

Removal of Cu (II) in Water by Using Adsorbent Based on Volcanic Ash of Mount Kelud in Indonesia

Eko Siswoyo, Annisa Firachmatika, and Ridho Babel Kautsar

Abstract—Low-cost adsorbent was prepared from volcanic ash of Mount Kelud in Indonesia which erupted in 2014 and remained million cubic of ash. The purpose of this study was to investigate the adsorption capacity of volcano ash to remove Cu(II) in water. Some parameters such as mass of the adsorbent, pH of solution, and shaking time were investigated in order to know the adsorption ability of the adsorbent. FTIR and SEM were utilized in order to know the functional group and surface of adsorbent. The presence of carboxyl and hydroxyl functional groups in this adsorbent were important in the process of adsorption. It was found that pH 6 of solution and 120 minutes of shaking time was a suitable condition for this adsorbent in adsorbing copper ion. Langmuir isotherm adsorption model was fit for this adsorbent and the adsorption capacity for Cu (II) was 82.64 mg/g.

Index Terms—Copper, low-cost adsorbent, mount Kelud, volcanic ash.

I. INTRODUCTION

Removal of transition or heavy metal ions from water is one of most serious environmental problems and the search for economically feasible technologies continues [1]. The pollutions with heavy metal have become public concerns because of its potential damage to human health and environments. The high concentration of copper, one of most toxic metals, is very dangerous for human being and ecosystem. It can be released to the environment from many kinds of industrial activities such as ceramics, metal plating, textile, etc [2].

The sources of copper contamination in some water area in Yogyakarta city, Indonesia mostly caused by some handy craft industries in the city. Many home industries produce handy craft made from silver and during the production they remain wastewater containing copper in high concentration. The amount of copper in some waste water of handy craft industries is up to 11,46 mg/l [3]. This amount of Cu is over than the standard of Indonesian government (1 mg/l). It is well known that heavy metal ion such as copper is accumulated in the livings and human body and its influence might be found out after several years. Therefore, even the low concentration of copper in water is still potential for kidney damage, bone damage, cancer, disturbing the respiratory and reproduction system due to the accumulation effect [4]. The concentration of copper in aquatic environment of some developed country

is generally much lower comparing to developing country such as Indonesia. The concentration of copper ion in the water area of Jakarta, the capital of Indonesia, was sometimes until 13.81-193.75 mg/l, higher than the standard of Indonesian government (1 mg/l) [5].

Many technologies have been developed to solve the contamination problem of heavy metals, those are, membrane technology, ion exchange, phytoremediation, adsorption, etc [6]. Activated carbon is a common adsorbent widely used in many countries. However, this material is high cost, therefore alternative materials are required as a raw material of adsorbent for removal of heavy metal ions in water [7].

The volcanic ash has some minerals such as iron (Fe), manganese (Mn), silicate (Si), Aluminum (Al), Calcium (Ca), Potassium (K) and Phosphor (P). It was reported that volcano ash of Mount Kelud has 45.9% of SiO₂ and mineral which can increase pH of soil [8]. The volcano ash is potential as adsorbent because it has high amount of Silicate. Recently, some studies on the development of low-cost adsorbent based on volcanic ash to remove heavy metal ions are conducted in some countries. Babel and Opiso (2007) reported that the adsorption capacity of ash from Mt. Isarog and Mt. Mandalangan for removal of Cr were 0.864 and 0.171 mg/g, respectively. The amount of clay on ash from Mt. Isarog and Mt. Mandalangan were 44.2 and 5%, respectively [9]. It was clear that the characteristic of the ash is different even though from same country. The characteristic of ash is influenced by the characteristic of the mountain, therefore, study on the development of low-cost adsorbent based on ash from various mountain is still interesting, because the adsorption capacity of each ash is probably different for removal of heavy metal ions in water or wastewater. Considering the huge availability of ash after eruption and its high adsorption capacity, it is urgent to study on the development of alternative adsorbent based on volcanic ash.

In the present study, we develop an alternative low-cost adsorbent based on ash of Mount Kelud in Indonesia which erupted in 2014 and resulted millions cubic of ash. The aim of this study was to know the ability of volcanic ash of Mount Kelud as raw material of adsorbent to remove copper ion in water on batch system.

II. MATERIALS AND METHODS

A. Preparation of Adsorbent

The low-cost adsorbent utilized in this research was prepared by using volcanic ash of Mount Kelud in Indonesia which erupted in 2014 and remained million cubic of ash. The ash was collected in Yogyakarta city several months after

Manuscript received September 22, 2015; revised November 12, 2015.
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eruption of Mount Kelud.

The volcanic ash was washed with distilled water and dried at 100°C for 24 hours. After cooling it at room temperature, the ash were crushed into powder form and then sifted with a 50 mesh sieve. The powdery volcanic ash were used as the adsorbent to adsorb copper ion from the water. The stock solution of copper ion (Cu²⁺) was prepared with Cu(NO₃)₂·4H₂O of WAKO Pure Chemical Co (Osaka, Japan).

Some instruments such as Scanning Electron Microscope (SEM) and Fourier Transform Infra Red (FTIR) machines were employed in order to know the surface morphology and active functional groups of the adsorbent.

B. Process of Adsorptions

Adsorption process in this study was conducted by the batch system. Parameters such as mass of adsorbent, pH of the solution, shaking time and the concentration of cadmium ion in the solution were investigated in order to know the ability and the optimum condition for adsorption using this adsorbent. In order to estimate the effect of mass of the adsorbent, 50, 100, 200, 300, 400 and 500 mg of adsorbent was added to 50 ml of copper solution and agitated at 150 rpm for 2 hours using a magnetic stirrer (Thermo Scientific). The influence of pH on the adsorption of copper ion was investigated by using the solution of pH 3, 4, 5, 6, 7 and 8. Acetic acid, HNO₃ and NaOH were utilized to adjust the desired pHs of solution. Various stirring time from 15 to 120 minutes was applied to know the influence of stirring time on the adsorption of copper ion. After equilibrium, the solution was filtered and then the concentration of copper ion in supernatant solution was determined using Atomic Absorption Spectrophotometer (Avanta, GBC).

The efficiency of adsorption is calculated by using the following equation:

$$E = \frac{C_0 - C_1}{C_0} \times 100\% \quad (1)$$

where:

E = efficiency of removal (%)

C_0 = initial concentration of Cu (mg/l)

C_1 = concentration of Cu after stirring time (mg/l)

III. RESULTS AND DISCUSSION

A. Characteristic of Adsorbent

The surface morphology of ash was determined by using Scanning Electron Microscope (SEM) in different magnification as like shown in the Fig. 1. It can be seen that there are some pore on the surface of the ash. The high porosity and large surface area are important for the adsorption of some metal ions in water.

FTIR analysis was employed in order to know the presence of some functional groups on the surface of the adsorbent. The strong peak between 3200-3550 cm⁻¹ indicated the presence of alcohol functional group (-OH). The adsorbent has strong peak at 1635.28 cm⁻¹ indicated the stretching vibration absorption band of C=O. The bands observed at

1054.36 cm⁻¹ represent stretching bands of Si-O-Si groups [10]. The presence of these functional groups might participate in the adsorption of copper ion in water.

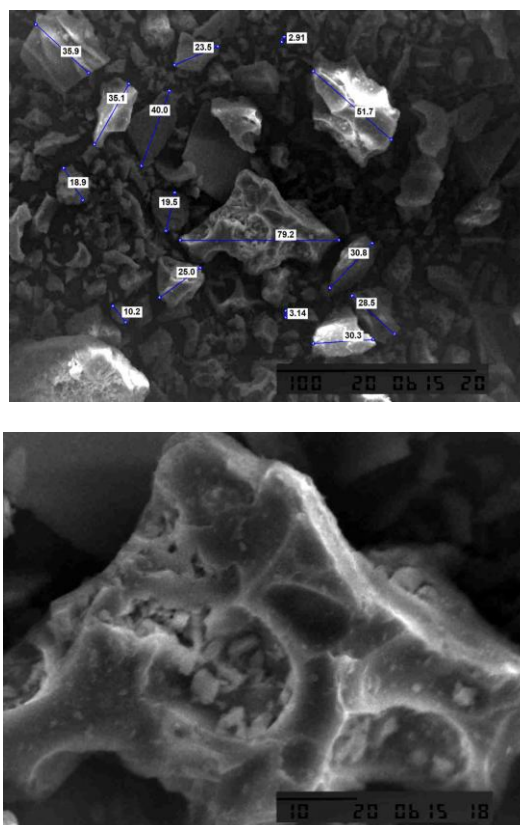


Fig. 1. SEM photograph of adsorbent (a) magnification 500x (b) magnification 2000x.

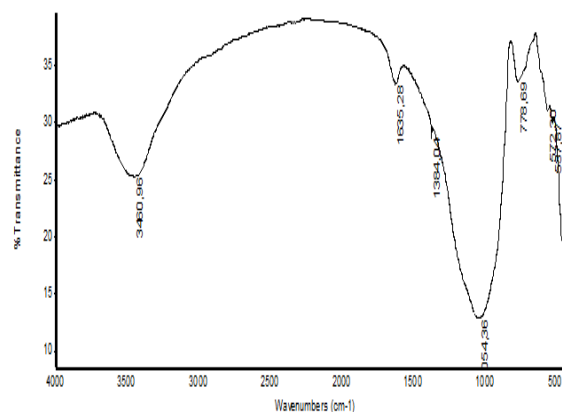


Fig. 2. Result of FTIR test of the adsorbent.

B. Effect of Mass of Adsorbent

Fig. 3 illustrates the removal efficiency of copper ion for different mass of adsorbent. Increasing the mass of adsorbent led to the enhancement of the adsorption efficiency of copper ion in the water. The adsorption efficiency for copper ion increased by increasing the mass of the adsorbent and became almost constant over 100mg. For 50 ml of copper solution, the favorable mass of adsorbent was 100 mg, where the adsorption efficiency was 77%. The increase of the adsorption efficiency of copper ion is due to the greater availability of the binding sites or surface area [11].

C. Effect of pH of Solution

The binding of Cu(II) with surface functional groups

strongly depended on the pH of solution. The effect of pH on the adsorption of 10 mg/l copper ion is shown in the Fig. 4. The removal efficiency of copper ion increased with pH of the solution because copperion forms complex with some functional groups in the adsorbent. The removal of metal cation at any pH was much greater than that by hydroxide precipitation. Adsorption of metal cation on adsorbent depends upon the nature of adsorbent surface and the distribution of metal species which distribution also depends on the pH of the solution [12]. The removal efficiency of copper decreased with the decrease of pH, because protons compete with metal ion for the adsorption sites on the adsorbent surface as well as the ion existing decrease of negative charge by association of the functional group with proton. The increase in metal ion removal as pH increase can be explained on the basis of the decrease in H⁺ on the surface, which results in less repulsion with adsorbing metal ions [6] and [13]. Rao M. M, (2006) reported that when point of zero charge of adsorbent was 5.7, where under 5.7 of pH, the surface of adsorbent was positively charged and adsorption of metal ion was low due to the electrostatic repulsion. Another researcher mentioned that in the highly acidic medium, the dissolution of the adsorbent occurs to a consequent decrease in the active sites. In this condition, the adsorbent surface is highly protonated, which is not favorable for the uptake of copperion because of the electrostatic repulsion [14] and [7].

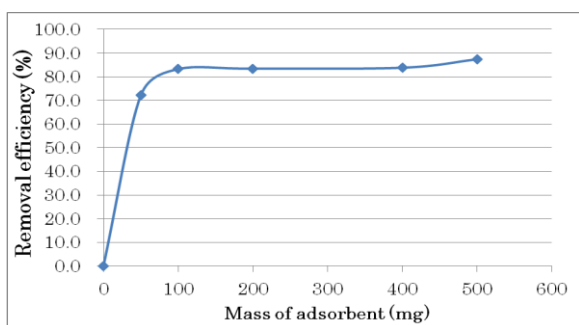
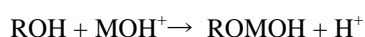
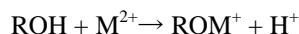
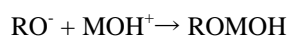
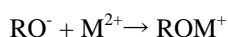


Fig. 3. Effect of mass of adsorbent on adsorption of copper ion (the pH of solution was 6.0, stirring time 2 hours for 50 ml of 10 mg/l Cu(II)).

In this study, it was confirmed that copper ions were precipitated at the higher pH than 7. The ideal pH for adsorption of 10 mg/l of copper solution was within the range of 5 to 7. The possible mechanisms of adsorption are shown as follows.



where RO⁻ denotes a negatively charged surface, ROH denotes a neutral surface and M denotes metal such as Cu.

D. Effect of Stirring Time

The effect of stirring time on the adsorption of copper ion is shown in Fig. 5. The equilibrium adsorption for 10 mg/l of copper was achieved after around 15 minutes with 92% adsorption capacity and then became 94% after 2 hours of

stirring. This result is necessary because the equilibrium time is considered for the application of economical wastewater treatment plant [11].

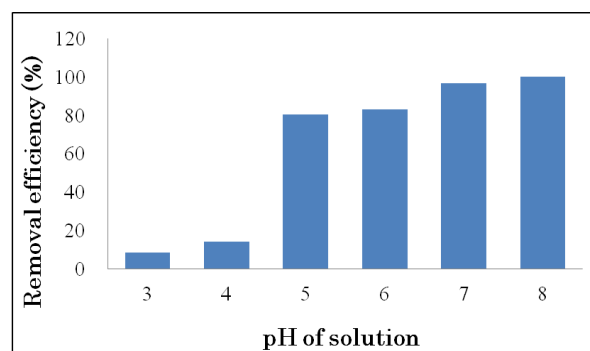


Fig. 4. Effect of pH of solution for Cu adsorption (adsorbent was 100 mg, stirring time 2 hours for 50 ml of 10 mg/l Cu(II)).

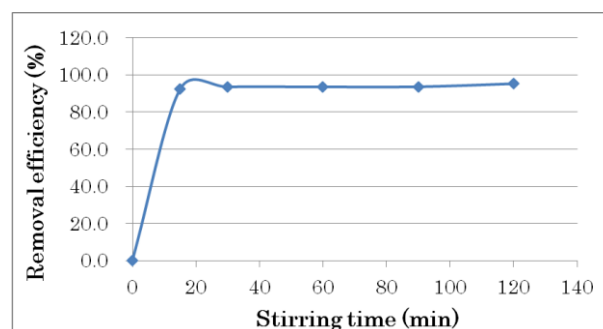


Fig. 5. Effect of stirring time on the adsorption of Cu (10mg adsorbent was used for 50 ml of 10 mg/l Cu(II) at pH 6.0).

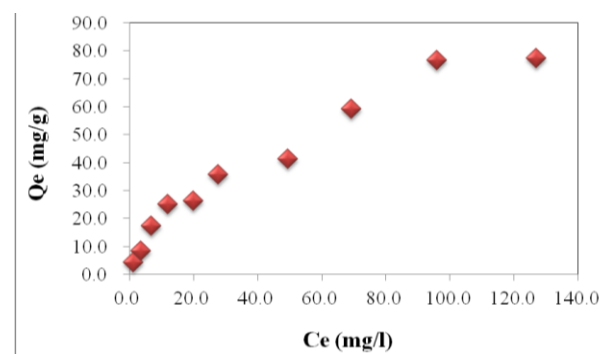


Fig. 6. Langmuir isotherm for adsorption of Cu(II) (100 mg adsorbent was employed for 50 ml Cu(II) solution of pH 6.0, and for 2 hours of stirring time).

E. Isotherm of Adsorption

The adsorption isotherm is shown in the Fig. 6. The Langmuir isotherm model was applied to the equilibrium constant of adsorption by the equation 2.

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{KLq_m} \quad (2)$$

where C_e is the equilibrium concentration (mg/l), q_e is the adsorbed amount of cadmium at equilibrium (mg/g), q_m and K_L are the constants of Langmuir related to the adsorption capacity and energy of adsorption, respectively. From the equation above, a plot of C_e/q_e versus C_e will be used to determine the values of q_m and K_L as the tangent and intercept of the curve. The value of q_m, K_L, and R² determined from the above equation were 82.6 mg/g, 0.042, and 0.9713,

respectively.

The characteristics of the Langmuir isotherm can be explained due to a dimensionless constant of the separation factor or equilibrium parameter, R_L , which is defined as:

$$R_L = 1 / (1 + K_L C_0) \quad (3)$$

where K_L is the Langmuir constant and C_0 is the initial concentration of copper ion in the solution. The R_L value indicates the shape of the isotherm as follows:

| | |
|---------------|--------------|
| $R_L > 1$ | Unfavorable |
| $R_L = 1$ | Linear |
| $0 < R_L < 1$ | Favorable |
| $R_L = 0$ | Irreversible |

The R_L value between 0 and 1 is favorable adsorption [15]. The R_L values for the concentrations of 10 and 100 mg/l of copper were 0.707 to 0.192, respectively. It means that the adsorbent was favorable adsorption for copper ion in water. The comparison of this adsorbent with some materials can be seen in Table I. Compared to the other materials, this adsorbent is quite good and could be considered as a low-cost adsorbent in the near future.

TABLE I: COMPARISON OF ADSORPTION CAPACITY WITH OTHERS MATERIALS

| Adsorbent | q_m (mg/g) | pH | Reference |
|-------------------------|--------------|-----|------------|
| Industrial oil sludge | 74.28 | 7.4 | [1] |
| Dewatered sewage sludge | 63.48 | 8.8 | [1] |
| Tea industry waste | 8.64 | 6 | [16] |
| Saw dust | 1.79 | | [17] |
| Peat | 12.07 | | [18] |
| Fly ash | 1.39 | | [19] |
| Rice straw | 2.54 | 5 | [20] |
| Volcanic ash | 82.64 | | This study |

IV. CONCLUSION

The ability of volcanic ash of Mount Kelud as adsorbent for removal of copper in water is good and the application of this material will give some advantages such as reducing amount of volcanic ash and producing an alternative low-cost adsorbent for removal of heavy metal ions in water. The adsorption capacity volcanic ash of Mount Kelud in Indonesia may due to the presence of some functional groups on the ash.

ACKNOWLEDGMENT

The authors thank to Department of Environmental Engineering, Faculty of Civil Engineering and Planning, Islamic University of Indonesia and Laboratory of Environmental Quality for financial support and facilities during this research.

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