GEOPOLYMER FROM METAKAOLIN AND BIOMASS ASH FOR Cu(II) IONS ADSORPTION FROM AQUEOUS SOLUTIONS: KINETICS AND ISOTHERM STUDIES

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ABSTRACT

The utilizations of geopolymer as adsorbent in the treatment of wastewater containing heavy metal or dyes have shown encouraging results. In this paper, geopolymer synthesized from alkaline activation of metakaolin and biomass ash was utilized as adsorbent for Cu(II) ions from aqueous solutions. Adsorption of Cu(II) ions by geopolymer followed Langmuir isotherm model which adsorption occurred on geopolymer surface by forming monolayer of adsorbate molecule with maximum adsorption capacity of 58.824 mg g^{-1}. Furthermore, pseudo-second order kinetics model was more suitable to describe adsorption of Cu(II) ions by geopolymer.

Keywords: adsorption, biomass ash, copper, geopolymer, metakaolin.

INTRODUCTION

Geopolymer is inorganic polymer with Si-O-Al bonds synthesized from alkaline activation of alumino-silicate materials at low temperature, generally below 100°C [1]. Metakaolin (Si_2O_5,Al_2O_2), obtained from calcination of kaolin ($Al_2O_3.2SiO_2.2H_2O$), is alumino-silicate material that has been widely used as geopolymer raw material [2]. Another source of alumino-silicate materials is solid waste from combustion such as fly ash and biomass ash. Biomass ash containing high silica, e.g. bamboo ash, can be used as geopolymer raw material [3].

Geopolymer having three dimensional porous structure has been applied for wastewater treatment as adsorbent of heavy metals [4, 5]. Adsorption has been widely used for heavy metal removal from wastewater because the process is simple, economical, and efficient [6, 7]. Applications of geopolymer from metakaolin as heavy metal adsorbent had been conducted on Cd, Cr, Cu, Pb [8]; Cs, Pb [9]; Zn, Ni [10]; and Pb [11]. Meanwhile, geopolymer from metakaolin and biomass ash had been applied as Pb adsorbent [12]. The use of geopolymer from biomass ash along with metakaolin as heavy metals adsorbent is interesting to study because it is one of the efforts to utilize solid waste to treat wastewater.

In this research, geopolymer was synthesized from alkaline activation of metakaolin and biomass ash and then applied as Cu(II) ions adsorbent. Copper is one of common heavy metals in industrial wastewater such as from electroplating, metal surface finishing, and fertilizer production, that are very toxic even at low concentration [13, 14]. Factors affecting adsorption process, namely adsorbent dosage, pH, initial concentrations, contact time, were studied in addition to kinetics and isotherm adsorption studies.

EXPERIMENTAL
Materials

Materials used in this study were metakaolin, biomass ash, commercial sodium hydroxide flakes (purity of 98 %), and commercial sodium silicate solution (SiO_2 = 30 %, Na_2O = 9 %, H_2O = 61 %). Metakaolin was obtained from calcination of commercial kaolin powder in electric furnace at 550°C for 3 hours, while biomass ash was obtained from combustion of bamboo (*Gigantochloa apus*). Metakaolin contained SiO_2 = 53.9 % and Al_2O_3 = 42.4 %, whereas the biomass ash contained SiO_2 = 58.6 % and Al_2O_3 = 0.7 %.

Preparation of geopolymer

Geopolymer powder for Cu(II) ions adsorption was obtained from geopolymer paste preparing from metakaolin, biomass ash, and alkaline activator. The weight ratio of metakaolin to biomass ash was 4:1. Alkaline activator used was mixture of 10 N sodium hydroxide

solution and sodium silicate solution with weight ratio of 1:2. Metakaolin and biomass ash as alumino-silicate materials were mixed with alkaline activator and stirred for 6 minutes. The weight ratio of alkaline activator to alumino-silicate materials was 1.1:1. The mixture was poured into 5x5x5 cm^3 mold and cured in mold. After 24 hours, geopolymer paste was removed from the mold and cured in oven at 60°C for 8 hours and then at room temperature for 28 days. Geopolymer paste then crushed and sieved with 60 mesh standard sieve to produce geopolymer powder as adsorbent.

Batch adsorption test

Geopolymer powder was used as adsorbent for 100 ml solutions of Cu(II) ions at room temperature (28°C) and constant stirring rate of 200 rpm. Solutions of Cu(II) ions were prepared from analytical grade of $CuSO_4.5H_2O$ with distilled water. Adsorption tests were carried out with varying adsorbent dosage (1 - 3 g L^{-1}), pH (3 - 7), initial concentration of Cu(II) ions solution (10 - 150 mg L^{-1}), and contact time (15 - 180 minutes). The concentrations of Cu(II) ions solutions were measured by Atomic Absorption Spectroscopy (AAS). The equation used to determine Cu(II) ions removal efficiency (%) is:

$$Cu(II)\ ions\ removal\ efficiency\ (\%) = \frac{C_0 - C_e}{C_0} x100 \tag{1}$$

where C_0 is the initial concentration of Cu(II) ions solution (mg L^{-1}) and C_e is the concentration of Cu(II) ions solution at equilibrium (mg L^{-1}). Meanwhile, the capacity of Cu(II) ions adsorption by geopolymer at equilibrium (q_e, mg g^{-1}) is calculated using equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where V is the volume of solution and W is the mass of adsorbent.

Kinetics and isotherm adsorption studies

Kinetics studies were conducted with pseudo-first order and pseudo-second order kinetics models. The adsorption kinetics can be expressed by the following equation:

$$\frac{dq_t}{dt} = k_n(q_e - q_t)^n \tag{3}$$

where q_t is the adsorption capacity at time t and k_n is pseudo-n^{th} order kinetics rate constant [15]. Equation (3) can be stated in the form of linear equation for pseudo-first order kinetics model:

$$\ln(q_e - q_t) = lnq_e - k_1t \tag{4}$$

and for pseudo-second order kinetics model:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \tag{5}$$

Isotherm studies were performed with Langmuir and Freundlich isotherm models. In Langmuir isotherm model, adsorption process occurs on homogeneous surfaces so that there is only one layer of adsorbate molecule on adsorbent surface and follows the equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{6}$$

where q_m is the maximum adsorption capacity and K_L is Langmuir constant related to adsorption capacity. In Freundlich isotherm model, adsorption process occurs on heterogeneous surfaces and can be expressed in equation:

$$q_e = K_F C_e^{1/n} \tag{7}$$

where K_F is Freundlich constant related to adsorption capacity and 1/n is related to adsorption intensity [16].

Characterization

Characterizations were undertaken on metakaolin, biomass ash, and geopolymer comprising X-ray diffraction (XRD) analysis and Fourier transform infrared spectroscopy (FTIR) analysis. XRD analysis was performed with Bruker D8 Advance instrument under following conditions: 40 kV, 35 mA, CuKα radiations, and 2θ: 5 - 80°, meanwhile FTIR analysis was performed with Shimadzu IR Prestige-21 instrument using KBr pellet technique in the wavenumber range of 4000 cm^{-1} - 400 cm^{-1}. Brunauer-Emmett-Teller (BET) surface area of geopolymer was also analyzed with Quantachrome Instruments. Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX) analysis was conducted on geopolymer before and after adsorption process with JEOL JSM-6510LA instrument.
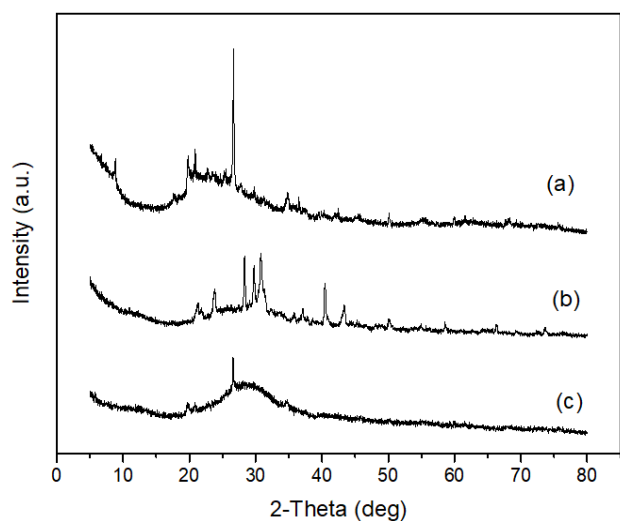
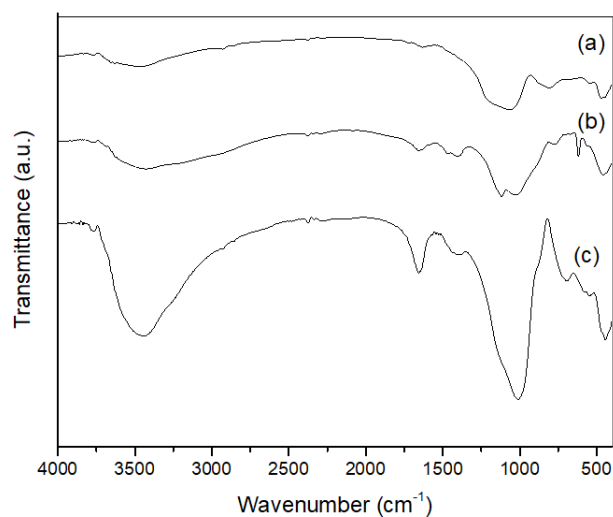Fig. 1. XRD patterns of metakaolin (a), biomass ash (b), and geopolymer (c).

Fig. 2. FTIR spectra of metakaolin (a), biomass ash (b), and geopolymer (c).

RESULTS AND DISCUSSION

Geopolymer from metakaolin and biomass ash

Metakaolin and biomass ash were used to synthesize geopolymer with alkaline activator, i.e. mixture of 10 N sodium hydroxide solution and sodium silicate solution. Geopolymer powder used as adsorbent had BET surface area of 57.119 $m^2 g^{-1}$. The results of XRD analysis of metakaolin, biomass ash, and geopolymer were showed on Fig. 1. Geopolymer had broad diffraction peak at 27 - 29º (2θ) indicating geopolymer formation [17]. Peak at approximately 27º (2θ) came from quartz [18]. From XRD analysis it had been known that amorphous structure in geopolymer was 66.9 %, while in metakaolin

was 62.9 % and in biomass ash was 56.3%, respectively. Geopolymerization can change structure in raw materials to be more amorphous which can cause the increase of adsorption sites [19]. FTIR spectra of metakaolin, biomass ash, and geopolymer were shown on Fig. 2 with functional groups presented on Table 1. Metakaolin, biomass ash, and geopolymer contained the same functional groups, namely Si-O (*in-plane bending vibrations*), HOH (*bending vibrations*), and -OH, HOH (*stretching vibrations*). The presence of Si(Al)-O (*asymmetrical vibrations*) functional group at wavenumber of 1010.70 cm^{-1} indicated formation of geopolymer [17, 20]. Meanwhile, the presence of O-C-O (*stretching vibration*) functional

Table 1. Functional groups on metakaolin, biomass ash, and geopolymer based on wavenumber (cm^{-1}).

Wavenumber (cm^{-1})				Annotations
Theoretical	Metakaolin	Biomass ash	Geopolymer	
469	472.56	457.13	445.56	Si-O (*in-plane bending vibrations*)
540	542.00	-	549.71	Si-O-Al (*bending vibrations*)
694	678.94	-	694.37	Si-O (*symmetrically stretching vibrations*)
798	808.17	-	-	Al-O (4 *coordinated* Al-O *stretching vibrations*)
1008	-	-	1010.70	Si(Al)-O (*asymmetrical vibrations*)
1080-1100	1072.42	1118.71	-	Si-O (*symmetrical vibrations*)
1400	-	-	1394.53	O-C-O (*stretching vibrations*)
1425; 1465;	-	1402.25; 1467.83	-	lignin
1600	1629.85	1658.78	1654.92	HOH (*bending vibrations*)
3400	3454.51	3427.51	3448.72	-OH, HOH (*stretching vibrations*)

Fig. 3. The effect of adsorbent dosage on the removal efficiency.
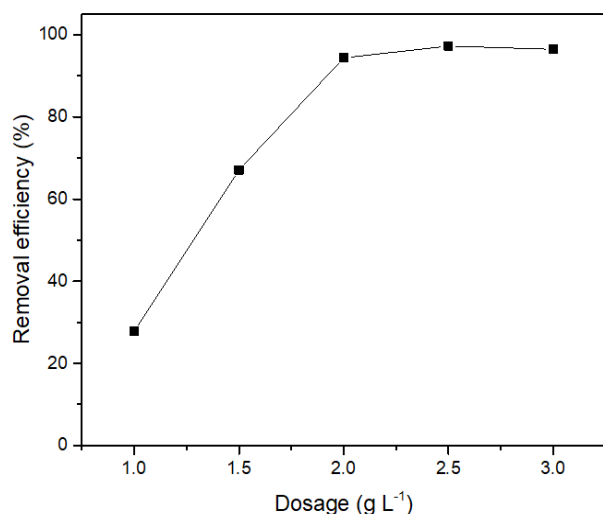

Fig. 4. The effect of pH on the removal efficiency.

group indicated the formation of carbonate from sodium hydroxide and atmospheric CO_2 [10].

Adsorption of Cu(II) ions by geopolymer
The effect of adsorbent dosage

The adsorption process with variation of adsorbent dosage was conducted at pH of 5, initial concentration of Cu(II) ions solution of 100 mg L^{-1}, and contact time of 120 minutes. The increase of adsorbent dosage from 1 g L^{-1} to 2 g L^{-1} caused the increase of the removal efficiency up to 94.35 %. After that, the removal efficiency seemed relatively constant with the increase of adsorbent dosage as shown on Fig. 3. The increase of adsorbent dosage generated the increase of available sites for Cu(II) ions adsorption and therefore the removal efficiency increased [21]. The geopolymer dosage of 2 g L^{-1} was optimum adsorbent dosage for Cu(II) ions adsorption.

The effect of pH

The effect of pH on the removal efficiency was shown on Fig. 4. Adsorption process was carried out at adsorbent dosage of 2 g L^{-1}, initial concentration of Cu(II) ions solution of 100 mg L^{-1}, and contact time of 120 minutes. The highest removal efficiency was obtained at pH of 5 which is similar to the result obtained by Cheng et al. [8] and Ge et al. [22]. Those researchers used geopolymer from metakaolin for Cu(II) ions adsorption. At pH of 3 and 4, there are more H_3O^+ ions in solutions that competes with Cu(II) ions to be adsorbed
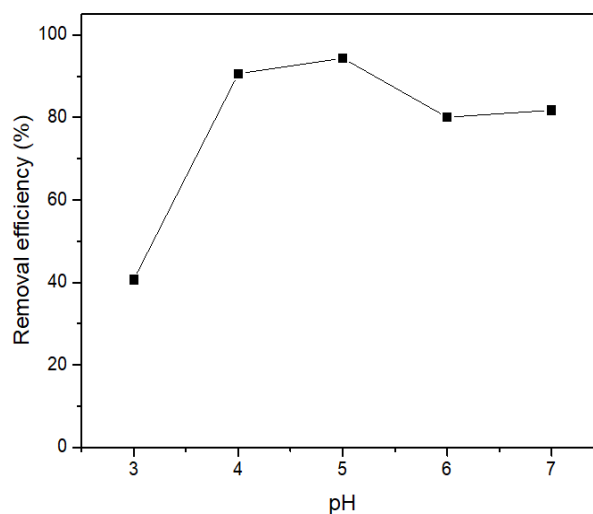
at geopolymer surface. However, the increase of pH higher than 6 will lead to Cu(II) ions precipitation as $Cu(OH)_2$ [23].

The effect of initial concentration

Variation of initial concentration in the adsorption process was done at adsorbent dosage 2 g L^{-1}, pH 5, and contact time 120 minutes. The increase of initial concentration tended to decrease the removal efficiency as shown on Fig. 5. At increase of initial concentrations up to 100 mg L^{-1}, the removal efficiencies were still above 90 %. The removal efficiencies dropped to 84.16 % and
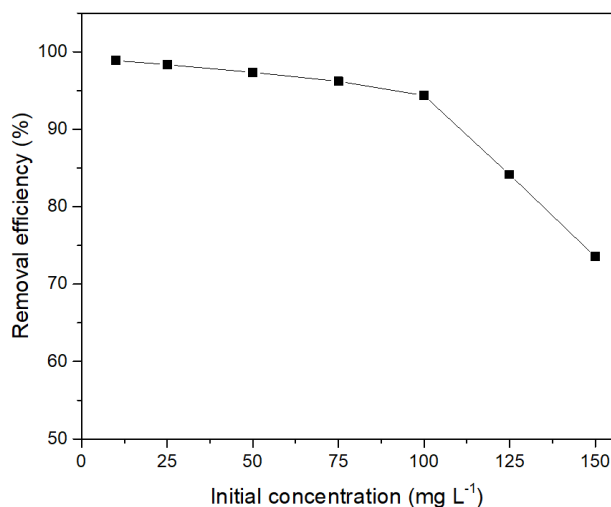

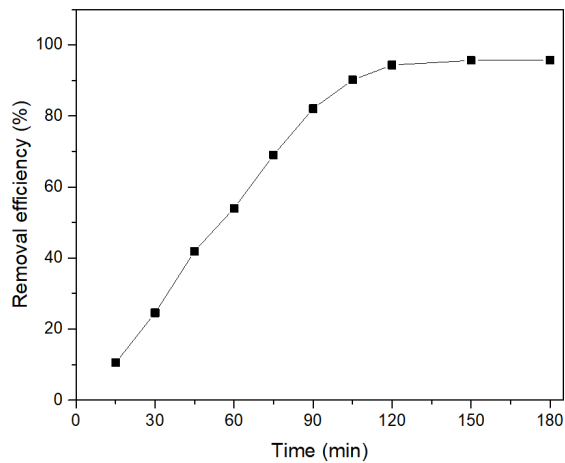Fig. 5. The effect of initial concentrations on the removal efficiency.

Fig. 6. The effect of contact time on the removal efficiency.

73.54 % at initial concentration of 125 mg L^{-1} and 150 mg L^{-1}, respectively. These were caused by adsorbent surface which became inadequate to adsorb Cu(II) ions so that some ions remained in the solution [24].

The effect of contact time

The adsorption process with varying contact time was carried out at adsorbent dosage 2 g L^{-1}, pH , and initial concentration 100 mg L^{-1}. The longer the contact time is, the higher the removal efficiency is. However,

the removal efficiency was relative constant after 120 minutes as shown on Fig. 6, indicating the adsorption process reached equilibrium in 120 minutes. Therefore, optimum contact time for Cu(II) ions adsorption was 120 minutes or 2 hours.

Geopolymer characterizations before and after adsorption process

Characterizations for geopolymer before and after adsorption process were conducted with SEM-EDX analysis. The results were shown on Figs. 7 and 8 with element compositions on geopolymer surface presented on Table 2. The content of Cu element on geopolymer surface after adsorption process seemed higher than that before adsorption process. This results confirmed that Cu(II) ions from solutions were adsorbed on geopolymer surface.

Kinetics studies

Kinetics studies on Cu(II) ions adsorption by geopolymer were carried out using pseudo-first order kinetics model and pseudo-second order kinetics model approaches. Fig. 9 and Fig. 10 showed linear plot of pseudo-first order kinetics model (t vs $log(q_e - q_t)$) and pseudo-second order kinetics model (t vs t/q_t), respec-

Table 2. Element compositions from EDX analysis on geopolymer before and after adsorption process.

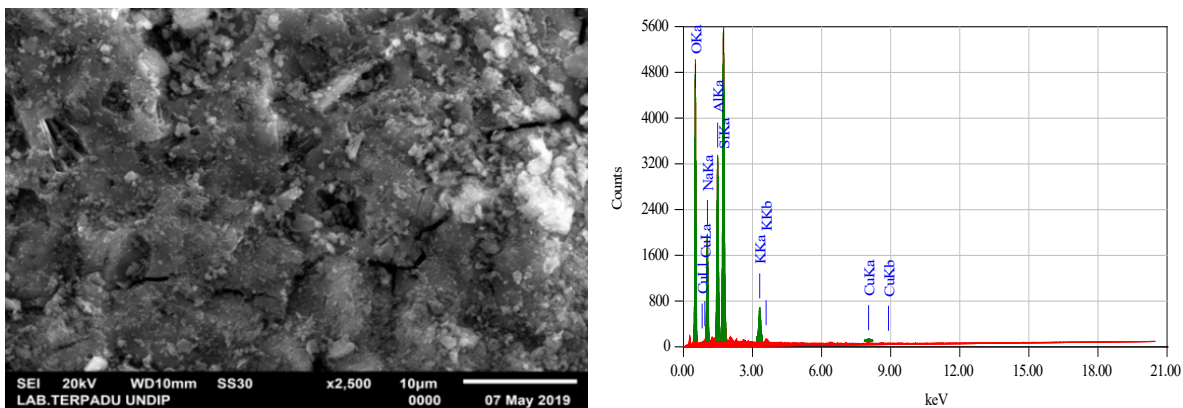| Compositions (%)	Geopolymer before adsorption process	Geopolymer after adsorption process
Si	46.47	46.62
Al	24.68	24.77
Na	20.93	9.04
K	6.83	8.60
Cu	1.09	10.97

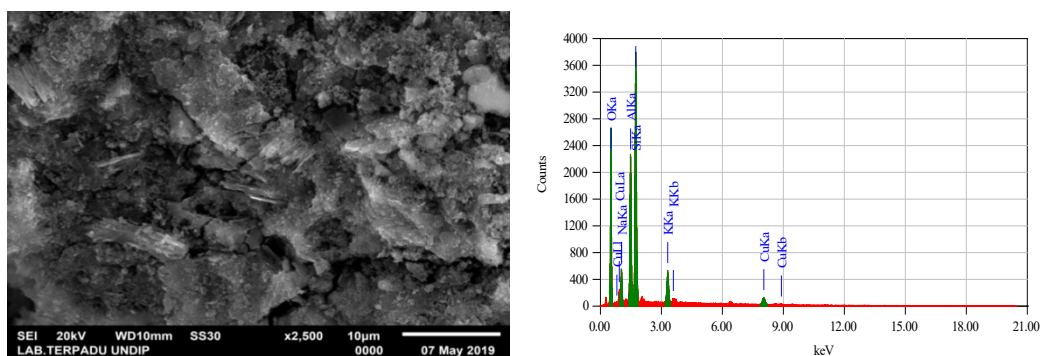Fig. 7. SEM-EDX analysis result of geopolymer before adsorption process.

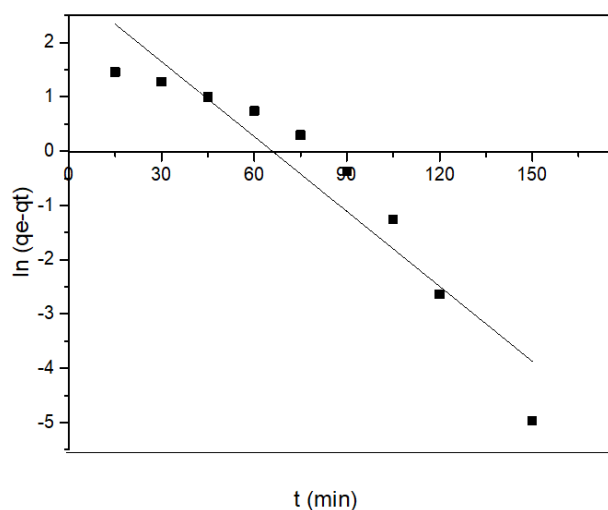Fig. 8. SEM-EDX analysis result of geopolymer after adsorption process.

Fig. 9. Linear plot of pseudo-first order kinetics model on Cu(II) ions adsorption by geopolymer.
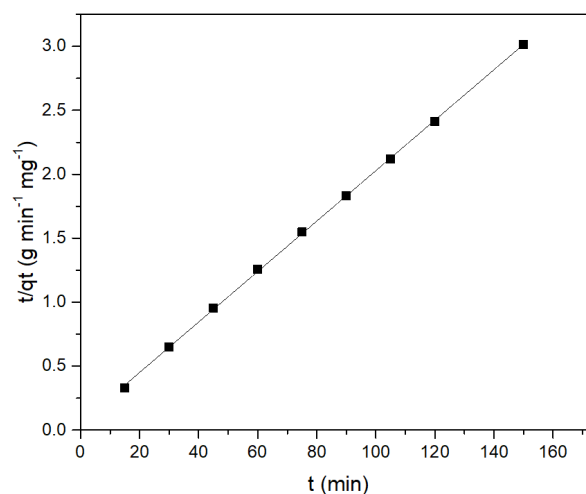

Fig. 10. Linear plot of pseudo-second order kinetics model on Cu(II) ions adsorption by geopolymer.

tively. Meanwhile, Table 3 presented kinetics parameters for each model. Cu(II) ions adsorption by geopolymer followed pseudo-second order kinetics model with coefficient of correlations (R^2) close to 1, i.e. 0.999. This result indicates that adsorption rate controlled by chemisorption which adsorption capacity of Cu(II) ions is proportional to the active sites on the surface of the adsorbent, namely the negative $[AlO_4]^{5-}$ tetrahedrons in geopolymer [25, 26]. Kinetics studies by Cheng et al. [8] on Cu(II) ions adsorption by geopolymer from metakaolin also showed the same result.

Isotherm studies

Isotherm studies on Cu(II) ions adsorption by geopolymer were conducted based on Langmuir and Freundlich models. Linear plot of Langmuir isotherm model (C_e vs C_e/q_e) and Freundlich isotherm model (log C_e vs log q_e) were shown on Fig. 11 and Fig. 12, respectively. The obtained adsorption isotherm parameters were presented on Table 4. Langmuir isotherm model had coefficient of correlations (R^2) higher compared to Freundlich isotherm model. This indicates that adsorption of Cu(II) ions by geopolymer followed Langmuir

Table 3. Kinetics parameters on Cu(II) ions adsorption by geopolymer.

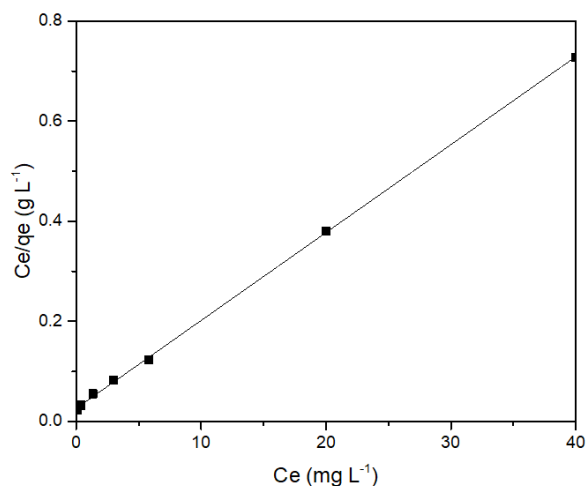| Pseudo-first order kinetics model			Pseudo-second order kinetics model		
q_e (mg g^{-1})	k_1 (min^{-1})	R^2	q_e (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
20.676	0.046	0.898	52.632	0.006333	0.999

Fig. 11. Linear plot of Langmuir isotherm model on Cu(II) ions adsorption by geopolymer.
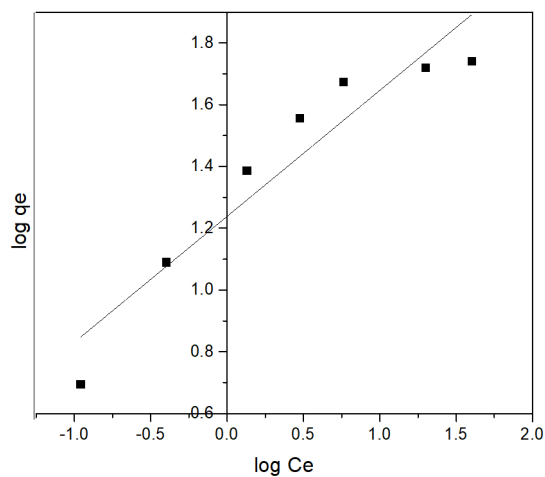

Fig. 12. Linear plot of Freundlich isotherm model on Cu(II) ions adsorption by geopolymer.

isotherm model which there is only one layer of adsorbate molecule on adsorbent surface [26, 27] with maximum adsorption capacity of 58.824 mg g^{-1}. The result obtained by Cheng et al. [8] also showed that Cu(II) ions adsorption by geopolymer from metakaolin followed Langmuir isotherm model.

Langmuir isotherm can be classified by dimensionless separation factor (R_L) calculated with the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (8)$$

The value of R_L classifies the adsorption to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$) [16]. The adsorption process of Cu(II) ions by geopolymer with initial concentrations of 10 - 150 mg L^{-1} has R_L value of 0.133 - 0.010 so that it can be classified as favorable adsorption.

The adsorption capacity of Cu(II) ions by various adsorbents was shown on Table 5. Geopolymer from metakaolin and biomass ash has higher adsorption capacity than other common adsorbents such as natural zeolite, fly ash, kaolin, and geopolymer from

Table 4. Isotherm parameters on Cu(II) ions adsorption by geopolymer.

Langmuir model			Freundlich model		
q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	n	K_F (mg g^{-1} (L mg^{-1})$^{1/n}$)	R^2
58.824	0.654	0.999	2.457	17.298	0.903

Table 5. Adsorption capacity of Cu(II) ions by various adsorbents.

Adsorbent	Adsorption capacity (mg g^{-1})	Operating condition	References
Activated carbon	75.0	pH=3.5, T=25 ºC	[28]
Natural zeolite	5.269	pH=3.5, T=20 ºC	[29]
Fly ash	21.50	pH=6.4, T=40 ºC	[30]
Kaolin	10.8	pH=5, T=ambient	[31]
Geopolymer from fly ash	152.31	pH=6, T=45 ºC	[24]
Geopolymer from metakaolin	48.78	pH=4, T=25 ºC	[8]
Geopolymer from metakaolin and biomass ash	58.824	pH=5, T=28 ºC	This study

metakaolin. This indicates that geopolymer from metakaolin and biomass ash has potential to be used as Cu(II) ions adsorbent.

CONCLUSIONS

Geopolymer had been synthesized from metakaolin and biomass ash with alkaline activator (mixture of 10 N sodium hydroxide solution and sodium silicate solution) and showed amorphous structure that supports its use as adsorbent. The optimum removal efficiency of Cu(II) ions by geopolymer was obtained at adsorbent dosage 2 g L^{-1}, pH 5, initial concentration 100 mg L^{-1} and contact time 120 minutes. Application geopolymer as adsorbent for Cu(II) ions from aqueous solution followed Langmuir isotherm model and pseudo-second order kinetics model.

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