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Synthesis of Pervious Geopolymer from Coal Fly Ash and Bagasse Fly Ash for Copper Removal

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Geopolymer has recently gained popularity as an eco-friendly material because of its potential to valorize waste. It is a new class of inorganic material formed upon dissolution of aluminosilicate in the presence of an activating solution. The aluminosilicate minerals become reactive and then form into aluminosilicate oligomers. While most of the study in geopolymer research is focused on cement and concrete industry, it also gained attention as an alternative material for solving environmental pollution in water. This study thus explores the use of combining coal fly ash and bagasse fly ash as the aluminosilicate source to produce pervious geopolymer for the treatment of copper-contaminated water. While coal fly ash (CFA) is a by-product of a coal-fired power plant, bagasse fly ash (BFA) is a waste product of the co-generation plant of sugar mills from burning bagasse. These raw materials were mixed with coarse aggregates and activating solution composed of sodium hydroxide and sodium silicate to produce a pervious geopolymer. The effects of the mix proportions of CFA and BFA on the compressive strength, porosity, and permeability of pervious geopolymer were investigated. Moreover, the copper removal efficiency of pervious geopolymer was determined using atomic absorption spectroscopy (AAS). The findings revealed that pervious geopolymer is a promising material that could remove copper at 67–87% efficiency.

1. Introduction

Rapid industrialization has contributed to the increase in toxic metal contamination in the environment. One of the contributors to the presence of toxic metals in water is the mining industry. Various studies have shown that prolonged exposure to these wastes may greatly affect human health due to their hazardous and carcinogenic properties. This industry produces a waste product called acid mine drainage (AMD) which is characterized by having low pH or acidity due to the presence of hydronium ions formed from oxidation. Untreated acid mine drainages could cause serious environmental consequences in aquatic and soil ecosystems. Therefore, proper management of these wastewaters should be of top priority (Aguiar et al., 2018). One of the significant mining disasters that had struck the Philippines was the 1996 Marcopper mining tragedy in which the company's open-pit burst and contaminated a nearby river with copper mine tailings that eradicated marine life (de la Cruz, 2017). This incident was critical enough that it paved the way for the revision of the country's mining policy. Hence, this study focused on remediation through the removal of Cu from the contaminated water.
Acid mine drainage, which is comprised of heavy metals, is treated in two approaches: active and passive treatment systems. Active treatment typically involves the use of mechanical equipment and chemicals that requires regular operation and maintenance making it more expensive as compared to passive treatment (Younger et al., 2002). Passive treatment system depends on natural, physical, geochemical, and biological processes that contain neutralizing material with a long lifespan which requires minimal human input (Skousen et al., 2000). Permeable reactive barrier or PRB is a passive and low-cost in-situ treatment which prevents cross-contamination with surface waters and doesn't require any waste disposal (Moodley et al., 2018). One of

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the materials that can be considered in developing PRB is the use of geopolymer. For example, Novais et al., (2019) developed an innovative 3 mm spheres made from fly-ash based geopolymer and found out that it is more efficient than that of powdered type geopolymer. The porous nature of geopolymer and its chemical similarity with zeolites made it more interesting (Rasaki et al., 2019). However, investigating the characteristics and optimizing the formulation of aluminosilicate material for geopolymerization to meet the desired specification is of significant importance (Sumabat et al., 2015).

Pervious geopolymers are inorganic substances synthesized from an aluminosilicate substance in an alkaline environment. They are incorporated with aggregates to induce channels (Nikolov et al., 2017). They are potential substitutes to concrete because of their enhanced properties and environment friendly fabrication process (Zaetang et al., 2015), but it is gaining attention due to its features such as ion-exchange capability (Javadian et al., 2015). The heavy metal removal efficiency of pervious geopolymer showed promising result as it outweighs the performance of porous geopolymer monolith (Tan et al., 2020). However, most of research only evaluated the material's capabilities particularly their adsorptive properties in batch processes. There was limited investigation on utilization of biomass fly ash in the production of geopolymers. This study highlighted the addition of bagasse fly ash into the blends of the geopolymer. This study aims to produce a pervious geopolymer by incorporating bagasse fly ash in the aluminosilicate precursor for the removal of copper, a heavy metal constituent of acid mine drainages.

2. Materials and method

This study requires the fabrication of a pervious geopolymer and its evaluation in terms of its copper removal from an aqueous solution. Bagasse fly ash and coal fly ash which serve as the aluminosilicate sources were mixed with coarse aggregate to produce pervious geopolymer.

2.1 Material

Coal fly ash was sourced from a thermal powerplant situated in Central Luzon, Philippines, while bagasse fly ash was collected from a company situated in South Luzon, Philippines. Reagents that were used for the preparation of the alkali activator were 10 M sodium hydroxide and sodium silicate solution using the formulation recommended in Arafa et al. (2017). Additionally, coarse aggregates with sizes ranging from 4.75 – 9.5 mm were incorporated to induce connected porosity and to increase permeability. The cylindrical molds used were fabricated from cylindrical PVC pipes with an inner diameter of 7 cm and height of 16 cm. To produce the aqueous copper ion solution, copper sulfate pentahydrate was used.

2.2 Method

The experimental procedure comprises the preparation of raw materials, synthesis of pervious geopolymer, and characterization of pervious geopolymer.

2.2.1 Preparation of materials

Chapter 2 The materials that require preparation were the bagasse fly ash and coal fly ash as well as the alkali solution and coarse aggregates. Both ashes and coarse aggregates were sieved while the alkali solution needs exact raw material measurements to achieve the component ratios.

Chapter 3 The bagasse and coal fly ash underwent elemental characterization employing X-ray fluorescence (XRF) analysis. This was done to determine the composition of the material. Both the bagasse fly ash and coal fly ash were sieved using mesh 200 to ensure uniform particle sizes. Using the bulk densities, the mixture of the fly ashes in different proportions was prepared which served as the source of aluminosilicate of the geopolymer production. The alkali activator was made from sodium hydroxide solution and sodium silicate solution. The 10M NaOH was made from analytical grade NaOH flakes dissolved in distilled water. It was then mixed with the sodium silicate solution to yield the activator. The mass ratio of sodium silicate solution and NaOH solution of 10:4 was utilized as an activator which was based on a previous study (Arafa et al., 2017). Synthetic acid mine drainage was prepared by dissolving copper sulfate pentahydrate ($CuSO_4{\bullet}5H_2O$) in distilled water to obtain a Cu^{2+} concentration of 25 mg/L. The pH of the solution was maintained at less than pH 4 with the use of concentrated H_2SO_4. The properties of synthetic acid mine drainage were based on the AMD discharge of an inactive open-pit copper mine in Marinduque, Philippines (Primo et al., 2006).

2.2.2 Synthesis of pervious geopolymer

The aluminosilicate base and the alkali solution were mixed with the coarse aggregates. The total fly ash to coarse aggregates ratio was 1:7 by mass while the alkali solution to total fly ash ratio was 1:2 by mass (Arafa et al., 2017). The resulting slurry was mixed manually. It was placed in a cylindrical PVC mold and was then allowed to rest for 30 mins. The slurry was cured inside an oven for 24 h at 60 °C and was demolded and allowed to stay in the same condition until the 7th day. Lastly, the samples were allowed to sit in ambient conditions until the 28th day. The synthesized pervious geopolymer was further characterized.

Table 1: Formulation of the aluminosilicate precursor

Set	Coal fly ash (ρbulk = 1.649 g/mL)		Bagasse fly ash (ρbulk = 0.424 g/mL)	
	% v/v	% w/w	% v/v	% w/w
A	100	0	0	0
B	75	92.11	25	7.89
C	50	79.54	50	20.46

2.2.3 Characterization of pervious geopolymer

For each of the analyses, all three proportions of the aluminosilicate blend listed in Table 1 were tested to evaluate the influence of the incorporation of bagasse fly ash. All sets of samples were done in duplicates. The following characterization and properties were investigated: compressive strength, morphology, porosity and permeability, and Cu2+ removal. The compressive strength of the geopolymer samples was determined by testing each sample using a universal testing machine (UTM). To investigate the morphological property of pervious geopolymer samples, scanning electron microscopy with energy dispersive X-ray Analysis (SEM EDX) was performed. Water permeability of the geopolymer samples was determined with the use of the constant head method. Continuous flow of water was allowed to pass through the geopolymer concrete until a steady flow rate was achieved. The porosity of the pervious geopolymer was measured using the weight of saturated and dry weight samples. The sample was then saturated with water and was immersed in a pool of water to measure the amount of water displaced. The difference between the weight of the saturated sample and its dry weight was considered the weight of water in pore space.

For the removal efficiency test, the prepared copper solution was placed in a reservoir and pumped in an up-flow configuration. Sample effluents were collected every 15 mins. These samples were treated and analyzed through atomic absorption spectrometry (AAS). The copper removal efficiency, R, of each sample, was calculated using the initial concentration, C0, and final concentration, Cf of the metal in ppm (Novais et al., 2016) as shown in Eq(1).

$$R\ (\%) = (C_o - C_f) / C_o \times 100 \qquad (1)$$

3. Results and discussion

3.1 Characterization of raw materials

The coal fly ash and bagasse fly ash were characterized to determine their composition. Table 2 shows the XRF analysis of coal fly ash and bagasse fly ash.

Table 2: Chemical composition of coal fly ash and bagasse fly ash

Component	Coal Fly Ash (% Mass)			Bagasse Fly Ash (% Mass)		
	Trial 1	Trial 2	Average	Trial 1	Trial 2	Average
MgO	8.52	9.37	8.95	-	3.14	3.14
Al2O3	14.74	15.50	15.12	4.54	4.40	4.47
SiO2	55.16	53.49	54.33	87.45	79.69	83.57
SO3	1.88	2.32	2.10	-	0.63	0.63
K2O	1.34	0.84	1.09	4.74	4.23	4.49
CaO	10.17	11.11	10.64	1.43	2.40	1.92
TiO2	0.43	0.54	0.49	-	-	-
Fe2O3	7.76	6.82	7.29	0.90	0.84	0.87
P2O5	-	-	-	0.95	4.67	2.81

High Si and Al content of coal fly ash indicate suitability as geopolymer precursors. Bagasse fly ash was observed to be dominantly composed of silica. The high silica content of bagasse fly ash was due to the combustible matter present when bagasse is burnt from. Despite the low alumina component of bagasse fly ash, this waste product is still viable as an aluminosilicate source for geopolymer synthesis as the molecular framework could exist as poly-sialate (-Si-O-Al-O-) or poly-siloxo (-Si-O-Si-O-) which are chemical groups with little to no aluminum (Davidovits, 2005).

3.2 Characterization of pervious geopolymer

3.2.1 Compressive strength, porosity, and permeability

Three samples for each bagasse fly ash concentration were made and subjected to a compressive strength test. The results are summarized in Figure 1. Based on the graph below, the maximum value for compressive strength is 1.6 MPa. The values for the compressive strength ranges from 1.2 – 1.6 MPa. A decreasing compressive strength is observed with increasing amounts of bagasse fly ash concentration. In comparison with other studies, the compressive strength of the pervious geopolymer samples was quite low. This was attributed to the materials used. Most of these studies utilized additives such as blast furnace slag and fine aggregates which resulted in stronger samples. Meanwhile, the permeability of each sample of pervious geopolymer concrete is determined using a constant head permeameter which ranges from 2.09 – 2.20 cm/s. The permeability could be directly related to porosity concerning age, binder, material type, and ash-to-coarse aggregates showing little influence on it (Arafa et al., 2017). The porosity values ranged from 37.0 % to 39.1 %. Porosity was also a factor to consider. Higher values were registered by the geopolymer samples that reduced the compressive strength (Arafa et al., 2017).

Figure 1: Compressive strength of pervious geopolymer with varying blends of aluminosilicate precursor

3.2.2 Copper removal efficiency

The copper removal efficiency of pervious geopolymer concrete was determined by comparing the AAS results of the initial and final copper concentrations of the solution. As seen in Figure 2, there is no apparent trend on the copper removal where all samples exhibit almost similar removal efficiency. Nonetheless, each sample has removed a significant amount of copper from the influent. The amounts of copper removed are in the range of 67 – 87% of its initial concentration. Moreover, the presence of active sorption sites allows the removal of heavy metal cations from a solution in contact with the geopolymer. Weak Van der Waals forces between the geopolymer surface and the metal cation are established as physical adsorption takes place.

Another factor that may significantly affect the removal mechanism of copper is pH. Adsorption is less at low pH compared to high pH because of H^+ ions competing against Cu^{2+} ions for the position on the active sorption sites. Since the hydrogen ion exists at a much lower concentration at high pH, the adsorption uptake of copper is greater. However, at high pH, precipitation of hydroxides may occur. The effluents from each trial of heavy metal removal have a pH of 9.30 – 9.76. The solubility of $Cu(OH)_2$ is the least at pH 10. Since washing the geopolymer concrete samples has only reached an equilibrium of pH 10 after three weeks, passing a pH 4 copper solution through the geopolymer concretes can increase the pH and precipitation may have initiated as observed in the bluish color of the effluent from each trial. With this, it may be inferred that $Cu(OH)_2$ precipitates may have adhered to the surface of the geopolymer concrete. Hence, desorption through simple washing of the samples may include precipitates, together with the adsorbed copper cations.

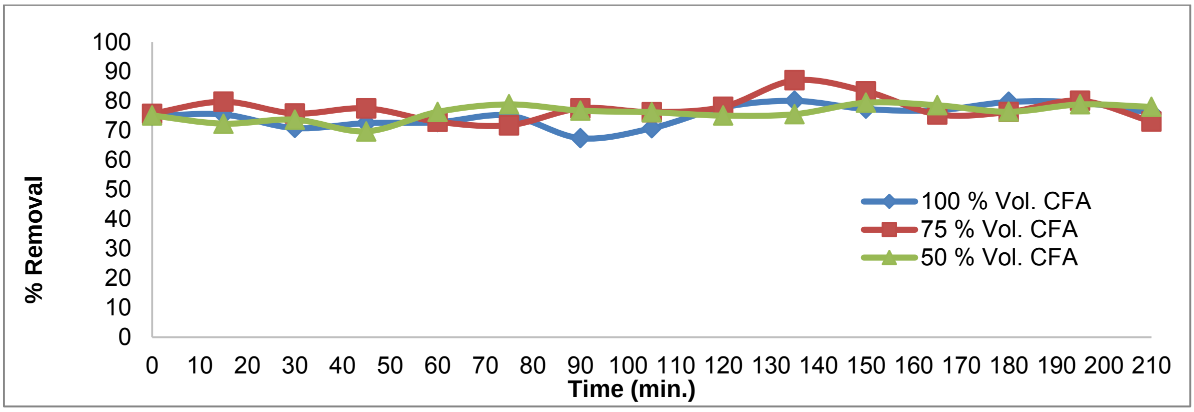

Figure 2: Plot of copper removal (%) against time (min.)

3.2.3 Morphological property

The morphological property of pervious geopolymer is shown in Figure 3. It is evident that incorporating more bagasse fly ash into the aluminosilicate precursor induces the formation and enlargement of microcracks which are undesirable in terms of structural strength. The decrease in strength can be attributed to more formation of microcracks as shown in Figure 3. Meanwhile, comparing the SEM images of the pervious geopolymer's surfaces before and after the metal removal test, it is evident that there is an increase in the amount of copper present. There are spherical-shaped particles present on the geopolymer surface after the test that, according to Bai & Williams (2014), are copper particles.

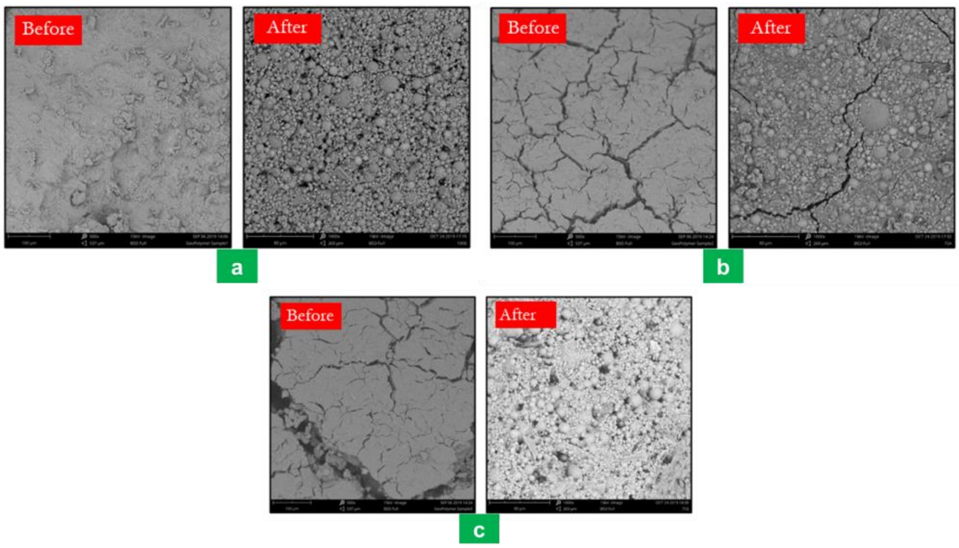

Figure 3: SEM images before and after copper removal tests of (a) 0 % BFA, (b) 25 % BFA, and (c) 50 % BFA pervious geopolymer concrete samples

4. Conclusions

A pervious geopolymer is developed using bagasse fly ash and coal fly ash as the aluminosilicate sources. The compressive strengths of the geopolymer concrete range from 1.2 – 1.6 MPa. The lower values of compressive strength may be attributed to the lack of additives, other than aggregates. Additives are proven to improve the compressive strength of the geopolymer. It is also worthy to note that the decrease in compressive strength may be associated with microcrack formations. There is an observable increase in these microcracks as the BFA/CFA ratio is increased. The permeability range of 2.09 – 2.20 cm/s and porosity range of 37.0 – 39.1 % were recorded. The minimal change in these values considering the variation in aluminosilicate sources may be due to the fixed size of aggregates used in the study. These two quantities are found to be directly proportional. Nonetheless, the permeability of the samples is comparable with the standard and is slightly affected by

BFA/CFA ratio. Meanwhile, the porosity of the samples is independent of BFA/CFA ratio and is found to affect the compressive strengths. The average copper removal efficiencies of the pervious geopolymer samples were within the range of 67 – 87 %. The removal mechanisms of the pervious geopolymer samples are determined to be both adsorption and precipitation, which may have happened simultaneously. An increase in the amount of copper as shown in the SEM-EDX analysis suggests that physical adsorption of the heavy metal occurs by passing a synthetic copper solution to the samples. The observed color and pH of the effluent samples may denote precipitation. To obtain the most promising pervious geopolymer concrete using the employed raw materials, optimization of the formulation with respect to the properties is recommended. Nevertheless, the pervious geopolymer concrete fabricated with bagasse fly ash and coal fly ash as the aluminosilicate materials are found to be comparable to those geopolymer concretes from literature and is a possible PRB for heavy metal removal in acid mine drainage.

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