The characterization of Merapi volcanic ash as adsorbent for dyes removal from batik wastewater

S Salamah¹ and E T Wahyuni²

¹Department of Chemical Engineering, University of Ahmad Dahlan, Prof. Soepomo Street, Yogyakarta 55164
²Department of Chemistry, University of Gadjah Mada, Sekip Utara Street, Yogyakarta 55281

¹sitisalamah@che.uad.ac.id, ²endtriw@yahoo.com

Abstract. In this paper, characterization, acid and base treatments, and adsorption assessment of the ash have been carried out to verify the ability of Merapi volcanic ash as an adsorbent. The characterizations were performed to determine the chemical composition by using ICP and surface area and pore volume by using surface area analyzer. The adsorbent ability was tested for removal of dyes, represented by naphtol standard, and Batik wastewater. The adsorption was carried by batch technique, in which adsorbent dose and adsorption time were varied to obtain the optimum condition. From the characterization, it is obtained that Merapi volcanic ash contains Si and Al as mayor elements, Fe, Ca, Mg, Na, and K with low percentage, and As, Mo, Cd, Cr, Cu, Mn and Pb with trace level. The adsorption study indicates that the Merapi volcanic ash can adsors the batik waste water and the adsorption increase by the increase in the weight of 49.6 % and stirrer time 50 minute can adsorb dyes waste of 3.9 gr/ml. Volcano ash is less suitable if it is used as adsorbent compared to natural zeolite.

1. Introduction

Merapi volcano eruption has exploded ash in very high amount that led to air pollution and made high pile of the ash promoting the environmental problem. It has been reported that Merapi volcanic ash contains mayor elements including SiO₂ and Al₂O₃ [1] that are around 60 % and 20 % respectively, accompanied with minor as well as trace level elements. In addition, radioactive elements are also found in the ash [2]. Based on the chemical composition, the effect of the ash contaminating soil on the plant growth has been studied and concluded that small amount of ash could induce the plant growth, while large pale ash on the soil inhibited the growth [3, 4].

The high content of SiO₂ and Al₂O₃ in the volcanic ash, as found in clays [5] and zeolites [6], enables the ash to act as adsorbent. In addition, the ash also has large surface area that is ~ 10 m² per gram weight volcanic ash [7] that may give high adsorption capacity. The material high composition of silica and other metal oxides has the possibility to remove dye from wastewater [8]. However, the use of Merapi volcanic ash as adsorbent has not been explored yet. Furthermore, the eruption of Merapi Volcano was in rainy season, so that the volcanic ash distributed in open place was rinsed by the rain water. Such rinsing may remove some metals from the ash. This may cause the change composition and change the adsorption capacity of the ash.
Adsorption is a process by which a solid adsorbent attracts a component in solution its surface through a physical or chemical interaction [9]. Based on the fact reported above, the adsorption ability of the volcanic ash, before and after rinsing, is interesting to be studied. Batik waste water was selected as a waste model that was treated with volcanic ash adsorbent, because many Batik industries are existing in Yogyakarta.

The large number of Batik industries create very high volume of the waste water, contents high level of dyes. The contamination of dyes in the environment including rivers leads to the environmental damage and health problem [8, 10]. The removal of dyes waste water from Batik industry has to be carried out before being disposed to the environment. Several methods have been used for removal dyes in Batik waste water [11]. Several adsorbents such as zeolite [11], modified clay [11], and activated carbon [12] can be used to manage the waste of Batik production in Yogyakarta [13]. Effectiveness of waste management has been studied for removal dyes from Batik waste water. However, removing the dyes from the waste by using volcanic ash has not been examined. In this paper, a study on dyes removal from Batik waste water by using volcanic ash as adsorbent, whether fresh/before rinsed and after rinsed is reported.

2. Experimental
This section explains the procedure of proposed experiment.

2.1. Material
Volcanic ash obtained from the eruption of Merapi Volcano on Oct 26, 2010 at radius ± 28 km from the peak of southern side, Sinduadi village, Mlati, Sleman (before and after, Naphthol dyes used in batik coloring, Naphthol α powder, Ethanol, Aquadest, HCl pro analyst, NaOH crystal, Filter paper Whatman 42 and pH paper were used in this research without any purification.

2.2. Instrumentation
Surface area analyzer NOVA 100, ICP (Ion coupled plasma), UV-Vis Spectrophotometer, Glass tools, Sieve (100 mesh size) model RX-86, Heater and magnetic stirrer, Dryer oven (Precision model 17), Digital scale Mettler AE 163, Grinder, Buncher funnel and vacuum pump, Vacuum oven (Yamamoto Scientific, LTD), Thermometer and a set of reflux tools and stopwatch were used in this research.

2.3. Procedure
2.3.1. Preparation of naphthol dyes solution. Naphthol dye powder, as a standard dye, as much as 0.4 gram; 0.3 gram; 0.2 gram and 0.1 gram was dissolved in 10 ml of cold water, while naphthol salt as a dye model was dissolved in 1 L of boiling water.

2.3.2. Determination of the chemical composition in Merapi volcanic ash. Merapi volcanic was dried at 100°C then sieved with 100 mesh sieve. The 100 mesh volcanic ash powder then was analyzed by ICP Analyzer.

2.3.3. Preparation of Merapi volcanic ash for adsorbent. The 100 mesh volcanic ash powder as much as 150 grams was mixed with 1 M HCl 125 ml and refluxed with three-neck flask for 4 hours at 60 °C by stirring gently using a magnetic stirrer. The ash was separated from the mixture by filtering and then rinsed with water to remove the HCl excess. Then, the rinsed ash was neutralized using by stirring for 4 h using 200 mL of 1 M NaOH. The Merapi volcanic ash was rinsed again with aquadest until the pH is 7 and dried in the oven for 2 hours at 100°C. These steps of preparation for volcanic ash were repeated in natural zeolite preparation to prepare the natural zeolite as adsorbent.

2.3.4. Adsorption of batik dyes using Merapi volcanic ash. Make a standard curve for various concentrations of dyes and analyzed the absorbance by spectrophotometer. Then making naphthol dyes solution and then measuring the concentration using spectrophotometer. Then pour the Merapi volcanic ash with variation of a certain weight (10 grams, 20 grams, 30 grams, 40 grams, and 50 grams) in 200 mL batik waste solution, and then stirred using a mercury stirrer for 10 minutes. After
stirring for 10 minutes, the mixture was precipitated for 24 hours, and then centrifuged for 10-15 minutes. The absorbance of the sample was then measured by using a spectrophotometer and the concentration was calculated with the aid of a standard curve that was created.

2.3.5. The influence of stirring time. Taking the volcanic ash with the most optimal datum of data that has been obtained through the previous experiments. Stirring the ashes for 4 minutes. After that, repeat steps 1-2 for stirring time 10 minutes, 20 minutes, 30 minutes, 40 minutes, and 50 minutes. After stirring, the mixture was precipitated for 24 hours, and then centrifuged for 10-15 minutes. Then, measure the absorbance of the sample with a spectrophotometer. Measure the concentration of the sample with the aid of a standard curve has been made.

3. Result and discussion
This section presents and discusses the experiment results.

3.1. Chemical composition of the Merapi volcanic ash
The chemical composition of the volcanic ash determined by ICP (Inductivity Coupled Plasma spectrometers), both before rinsed/fresh and that of after rinsed is presented in table 1 for mayor elements and that of for heavy metals is in table 2.

**Table 1.** The content of mayor elements in Merapi volcanic ash.

| No | Element | volcanic ash (mg/kg) | volcanic ash + water (mg/kg) |
|----|---------|----------------------|-----------------------------|
| 1  | Al      | 62890                | 39590                       |
| 2  | Ca      | 39500                | 16010                       |
| 3  | Fe      | 54040                | 31660                       |
| 4  | Mg      | 9773                 | 4944                        |
| 5  | Na      | 22440                | 13640                       |
| 6  | P       | 765.4                | 113.1                       |
| 7  | S       | 907.7                | 815.6                       |

**Table 2.** The content of heavy hazard metals in the volcanic ash.

| No | Element | volcanic ash (mg/kg) | volcanic ash+ water (mg/kg) |
|----|---------|----------------------|-----------------------------|
| 1  | As      | 8.948                | 8.302                       |
| 2  | Cd      | 1.295                | 0.839                       |
| 3  | Cr      | 3.88                 | 2.262                       |
| 4  | Cu      | 7.407                | 2.492                       |
| 5  | Mn      | 1310                 | 796                         |
| 6  | Mo      | 1.436                | 1.436                       |
| 7  | Ni      | 2.767                | 1.623                       |
| 8  | Pb      | 10.14                | 11.70                       |
| 9  | Zn      | 160.6                | 72.34                       |

Table 1 and [5] showed that Merapi volcanic ash contains SiO$_2$ and Al$_2$O$_3$ in high level accompanied by other mayor elements. Based on this data, it is clear that the volcanic ash has the potential to be used as an adsorbent by providing silanol and aluminol as the active adsorption sites. According to [8], charcoal has a structure like aluminum silicate which has the possibility to be used as an adsorbent. In addition, as seen in table 2, some hazardous metals in very low quantities were found in the volcanic ash.
The presence of the hazardous metals made the ash harmful to the body as it can cause lung problems when the ash-polluted air is inhaled. Moreover, when the ash contaminates water including open well and rivers, biota may be dead and people may get health problems. Furthermore, data in both tables indicate that the rain water has made the content of all metals, except for Pb and Si, decreased. The decrease is caused by releasing the metals in the rain water. Such releasing makes the content of Si increased, that may provide more active adsorption sites.

Merapi volcanic ash contains hazardous metals (As, Cd, Pb, and sulfur) in small quantities, also contain other metals which is in large enough quantities e. g. aluminum (Al), calcium (Ca), iron (Fe), and sodium also phosphorus (P). These results also indicate the metal content in the volcanic ash exposed to rain is mostly decline, it was likely due to the metals dissolve in water, and pouring rain water can dissolve some of the metals contained in the ash. The metal content of volcanic ash can be utilized such as a mixing compound cement manufacturing. According to [5] in addition to Al and Ca also contains silica which is quite high, thus allowing the use of ash as a basis for the manufacture of cement-based material.

3.2. The surface characters of Merapi volcanic ash

Measurement of the specific surface area, total pore volume and pore radius average conducted to determine how large specific surface area and pore distribution of ash that can be used as an adsorbent. This measurement was done because the specific surface area of the sample will indirectly affect the adsorption ability of the sample. According to [14] with increasing adsorption on the surface of the powders, the possibility of formation of a product which is expressed as the concentration of reactants that can be adsorbed will increase. Data specific surface area, total pore volume and pore radius average volcanic ash are presented in table 3.

| Sample            | Parameter              | Test result | Unit    |
|-------------------|------------------------|-------------|---------|
| Merapi Volcano ash| Specific surface area  | 4.100       | m²/g    |
|                   | Total pore volume      | 5.234 x 10³ | cc/g    |
|                   | Pore radius average    | 25.531      | Å       |
| Merapi            | Specific surface area  | 4.297       | m²/g    |
| Volcano ash +     | Total pore volume      | 5.241 x 10³ | cc/g    |
| water             | Pore radius average    | 24.39       | Å       |
| Natural zeolite   | Specific surface area  | 29.366      | m²/g    |
|                   | Total pore volume      | 5.241 x 10³ | cc/g    |
|                   | Pore radius average    | 18.183      | Å       |

Table 3 showed that the Merapi volcanic ash specific surface area and specific pore area are quite large and thus have the potency as an adsorbent. As a comparison, Y-zeolite which is zeolite synthesis produced in Japan [15] has a specific surface area of 475.94 m²/g and specific pore area of 29.366 m²/g and the fly ash which is a product of coal combustion has a specific surface area between 170 to 1000 m²/kg or 0.170 to 1 m²/g [7], both are the adsorbents widely used nowadays. The specific surface area of Merapi volcanic ash increased after affected by rain water. It is probably because some of the metals are dissolved in rain water and thus it increases its specific surface area. This is also supported by the reduction in the metal content of the volcanic ash exposed to rain.

3.3. volcanic ash utilization as dyes adsorbent

The weight of volcanic ash used as an adsorbent is 10 grams, 20 grams, 30 grams, 40 grams and 50 grams, minutes. Once adsorbed by stirring, the solution was precipitated for 24 hours and centrifuged for 15 minutes and then analyzed for absorbance.
The adsorption experimental was carried out by batch technique, in which the influences of adsorbent mass and stirring time are studied to obtain the optimum adsorption conditions. The influence of the volcanic ash mass on the dyes adsorption is presented as table 4 and 5.

Table 4. The influence of the volcanic ash on the dyes adsorption.

| No | volcanic ash weight (gr) | Adsorption Concentration | Adsorption (%) |
|----|--------------------------|--------------------------|----------------|
| 1  | 10                       | 1.639                    | 20.594         |
| 2  | 20                       | 1.797                    | 22.572         |
| 3  | 30                       | 2.434                    | 30.576         |
| 4  | 40                       | 3.301                    | 41.458         |
| 5  | 50                       | 3.952                    | 49.641         |

Table 4 showed that the more Merapi volcanic ash used as adsorbent represented by the increase in volcanic ash weight, the more wastewater that is adsorbed. This is because the more materials used as adsorbent, the more the pore area increased, and thus the more wastewater color being adsorbed.

Table 5. The influence of the natural zeolite on the dyes adsorption.

| No | Natural Zeolite weight (gr) | Adsorption Concentration | Adsorption (%) |
|----|----------------------------|--------------------------|----------------|
| 1  | 10                        | 4.654                    | 50.454         |
| 2  | 20                        | 7.876                    | 61.241         |
| 3  | 30                        | 5.678                    | 71.314         |
| 4  | 40                        | 6.186                    | 77.699         |
| 5  | 50                        | 6.286                    | 78.958         |

Table 5 showed that the more zeolite being used as adsorbent represented by the increase in zeolite weight, the more wastewater being adsorbed compared with wastewater adsorbed by Merapi volcanic ash. This is because the zeolite has a specific pore area of 29.366 m²/g larger than volcanic ash which only has a specific pore area of 4.1 m²/g hence the wastewater adsorbed is more than those adsorbed by volcanic ash. If it is compared with volcanic ash adsorbent, zeolite adsorbed 30% even up to 60% more than volcanic ash. This is because of specific pore area of zeolite which is larger than volcanic ash.

3.4. The influence of the stirring time to adsorption

The influence of the stirring time was examined by running the adsorption experiment with time variation by volcanic ash and natural zeolite. The result of the adsorption in various stirring times is displayed as figure 1.

Figure 1 shows that the longer the time or stirring, the more wastewater being adsorbed. The optimal amount of wastewater absorbed by volcanic ash is 3.98 gr/ml with the percentage of 50 %, while zeolite absorbed more amount of wastewater which is 6.3 gr/ml with the percentage of 79.4 %. This is because by prolonging the stirring time until the optimal time, the longer the contact between the adsorbent and the wastewater and the closer to perfect the adsorption process.
Figure 1. The influence of the stirring time on the dyes adsorption.

The comparison of adsorbed color concentration between stirring time of volcanic ash and zeolite showed that zeolite has higher adsorption ability which reaches 79.4%. This is because zeolite has larger specific surface area than volcanic ash. Natural zeolite has a specific surface area of 29.366 m²/g whereas Merapi volcanic ash has a specific surface area of 4.100 m²/g. The research showed that Merapi volcanic ash is less suitable if used as adsorbent if it is compared to other adsorbent which has larger specific surface area.

4. Conclusion
Merapi volcanic ash contains heavy metals such as Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Manganese (Mn), Molybdenum (Mo), and Lead (Pb) with varying concentrations and a maximum of 10 mg/kg. It also contains other metal elements such as Aluminum (Al), Calcium (Ca), Iron (Fe), and Sodium (Na). Merapi volcanic ash has a surface area of 4.100 m²/g, pore volume of 214.47 x 10⁻³ and the mean pore of 214.47 x 10⁻³. Based on this result, it can be concluded that Merapi volcanic ash can be used as an adsorbent and when the volcanic ash is used as an absorbent of batik waste water, it works optimally at a weight of 50 grams can adsorbent dyes of 49.6% and stirring time 50 minutes can adsorbent dyes of 3.98 gr/ml. Merapi Volcano ash is less suitable if used as adsorbent if it is compare natural zeolite.

Acknowledgement
This research was supported by Research and Development Institute of Ahmad Dahlan University grant No: M-75 / LPP-UAD / I/2014.

References
[1] Delmelle P 2005 Surface Area, Porosity and Water Adsorption Properties of Fine Volcanic Ash Particles. *Bull. Volcanology* vol 67 pp 160-9
[2] Clift P D and Fitton J G 1998 Trace and rare earth element chemistry of volcanic ashes from sites 918 and 919: Implication for Icelandic Volcanism *Proc. of the Ocean Drilling*
[3] Brotopuspito K 2012 Physics of the Volcano *Inaugural Speech Professor of Geophysics* (Yogyakarta: University of Gadjah Mada)
[4] Wilson T M, Stewart C, and Cole J 2007 Impact on the 2006 Eruption of Merapi Volcano, Indonesia on Agriculture and Infrastructure (Indonesia: GNS Science Report)
[5] Wahyuni E T 2012 Determination of volcanic Ash Chemical Composition from Merapi
Volcano Eruption *J. Human and Environmental* vol 19 pp 150-9

[6] Salamah S 2016 Utilization of Kelut's Volcanic Ash as the Aggregate Mixture of Concrete Brick *J. Key Engineering Material* vol 718 pp 196-200

[7] Pratama Y, Putranto H T 2007 Fly Ash Coal Conversion to Zeolite for Removal of Chromium and Nickel from Wastewaters (www.majarikanayakan.com)

[8] Kusmiyati, Listiyanto P A and Vitasari D 2017 Coal Bottom Ash and Activated Carbon for Removal of Vertigo Blue Dye in Batik Textile Waste Water: Adsorbent Characteristic, Isotherm and Kinetic Studies *J. WALAILAK Sci & Tech* vol 14 no 5 pp 427-39

[9] Bediako J K, Wei W, Y-S Yun 2016 Conversion of Waste Textile Cellulose Fibers into Heavy Metal Adsorbents *Journal of Industrial and Engineering Chemistry* vol 43 pp 61-8

[10] Hernaningsih T 2016 Industrial Wastewater Treatment Technology Review by Electrocoagulation Process *J. Environmental Engineering* vol 9 pp 31-46

[11] Riyanto 2015 Discovery New Technique for Batik Wastewater Treatment *J. Research Outcome in Sleman Regency* vol 2 pp 65-77

[12] Setyaningsih H 2007 Batik Wastewater Treatment with Chemical Process and Activated Carbon Adsorption *Post Graduate Thesis* (Jakarta: University of Indonesia)

[13] Al Rasyid M R and Asri R W P 2017 Waste Prevention Effectiveness of Batik Production in Yogyakarta, Indonesia, *Proceeding of The 2nd International Conference on Sustainable Innovation* pp 437-81

[14] Gasser R P H 1985 *An Introduction to Chemisorption and Catalysis by Metal* (Oxford: Clarendon Press)

[15] Salamah S, Trisunaryanti W and Triyono 2011 Influence of total metal contents in catalyst Ni/Pd/zeolite Y on fuel hydrocracking asphalt fraction from Buton asphalt with semi bath reactor, *Proceeding of The 7th Indonesia Zeolite Conference ITS Surabaya*