent and adsorbate; when \( 1/n \) is equal to 1, this means a linear adsorption, leading to identical adsorption energies for all the sites (Febrianto et al., 2009).

3 Results and Discussion

3.1 Characterization of raw materials

The elemental composition of the raw materials are shown in Table 2. CFA is classified as Class F fly ash under ASTM C618-05 since the sum of the silica, alumina, and iron oxide is 72.82%, which is greater than 70%. Also, the Si:Al ratio of CFA is 2.42:1, which is a suitable material for geopolymer products applied in low carbon-dioxide-emission cements and concretes, and toxic waste encapsulation or adsorption. On the other hand, CTW and SBE have Si:Al ratio of 3.79:1 and 6.17:1, respectively, which means it can be used as adhesives in various industries operating at 200 to 600 °C (Dimas et al., 2009; Timakul et al., 2015).

| COMPOSITION | CFA | CTW | SBE |
|-------------|-----|-----|-----|
| SiO₂        | 47.5| 67.78| 60.50|
| Al₂O₃       | 19.6| 17.87| 9.80 |
| CaO         | 12.3| 1.21 | 4.15 |
| Fe₂O₃       | 5.72| 5.52 | 8.79 |
| K₂O         | 3.00| 1.02 | -    |
| MgO         | 4.70| 0.95 | 4.59 |
| Na₂O        | 1.96| -    | -    |
| TiO₂        | 0.63| -    | 0.96 |
| SO₃         | 3.20| 0.060| -    |
| P₂O₅        | 0.095| 5.18|
| BaO         | 0.11| -    | -    |

| Moisture Content | 0.30 | - | 1.94 |

3.2 Dissolution test

Geopolymerization is highly dependent on the reactivity of the materials used. Table 3 shows that CFA has the highest dissolution rate of 46% among the three raw materials, followed by SBE at 41.60%, then CTW at 27.60%. CFA and SBE are reactive due to their amorphous properties, while CTW has the lowest reactivity because of its crystal structure (Mas et al., 2015).
3.3 Optimum ternary mixture ratio

Table 4 shows the compressive strength and density of sodium aluminosilicate monoliths produced from the mix design of the raw materials.

| MIX RATIO | Compressive Strength (CS) (MPa) | Mass (g) | Density (D) (kg/m³) |
|-----------|--------------------------------|----------|---------------------|
| R1        | 20                             | 205.04   | 1564.0              |
| R2        | 6                              | 228.20   | 1740.7              |
| R3        | 0                              | 198.15   | 1511.5              |
| R4        | 14                             | 203.25   | 1550.4              |
| R5        | 6                              | 227.29   | 1733.8              |
| R6        | 0.4                            | 173.60   | 1324.2              |
| R7        | 12                             | 205.04   | 1564.0              |
| R8        | 2                              | 199.61   | 1522.6              |
| R9        | 0                              | 192.71   | 1470.0              |
| R10       | 2                              | 206.33   | 1573.9              |

Based on the statistical analysis of these data, the best fit model for both responses is quadratic equation as shown below. For compressive strength (CS) equation (4), linear model terms A, B, and C, as well as AB and AC are all significant terms since their P-values are less than 0.10, as shown in Table 5. However, model term BC will not be included since its p-value is 0.1251. On the other hand, for density (D) equation (5), all model terms are considered significant.

\[
CS = 20.62A + 5.67B + 0.40C - 3.36AB - 21.91AC \quad (4)
\]

\[
D = 1554.78A + 1741.36B + 1501.98C - 362.98AB + 808.66AC - 1163.38BC \quad (5)
\]

For optimization, the desirability function was used wherein the compressive strength was set to 12 MPa, meeting the minimum requirement of 11.7MPa from ASTM C90-14 for moderately-loaded, lightweight load bearing concrete, while density was minimized, with a maximum value of 1680kg/m³ in accordance with PNS ASTM C332:2013, as shown in Table 7.

| COMPOSITION | GOAL | LOWER LIMIT | UPPER LIMIT |
|-------------|------|-------------|-------------|
| A (CFA)     | is in range | 0 | 500 |
| B (CTW)     | is in range | 0 | 500 |
| C (SBE)     | is in range | 0 | 500 |
| Compressive Strength | target = 12 | 11.7 | 14 |
| Density     | Minimize | 0 | 1680 |

The resulting ternary plots for compressive strength and density are shown in Figure 2. The green-shaded region in the figures indicates the possible mix ratios of the raw materials that would meet the desired properties of the product.

Figure 2(a) and Equation 4 indicates that the increase in the compressive strength of sodium aluminosilicate monolith is due to the CFA. Moreover, SBE and CTW decrease the compressive strength of the product as shown by the downward slope in the response surface plot. The effect of SBE to decrease the strength may be attributed to the remaining residual oil after leaching since oil reacts to sodium hydroxide to form soap through saponification.

On the other hand, all materials contributed linearly to the density of the product as shown in Figure 2(b) and Equation 5, but a higher proportion of SBE and CTW would give a lower density. From this, the optimum mix ratio for the production of sodium aluminosilicate monolith is 55.95% CFA, 38.73% CTW and 5.31% SBE, with a desirability of 0.283.
Figure 2. Response surface plots of a) the compressive strength b) density of sodium aluminosilicate monoliths

3.4 Methylene blue (MB) adsorption determination

To determine the adsorption mechanism, the results are fitted into the Langmuir and Freundlich isotherm plots as shown in Figure 3.

The Pearson correlation coefficient of Freundlich isotherm plot is closer to 1, therefore the adsorption behavior can be fitted to this model. Based on the equation given by the Freundlich isotherm, the adsorption intensity \((1/n)\) is equal to 1.63, this means that sodium aluminosilicate monoliths gave a favorable adsorption behavior. On the other hand, the Freundlich constant obtained is 0.07 for sodium aluminosilicate monoliths.

3.5 Characteristics of produced sodium aluminosilicate monolith

The produced sodium aluminosilicate monolith was subjected to a quantitative analysis as per ASTM C0109/C0109M: Standard Test Method for Compressive Strength of Hydraulic Cement Mortars and was found to conform to the specifications of ASTM C90-14 for moderately-loaded, lightweight load bearing concrete (minimum compressive strength of 11.7MPa and maximum density of 1680 kg/m\(^3\)) by exhibiting the following properties: average compressive strength of 12.4 MPa, density of 1310 kg/m\(^3\), and porosity of 17.03%. Furthermore, adsorption capacity was tested through UV-vis spectrophotometer resulting to methylene blue adsorption intensity of 1.63% and a Freundlich constant of 0.07.

4 Conclusion

The production of sodium aluminosilicate monolith has been obtained through geopolymorization of coal fly ash (CFA), ceramic tile wastes (CTW) and spent bleaching earth (SBE). In this study, the properties of monolith produced from the ternary mixture of 56-39-5 by mass ratio of CFA-CTW-SBE and an alkali solution containing 80% 8M NaOH and 20% sodium silicate conformed to the specifications set by ASTM C90-14, and ASTM C332. The product obtained compressive strength of 12.4MPa and 1310 kg/m\(^3\) density. Furthermore, due to the addition of hydrogen peroxide, the product obtained a porosity of 17.03% and methylene blue adsorption intensity of 1.63% signifying that the product may be used as an adsorbent for wastewater treatment.
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