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Effects of Fly Ash Geopolymer Leachate Alkalinity on Lethality of Freshwater Climbing Perch, *Anabas testudineus*

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ABSTRACT

The application of geopolymer materials from industrial waste as binder to cast concrete contributes to a reduction of carbon dioxide than ordinary Portland cement but still contribute to other environmental adverse effect such as freshwater toxicity. The leaching of alkali from geopolymer building materials increases the alkalinity or pH values of affected water body and can cause damage the biotic ecosystem and aquatic organisms. The increasing level of alkalinity which is pH values from the leaching of geopolymer materials and ordinary Portland cement caused the lethality of *Anabas testudineus* (climbing perch) were determined. A 50mm x 50mm x 50mm dimensional fly ash geopolymer paste with 12M NaOH solution (Na₂SiO₃ : NaOH = 2.5:1) and a 50mm x 50mm x 50mm dimensional ordinary Portland cement with the ratio of (Solid : Liquid = 3 : 1) were immersed accordingly into each cylindrical containers that contained an *Anabas testudineus* (climbing perch) in 500ml paddy swamp water. The fishes were observed and the pH readings were calculated. The test was ended when all the fishes were dead. Finally, the mortality limit pH value of *Anabas testudineus* for fly ash geopolymer paste is at pH 11.0, while ordinary Portland cement is at pH 11.5. The peak of alkali leaching of fly ash geopolymer paste is between 0.5 – 1.0 hours while for ordinary Portland cement is between 0.25 – 0.5 hours. As the conclusion, ordinary Portland cement gives severe adverse effects to the mortality of *Anabas testudineus* compared to fly ash geopolymer paste due to the leaching of OH⁻ and other alkali anions. *Anabas testudineus* can live 10 hours in fly ash leaching media but only can live 1 hour in ordinary Portland cement leaching media.

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1. Introduction

The contribution to carbon emissions from the ordinary Portland cement (OPC) concrete can be reduced by the substitution of geopolymer materials (Al-Bakri Abdullah et al., 2012). With growing environmental demands in terms of low carbon, geopolymer concrete has merged as environmentally construction material with great potential to complement OPC (Sufian Badar, Kupwade-Patil, Bernal, Provis, & Allouche, 2014). The development of green technology in the construction industry since 10 years ago is something to be proud of Malaysia.

Geopolymer is the mixture of aluminosilicate precursor material such as fly ash, alkaline reagent like sodium or potassium soluble silicates with a molar ratio
MR SiO2:M2O ≥ 1.65, M being Na or K. Geopolymer is hardening in room temperature (Al-Bakri Abdullah et al., 2012). Several alternative geopolymer materials were invented in Malaysia such as fly ash, POFA, kaolin, metakaolin, and dolomite based geopolymer materials to achieve sustainable development especially in the building and construction sector (Zain, Abdullah, Hussin, Ariffin, & Bayuaji, 2017).

One of the geopolymer application is concrete binder. The application of geopolymer materials from industrial waste as binder to cast concrete, e.g. fly ash, slag and mud potentially contributes to a maximum reduction of 80% carbon dioxide emission in construction projects compared with OPC based on heat balance comparison study (Arnaud, 2014). However, when compared fly ash geopolymor with the OPC life cycle, fly ash geopolymer concrete was still able to reduce the effects of global warming potentials, but it is rather gave a negative impact on some aspects of the environment such as abiatic depletions, human toxicity, freshwater ecotoxicity, terrestrial ecotoxicity and acidification (Zain et al., 2017).

Habert, D’Espinose De Lacailleer, & Roussel (2011) reported that geopolymer concrete has a higher environmental impact regarding other impact categories than global warming impact due to the heavy effects of the production of the sodium silicate solution, whilst geopolymor concrete made from fly ashes or granulated blast furnace slags based require less sodium silicate solution in order to be activated. They therefore have a lower environmental impact than geopolymer concrete made from pure metakaolin.

Geopolymer has an effective immobilization system in order to adsorb heavy metal contaminant and the need to establish the main processing variables and their effects on the final product are becoming of increasing interest to researchers (Phair & Van Deventer, 2001).

From previous research, the immobilization of copper and lead in geopolymor binders mainly affected by the kinetic leaching of the materials, the effect of pores and particle size during leaching process (Van Jaarsveld, Van Deventer, & Schwartzman, 1999).

During geopolymerization, the dissolution of Al and Si from fly ash was greatest in NaOH solutions while the dissolution of Ca and Mg was greatest in KOH solutions. Thus, increasing the solid: liquid ratio decreased the dissolution of Ca and Mg. Geopolymer concrete made from fly ashes or granulated blast furnace slags based require less sodium silicate solution in order to be activated. They therefore have a lower environmental impact than geopolymer concrete made from pure metakaolin.

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Karuppuchamy, Ananthkumar, & Raghavapriya (2018) reported that the pH or alkalinity of alkali activator solution was affected by varied mixed proportion of the materials, curing temperature and curing duration where the alkalinity of stimulated pore solution was measured in pH by the range of 10.2 to 11.7 for fly ash geopolymor materials.

Leaching is a method to remove soluble components from a solid matrix. Kim, Kazonich, & Dahlberg (2003) described leaching in a very simple equation. Material (leachee) + leachant → leachate. It can be assumed that the material to be leached is known, although its physical and chemical or mineralogical properties will affect the final result.

Leachability of trace elements and heavy metals of construction materials strongly depends on the water hardness, affected by the calcium concentration and the availability of hydro carbonate in the leachate (Hartwich & Vollpracht, 2017).

The leachability of the critical elements depends on the pH of the leachate (Engelsen et al., 2010). The changes in pH can alter the solubility by several order or magnitude. For many heavy metals, the leachability from cementitious materials increases as the pH decreases (Hartwich & Vollpracht, 2017).

Thus, the application of geopolymer materials as construction materials in aquatic and freshwater environment should be reconsidered. Zain et al. (2017) reported that even though fly ash concrete based still shows positive results to the environment because it produced almost half CO2 emission lower than OPC concrete during its production but fly ash geopolymer concrete based gave some low negative impacts to the environment especially towards abiatic depletions, human toxicity, freshwater ecotoxicity, terrestrial ecotoxicity and acidification.

It is supported by Hartwich & Vollpracht (2017) which stated that the overall concentration of water constituents plays an important role, by influencing the concentration equilibrium between the pore solution and the leachate. Water hardness and calcium concentration within leachate becomes the main factor. Hydro carbonate content caused a high buffer capacity in the leachate and it provides carbonate ions to react with calcium producing carbonate salt that reducing the pore structure in the materials and inhibit the rate of leachability.

Philip Bloch (2014) reported that large anthropogenic infrastructure such as major bridges in waterways can influence the ecological dynamics of the affected aquatic environment. These influences may affect behaviour, habitat use, fitness, and survival of endemic fishes.

Seventy-five percent of the available surface water resources (river water) in Malaysia are used for rice irrigation. However, many of the rivers in Malaysia suffer from pollution. Aquatic organisms are sensitive to pH changes and require a pH value from 6 to 9 to survive. Haque, Huang, & Lee (2010) reported from their water quality analysis at four main rivers of Northern Peninsular Malaysia, the pH values range from 5.10 to 8.15 with the average value 6.63. The highest pH value was found in Muda River while the lowest value was in downstream of Kerian River. All the pH values are within the permissible limit (Class IV) of Interim Water Quality Standards of Malaysia and suitable for agriculture irrigation.

Anabas testudineus commonly called as climbing perch is an extremely hardy, small, brown dark greenish-brown fish, originated from Southeast Asia. It is highly adapted to life in a seasonal tropical environment. It can tolerate very turbid brackish water conditions; possesses an accessory air-breathing organ that enables it to survive out of water for several days; and uses its highly mobile sub operculum and strong fin spines to pull itself over land to move. The fish has the ability to aestivate during the dry season. Under extreme circumstances it is even able to
aestivate for several weeks by burying itself into moist ground (Bhabananda & Shah, 2009).

It inhabits the majority of drainage systems across its native range and has been recorded in many different habitat-types including swamps, marshes, lakes, canals, pools, small pits, rice field, puddles, tributaries and main river channels. Though primarily a lowland freshwater species, it is also available in brackish coastal environments in some areas (Samuel Vinod Kumar, Little Flower Pascal, Samuel Tennyson, Muniyasamy Pandeeswari, Kalyanasundaram Dhinamala, Deepa Parris, Rajasinghe Raveen, Subramanian Arivoli, 2018). It is reported that most of the pollutants induce fish mortality, genotoxicity and histopathology thus impairing respiration, metabolism and enzyme activities in affected fishes (Suress M, Kalandar A, 2013). As reported by (McCarraher, 1971), from the 14 species of fishes tested, those with the most noteworthy tolerance to alkalinity was the Sacramento perch (perch type of fish); that survived 12-18 months in lakes where the total alkalinity ranged from 1000 to 2000 mg/liter with pH range 8.5 – 9.7. Perch not only appeared to have superior survival qualities for alkaline waters but is presently found living in several of the noncarbonated saline lakes of North Dakota, Colorado, and Nevada as reported by McCarraher & Thomas (1968).

The paper aimed to determine the pH values of leaching fly ash geopolymer paste which caused the lethality of Anabas testudineus. The specific lethality ranges from the leaching of OPC and fly ash geopolymer paste were also determined. The alkalinity adverse impacts between OPC and fly ash geopolymer paste were compared to explore their potential application in the aquatic ecosystem.

2. Materials and methods

2.1 Geopolymer and OPC paste sample preparation

In this study, geopolymer paste with the dimension of 50mm x 50mm x 50mm was made from class C fly ash based geopolymer mixed with alkaline activators which were sodium silicate (Na2SiO3) and 12M sodium hydroxide (NaOH) solution.

Sample was prepared according to (Al-Bakri Abdullah et al., 2012). Firstly, 12M NaOH solution was prepared by dissolving the pelletized NaOH in distilled water. Then NaOH 12M solution was mixed with Na2SiO3 solution to produce alkaline activator. NaOH was prepared 24 hours prior the preparation of alkaline activator. Then, NaOH 12M was mixed with Na2SiO3 within the ratio of 2.5:1 (Na2SiO3 : NaOH = 2.5:1). Finally, alkaline activator was later mixed with class C fly ash within the ratio of 2:1 (Fly ash : alkaline activator) and the mixture was stirred for about 30 minutes before being poured into a 50mm x 50mm x 50mm dimensional mould. For ordinary Portland Cement paste preparation, it was mixed within the ratio of (Solid : Liquid = 3 : 1). The mixture was stirred for about 5 minutes before being poured into a 50mm x 50mm x 50mm dimensional mould.

The prepared geopolymer paste mixture were placed in mould and were compacted. The samples were kept at ambient temperature for 2 hours and cured at 60°C in the oven for 24 hours (Farhana, Kamarudin, Rahmat, & Al Bakri, 2015). OPC paste were cured just in ambient condition for 24 hours.

2.2 XRF of fly ash geopolymer

Class C fly ash was obtained from cement factory CIMA, Perlis Malaysia. The chemical composition is listed in Table 1.

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>SiO2 (%)</th>
<th>CaO (%)</th>
<th>Fe2O3 (%)</th>
<th>Al2O3 (%)</th>
<th>MgO (%)</th>
<th>K2O (%)</th>
<th>TiO2 (%)</th>
<th>SO3 (%)</th>
<th>MnO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity</td>
<td>30.8</td>
<td>22.3</td>
<td>22.99</td>
<td>13.1</td>
<td>4.0</td>
<td>1.6</td>
<td>0.86</td>
<td>2.67</td>
<td>0.21</td>
</tr>
</tbody>
</table>

2.3 Acclimatization of test fishes

The study was conducted in CEGeoGTech laboratory, UniMAP Perlis. Healthy specimens of freshwater fish A. testudineus (climbing perch) were collected from Arau paddy field Perlis, Malaysia. Fishes were transported to the laboratory with proper covering and agitation. Fish were given prophylactic treatment by bathing twice in 0.05% potassium permanganate solution for 3 minutes to avoid any dermal infections and then immediately released into a cylindrical container containing paddy swamp water and maintained there for 7 days in a static condition. Fishes were acclimatized in laboratory conditions for one week.

The water quality parameters of the acclimation tank were studied at times. Only healthy fishes were selected for the experiment and the length and weight of the fishes were noted.

The physiochemical characteristics of water such as temperature, dissolved oxygen, pH or alkalinity, hardness, carbon dioxide and ammonia concentration were measured using potable water kit (NovoBlue 14 in 1 Water Quality Test Kit). The data obtained were analysed statistically to observe whether there is any influence of different concentrations on the mortality of fish. Statistical software SPSS version 16 was used at P < 0.05 to analyse the data via one-way ANOVA.

No mortality was recorded during this period. The fishes were fed with fish pelletized food daily. Fishes were fed on commercial feed produced by Daya Aquatics Sdn Bhd twice daily with 48 hours interval water changes. After acclimatization, fishes were kept in different cylindrical container.

2.4 Leaching test and fish lethality observation

For leaching test, HDPE cylindrical containers and a volume of 500ml paddy swamp water were used as leaching medium. Both containers were filled with one climbing perch. One container as a control and another one as a testing media. A 56 days age of fly ash geopolymer cube paste was unwrapped and placed into the solution.
Figure 1: a) 500 ml paddy swamp water with a climbing perch as control. b) 500 ml paddy swamp water with a climbing perch and a fly ash geopolymer paste cube and c) 500 ml paddy swamp water with a climbing perch and an OPC paste cube.

(testing media). Solution sampling was done in fixed intervals of 0.25, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 hours for pH monitoring. The physiological appearance and changes of those three climbing perch were also observed. The duration of the fishes death were also determined

Figure 1 indicates the setup of the experiment. Alive, healthy and disease free three climbing perch (weight 17gm and length 9cm) were used for the experiment. The fishes were transferred into three cylindrical containers of 500ml paddy swamp water. Each fish was located in one container.

The initial pH measurements and 10ml water samples of each medium were taken. Then, one container was taken as a control and another two containers were taken for the experiment.

A Fly ash geopolymer paste cube and an OPC paste cube were immersed into the each selected experimental medium. The fishes were observed and the pH readings were tabulated in a Table 3 of 1 hour time intervals. The rate of alkali leachability and pH readings were calculated. The test was ended until the fish dead.

3. Results and Discussion

3.1 Physico-chemical properties of water

The physico-chemical properties such as temperature, dissolved oxygen, pH, carbon dioxide and ammonia concentration of paddy swamp water were monitored during the acclimation period and tabulated in Table 2. There were no noticeable differences between the results of water in control medium and experimental medium.

According to Salma Akter, Akter, Ahmed, Akhand, & Islam (2008), the fluctuation of temperature should not exceed 4°C and similarly goes to oxygen content must be not diminish below 4 mg/L for warm water medium. In the present experiment, the temperature fluctuations was found between 25°C - 28°C and dissolved oxygen was within the normal range which was 4.8 - 6.5 mg/L. To avoid ammonia contamination from the food and fish excreta, water exchange was conducted once a day.

<table>
<thead>
<tr>
<th>Physico-chemical properties</th>
<th>Means ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>27.55 ± 0.20</td>
</tr>
<tr>
<td>Dissolved oxygen (mg/L)</td>
<td>6.10 ± 0.50</td>
</tr>
<tr>
<td>pH</td>
<td>7.0 ± 0.20</td>
</tr>
<tr>
<td>Carbon dioxide (mg/L)</td>
<td>9.6 ± 0.75</td>
</tr>
<tr>
<td>Ammonia (mg/L)</td>
<td>0.12 ± 0.01</td>
</tr>
</tbody>
</table>

3.1 Mortality and comparison of pH values during leaching and the observation of lethal effect under alkali leaching.

Exposed fish in different pH showed behavioural anomalies. Figure 2(a), Figure 2(b) and Table 3 indicate the observation of the experiment. At the beginning of the exposure of fly ash geopolymer medium, fish was alert, and stop swimming and remained static in position. It was happened in the first 0.5 hours (pH = 6.8). Faster opercular activities were observed as gasping and gulping for the air. It was happened from 0.5 hours onwards. The degree of such behavioural observations were clearly dependent upon the degree of alkalinity in the exposure media. The visible reactions of the treated fish was at 1.0 hours (pH = 10.4). Available evidence indicates that a minutes amount of alkali has the ability to cause abnormal behaviour performances in fish through impaired perceptive acuity (Parvin et al., 2011). During 4.0 hours (pH = 10.8), the fish swim erratically with jerky movements and hyperexcitability. At 7.0 hours (pH = 10.9), the fins became hard and stretched due to the stretching body muscles. During 9.0 hours (pH = 11.0), the fish secreted copious amounts of mucus from the whole body continuously, and the thick layer of mucus was deposited in the buccal cavity and gills. After 9.5 hours, fish lost its balance, became exhausted, loss consciousness and became lethargic within 10.0 hours (pH = 11.0) of exposure period. Then, it remained in a vertical position for a few minutes with the anterior side (mouth) up near the surface of the water, gasping for oxygen and the posterior (tail) turned downwards. At 10.5 hours, the fish settled at the bottom of the cylindrical container near the cubic solid and at 11.0
hours (pH = 11.0) of the exposure period, the fish abdomen in fly ash geopolymer media turned upward and died.

While in OPC media, fish was alert, stop swimming and remained static in position. It was happened in the first 0.25 hours (pH = 6.4). Faster opercular activities were observed as gasping and gulping for the air at the time interval. During 0.5 hours (pH = 10.3), the fish swam erratically with jerky movements and hyperexcitability. The fins became hard and stretched due to the stretching body muscles. During 1.0 hours (pH = 11.3), the fish secreted copious amounts of mucus from the whole body continuously, and the thick layer of mucus was deposited in the buccal cavity and gills. After 2.0 hours, fish lost its balance, became exhausted, loss consciousness and became lethargic within (pH = 11.5) of exposure. The fish was died at 2.0 hours (pH = 11.5). Only control fish was remained alive in this experiment.

Table 3 shows the pH values and the condition of the fishes in specific medium. The fish in OPC leaching medium died in 2 hours under the similar pH as the fly ash geopolymer medium because leaching rate in OPC medium is higher than in fly ash geopolymer medium.
4. Conclusion

OPC showed faster lethality rate than fly ash geopolymer. The mortality limit pH value of *Anabas testudineus* for fly ash geopolymer paste is at pH 11.0, while for ordinary Portland Cement is at pH 11.5. The peak of alkali leaching of fly ash geopolymer paste is between 0.5 – 1.0 hours while for ordinary Portland Cement is between 0.25 – 0.5 hours. Thus, OPC gives severe adverse effects to the mortality of *Anabas testudineus*, than fly ash geopolymer paste due to the leaching of OH- and other alkali anions. *Anabas testudineus* can live 10 hours in fly ash leaching media but only can live 1 hour in OPC leaching media. As the conclusion, OPC gives more adverse effect to the lethality of *Anabas testudineus* than fly ash geopolymer material. Since OPC paste and fly ash geopolymer paste released a very high amount of alkali during leaching, both of the pastes are not recommended to be used in aquaculture, agriculture and aquatic ecosystem.

5. References


