Effect of Solid to Liquid Ratio on Heavy Metal Removal by Geopolymer-Based Adsorbent

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Abstract. Microstructure of three-dimensional aluminosilicate which similar to zeolite cause geopolymer based adsorbent accepted in the treatment of wastewater. This paper presents an investigation on the copper removal from the wastewater by varying the solid to liquid ratio in the fly ash, kaolin and sludge-based geopolymer adsorbent. The adsorption test was conducted to study the efficiency of the adsorbent and the copper concentration was examined by using Atomic Adsorption Spectrometry (AAS). The optimum solid to liquid ratio with the highest percentage removal were 1.0, 0.5 and 0.8 for fly ash-based geopolymer, kaolin-based geopolymer and sludge-based geopolymer adsorbent.

1. Introduction

Great concern raises to water pollution since water constitutes a basic necessity for daily life. Rapid growth of industrial society leads to a significant increase in the demand of water. Discharge of wastewater without detail and adequate treatment give negative impact via contamination to the land and water. Among other issues, water contaminations by heavy metals are more pronounced especially when heavy metals are exposed to the natural ecosystem. Therefore, it is very necessary to treat heavy metal in wastewater from industrial. Adsorption become excellent alternative and central research focus due to effectiveness, simplicity and low cost [1].

Geopolymers, inorganic polymers or zeolites precursors was introduced to replace Ordinary Portland Cement (OPC) due to their unique properties in mechanical, chemical or fire resistance, high temperature resistance and superior durability toward acid attack [2-5]. In addition, compared to OPC, geopolymer being low emission of greenhouse gases and low energy consumption manufacturing process thus proposed as alternative building material to OPC. Reaction between aluminosilicate with an aqueous alkaline activator (mixing of sodium silicate and sodium hydroxide) produce a geopolymer structure consist of an amorphous network of SiO_4 and AlO_4 tetrahedral units similar to zeolite connected by oxygens and charge-balanced by hydrated alkali cations [6-8].

The advantage of geopolymerization method are environmental protecting, energy saving, no more high temperature techniques, compare to zeolite is the process of geopolymerization is simpler than that of zeolite and the temperature used is below 100°C [9, 10]. However, the fundamental different between zeolites and geopolymer, no sufficient time and space for paste to grow into a well crystallized structure during geopolymerization since the paste quickly transform into a hard geopolymer [11]. Nevertheless, decision choice of the source materials for making geopolymers should be take into account the cost, type of application, availability and demand in the market [12].

In the geopolymer, the process of alkali activation of alumino-silicate materials has not been fully described yet. The understanding by now, reaction of aluminosilicate in a strong alkaline environment create disintegration of siliceous bonds. Then, the phase start containing aluminum (Al) parts are formed result in producing zeolite precursor [13]. Geopolymer framework consist of Si-O-Al, negative charge of Al^{3+} balanced by the positive charge of alkali (Na^+) ions [14]. Al Bakri reported that the amount of Al in the aluminosilicate gel indicates the reactivity level of fly ash [15]. Thus, the ratio of raw material to alkaline activator affected the adsorbent efficiency.

Million tons of fly ash generated from power station creating the disposal problem. Utilization of fly ash in geopolymer is an excellent and beneficial alternative to overcome an abundant of fly ash byproduct [16, 17].There are two types of fly ash, class F and class C. Fly ash with class F considered as pozzolanic materials act as a binder which activated by alkaline solution [18]. Kaolin is a naturally occurring material composed primarily of fine-grained minerals; it is the most abundant mineral found in the earth. Kaolin is one source of alumino-silicate oxide source to synthesize geopolymer. Kaolinite possesses a slow dissolution of Al and require sufficient time for interactions among the source materials [19, 20]. Sludge contain settleable solid, organic chemical compound, biological flocs, inorganic and others. A few types of sludge such as primary sludge, secondary sludge, tertiary sludge, chemical sludge, humus sludge, surplus activated sludge and attached growth system sludge. Due to the its characteristic which is quite similar to the properties of kaolin, sludge having a potential to be raw material for geopolymer [21].

The mix design of geopolymer are divided into solid to liquid (S:L) ratio and sodium silicate to sodium hydroxide (Na_2SiO_3:NaOH) ratio. Geopolymer paste with low S:L ratio tend to have high viscosity and increase in the dissolution rate. The high content of alkaline activator lead to excessive OH- in the system, contribute to weakening the geopolymer structure [22]. Increase in the alkaline activator (containing sodium waterglass) will increase the Si content thus result in stronger Si-O-Si [23]. This is supported by Al Bakri, increasing the waterglass in the activator will increase the geopolymerisation reaction rate. In certain limit, the rate is negatively affected [24]. Alkaline activator used is to activate the binder in the geopolymerisation process which the combination of alkaline solution with waterglass. Alkali hydroxide is a strong base consist of metal cation and hydroxide ions. Alkali silicate comprise with metal cation used as activator in alkali activated binder usually sodium and potassium [25]. This research presents a performance of fly ash, kaolin and sludge-based geopolymer adsorbent. It proposes new technology of adsorbent in Malaysia which contribute to environmental friendly and economic.

2. Materials and methods

The materials used in this research are fly ash, kaolin, sludge. Geopolymer is a result of mixing raw material and alkaline activator solution. The adsorption test was conducted to study the efficiency of adsorbent.

2.1. Material preparation

For the raw material, fly ash was obtained from ManjungCoal-Fired Power Station, Lumut, Perak, Malaysia. Kaolin was purchased from Associated Kaolin Industries Sdn.Bhd while sludge was collected in the Arau Water Treatment Plant, Perlis, Malaysia. Alkaline activator consists of sodium silicate and sodium hydroxide. Sodium silicate supplied from South Pacific Chemical Industries SdnBhdwith chemical composition of 30.1% SiO_2, 9.4% Na_2O and 60.5% H_2O with the modulus

SiO_2/Na_2O of 3.2, density at 20°C of 1.4g/cm^3 and viscosity at 20°C of 0.4 Pa-s. Sodium hydroxide pallet with 98% purity supplied from Sigma-Aldrich Pty.Ltd.

2.2. Experimental procedure
According to the Figure 1, alkaline activator was produced by the result mixing of sodium silicate and 10M sodium hydroxide together for 5 minutes. Before mixing, NaOH pallet was diluted with distilled water then let it cooled down at room temperature for 1 day. The alkaline activator then was added and mixed homogenously with raw material to developaluminosilicategeopolymer adsorbent paste according to formulation in Table 1. The pastes were cured at temperature 100°C for 24 hours. The process was proceeded to crushing and sieving to obtain powder in size.
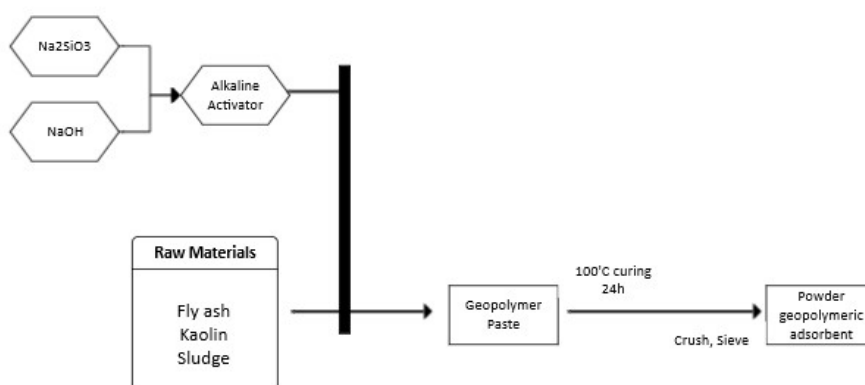

Figure 1. Preparation process of geopolymer-based adsorbent.

Table 1. Formulation use to produce geopolymeric adsorbent.

Raw material	NaOH:Na$_2$SiO$_3$	S:L
Fly ash	1.5	1.0
		1.5
		2.0
		2.5
		3.0
Kaolin	1.5	0.5
		0.6
		0.7
		0.8
		0.9
		1.0
Sludge	1.5	0.5
		0.6
		0.7
		0.8
		0.9
		1.0

2.3. Absorption test

This study performed an adsorption test to investigate the effectiveness of adsorbents to adsorb heavy metal. The initial pH of heavy metal solution was controlled to be lower than 5 for every adsorption test. Adsorption of 100mL of metal ions solutions was conducted by using orbital shaker. After adsorption, the supernatant was filtered by using filter paper. The changes in the concentration of heavy metal was analysed by using Atomic Adsorption Spectrometry (AAS).

Percentage removal efficiency was calculated using the following equation:

$$E(\%) = \frac{Co - Ce}{Co} \text{x } 100 \qquad (1)$$

E = Removal efficiency
c_o = Initial concentration
c_e = Final concentration

3. Results and discussions

Reaction in the adsorption occurs due to the ion exchange between the surface and the inside positions of the adsorbent. Figure 2 shows the percentage removal of heavy metal by different materials used and various solid to liquid ratio.
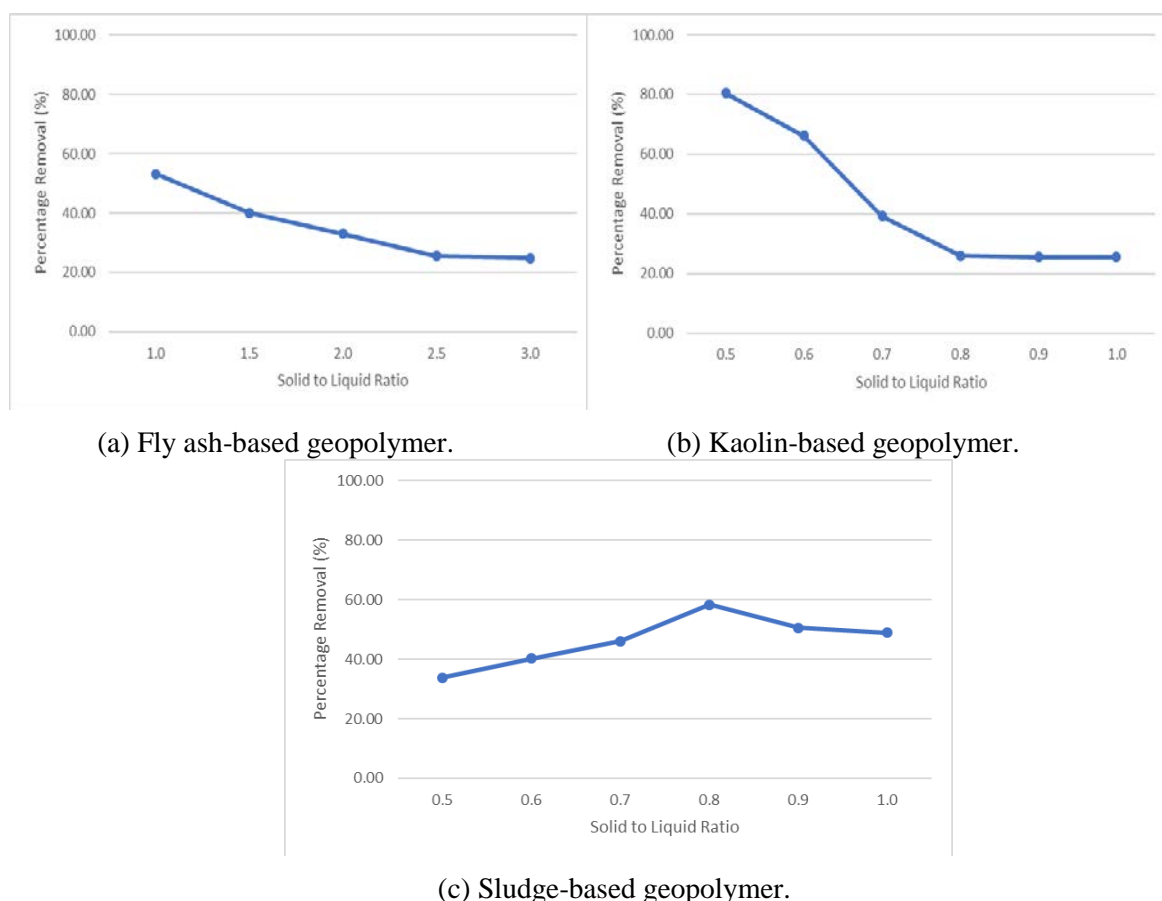

(a) Fly ash-based geopolymer.   (b) Kaolin-based geopolymer.

(c) Sludge-based geopolymer.

Figure 2. Percentage removal of copper removal by different geopolymeric adsorbents.

The optimum of solid to liquid ratio of fly ash-based geopolymer are 1.0 which 53% are taken out from the wastewater solution and 46% left behind. The graph 2(a) show the adsorbent efficiency decreased with the increase of solid to liquid ratio. Study by Liew reported that NaOH-fly ash

geopolymer observed crystalline and granular structure produced [26]. This show that, increase in the alkaline activator will increase in the adsorbent efficiency. The geopolymer phase thought to be reactive, dissolve by alkali metal. Some cations must be present to keep the structure neutrality or actively bonded into the matrix. Furthermore, the cation bonded via Al-O or Si-O bond by the substitution [27]. This result supported by Cheng and Luukkonen which use S:L ratio 1.3 and removed about 40.9 mg/g and 21.07mg/g [9, 28].

Kaolin-based geopolymer shows highest metal ions uptake among the adsorbents used. This may due to the properties of low reactivity of kaolin. Balancing of Graph 2(b) shows removal decrease with the increase of solid to liquid ratio then slightly different from 0.8 to 1.0. This show that the minimum solid to liquid ratio can be used is 0.8. About 80 percent of copper ions were removed from the solution at 0.5 ratio of solid to liquid. Yang reported that addition of alkali activated concentration is an important factor on other Si gel generation [29,30]. Furthermore, the percentage removal of copper is high. Although decrease the ratio will lead to increase in the removal, the ratio of kaolin/alkaline activator cannot be reduce because of its high workability [31].

Sludge contain 54% SiO_4 and 29% Al_2O_3, high percentage of Si and Al make this material suitable to be treated by alkaline activator to develop geopolymer structure. Solid to liquid ratio of sludge-based geopolymer adsorbent was studied from 0.5 until 1.0. Figure 2(c)shows0.8 (58 percent) is the best solid to liquid ratio copper removal from wastewater solution by adsorbent from sludge-based geopolymer. This indicated that at ratio 0.8, high chemical binding occurs in geopolymer or silicate phases. The minimum percentage heavy metal removal by adsorbent is 33%.This may due to lack alkaline activator as reported by El-Eswed that metal contaminations either by physical or covalent bonds (metal is bonded to the silicate chain or hydroxide links) [32].

4. Conclusions
The present work focused on the removal of copper heavy metal by using fly ash, kaolin and sludge-based geopolymer adsorbent. Different materials having different solid to alkaline activator ratio. The best solid to liquid ratio for every fly ash, kaolin and sludge-based geopolymer adsorbent is 1.0, 0.5 and 0.8 respectively.

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