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Production and Application of Aggregate Manganese Zeolite Greensand using Post Cartridge Micron as Absorbent Fe and **Mn** Ions

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Abstract. The purpose of this study was to produce an aggregate of fine manganese greensand and its applications using micron cartridge design for absorbing Fe³⁺and Mn²⁺ ions in the well water affected by the Lapindo mud. The fine manganese greensand was made using the flame spray pyrolysis. The combination of aggregate material and the bulk manganese greensand were performed with the adding filler with the varied compositions of CaO, CaCO₃, and white cement as the adhesive. Characterization of topography, morphology, and composition of aggregate manganese greensand was performed using SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-Ray). Applications of the aggregate manganese greensand and activated carbon were designed in several post cartridge microns for well water samples. Initial and final measurement the concentration of Fe and Mn solution using a calibration curve by AAS method (Atomic Absorbance Spectrophotometer). The results showed that the aggregate A with a composition of fine manganese greensand: bulk manganese greensand: CaCO₃: CaO and white cement is 2:5:1:1:1:1 and aggregate B (3:4:1:1:1) absorbed maxima ions of Mn (97.5%) and Fe (80.3%) in the well water sample, respectively. Besides, the profile of spectrum SEM-EDAX indicated the aggregate A and B interacting with filler which showed the active situs as exchange cation for absorbing Fe³⁺ and Mn²⁺ ions.

Keywords: well water, aggregate, zeolite, post cartridge micron, Lapindo mud

1. Introduction

Lapindo mudflow is the most significant environmental problem in Indonesia, and till now there is no solution yet. The blast of hot mud over several years has caused flooding of settlements and impacts on the environment. In the natural environment, the contaminant of Lapindo mud can contribute Fe



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and Mn and then enter in the freshwater system transformation processes. The decline in housing supply after the emergence of Lapindo disaster and their social identity were considered to solve those problems for sustainable future [1,2]. The high levels of Fe and Mn contaminations in water are of serious concern due to persistence in the sediment, coral environments and carcinogenicity to human beings [3–7]. The impact of high levels of Fe and Mn affect human health, especially the physiological anomaly of the liver. It was also stated that metals could not be destroyed biologically, but other ways are only transformed from one oxidation state or organic complex to another [8]. Investigation and reduction of Fe and Mn ions in well water caused the effect of Lapindo mud is needed to monitor the environmental contaminations.

Today, the application of new materials and technologies on water purification media is very prospective innovation. Some researchers used the nanotechnology material, which has several advantages including: (1) nanomaterials have greater energy than ordinary size material because it has a large surface area [9–11], (2) The magnetism rate will increase with the particle droplet size and decrease of surface area that can accurately increase the chemical absorption activity of the material [12,13]. One of the natural materials that can be used as an absorbent of Fe and Mn is a zeolite. Zeolite had potential as membrane systems that function as ultra-micro filtration, reverse osmosis, catalysts, and ion exchange systems to remove heavy metals [12,13]. However, zeolite in the form of manganese greensand aggregate has not been developed in Indonesia.

Here, we produced the manganese zeolite greensand absorbent aggregate and applied it in Post Cartridge Micron (PCM) for absorbing Fe and Mn ions in the well water closing with an area of Lapindo mud. Moreover, the design of PCM was installed in the pipeline of the well water for clean water needs in the affected area of Lapindo mud.

2. Methods

2.1. Preparation of Manganese Zeolite Greensand Aggregate and SEM-EDX test

Manganese zeolite greensand (K₂Z.MnO.Mn₂O₇) bulk size was milled using a grinder, and followed by using a flame spray pyrolysis tool to produce the fine powder manganese greensand zeolite. The manganese zeolite greensand and bulk manganese zeolite greensand were heated at 3.5 hours in the oven. These two materials then were mixed with various mass variations and CaO, CaCO₃ also white cement up to 100% composition (w/w) (Table 1). The material was aggregated by adding 500 ml of distilled water, stirred and then finally entered in PCM for 7 days. The formed of the manganese zeolite greensand aggregates with the various composition were tested for topographic characterization, morphology and metal distribution using Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX) JEOL Model JSM-7800F.

2.2. Application of aggregate in PCM

As shown in Figure 1a and b, the PCM is installed subsequently for absorbing Fe and Mn ions from well water. The well water samples were taken from 5 locations affected by Lapindo mud (Kenongo, Pesawahan, Candi Pari, Gedang, and Mindi). After measuring of Fe and Mn concentrations from 5 locations, we chose one of the well waters which had the highest concentrations of Fe and Mn for input sample to the installation of PCM. The concentrations of Fe and Mn before and after entered the PCM were measured by Atomic Absorption Spectrophotometer (AAS) Shimadzu 4000 using the calibration curve method.

3. Results and Discussion

3.1. Aggregate Manganese Zeolite Greensand

The manganese zeolite greensand aggregate as absorbent was successfully produced. The absorbent composition had an important role in the absorption of Fe^{3+} and Mn^{2+} ions. The result of the aggregate manganese zeolite greensand is listed in Table 1.

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Fine Manganese Greensand (%)	Bulk Manganese Greensand (%)	CaO (%)	CaCO ₃ (%)	White Cement (%)	Aggregate
20	50	10	10	10	А
30	40	10	10	10	В
40	30	10	10	10	С
50	20	10	10	10	D
60	10	10	10	10	Е

Table 1. The composition of product aggregates

As listed in Table 1, the A-E aggregates were used as absorbent materials in PCM for absorbing of Fe and Mn ions in areas affected by Lapindo mud. The concentration of Fe and Mn in the well water is listed in Table 2.

Table 2. Fe and Mn concentrations in well water samples

Sampling Location	Fe Concentration (ppm)±SD	Mn Concentration (ppm)±SD
Kenongo	$0.72{\pm}0.01$	5.31±0.13
Pesawahan	$0.76{\pm}0.04$	16.2 ± 15.6
Candi Pari	$0.66{\pm}0.01$	15.3 ± 4.86
Gedang	$0.72{\pm}0.07$	10.9 ± 5.92
Mindi	$0.69{\pm}0.01$	12.4±7.80

The concentration of Fe and Mn at 5 locations affected by Lapindo mud was higher than the value of the standard of clean water (Fe 0.1 ppm, Mn 4.6 ppm) as reported by Garbisu and Alkota, 2001 (Table 2). Especially the concentration of Fe and Mn, their contents in well water at the location of pesawahan (rice fields) recorded at 0.76 ppm and 16.2 ppm, respectively showed higher 7 and 4 times than standard values of clean water suggesting that Lapindo mud through geothermal processes contributed to Fe and Mn ions and then contaminated in the groundwater flows or wells. Besides, well water from the location of Pesawahan is closing with the source of Lapindo mud.

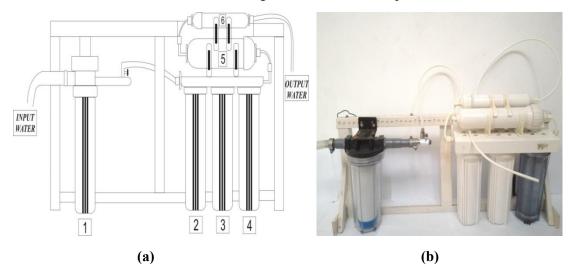


Figure 1. (a) Design of Water Purifier, (b), Water Purification Products

To test the effectiveness of Fe and Mn absorptions, the water purification instruments or PCM installation were designed (Figure. 1a and b). Well water sample was chosen from Pesawahan location as the input sample. The water sample was entered at 1-6 PCM, subsequently. PCM contained the activated carbon and fine manganese zeolite greensand with a variation of 5 aggregate (A-F) (Table 1). PCM 1, 2, and 3 contained activated carbon as an odor absorber, color bleach, and water purifier before entering PCM 4. PCM 5 and 6 adsorbed of Fe³⁺ and Mn²⁺ ions after reacting with manganese zeolite greensand aggregate. Besides, the functions of PCM 5 and 6 reduced the odor and made a clear solution.

Based on Table 3, it can be described that the best material absorbent composition for absorbing Fe concentration was aggregate B (30% Fine Manganese Greensand, 40% Bulk Manganese Greensand, 10% White Cement, 10% CaO, and 10% CaCO₃ or 3: 4: 1: 1: 1 compositions). The ability of this aggregate can absorb of Fe concentration from 0.76 to 0.13 ppm (80.3%). In addition, the best material absorbent for absorbing Mn contents was aggregate A (20% Fine Manganese Greensand, 50% Manganese Greensand Bulk, 10% white cement, 10% CaO, and 10% CaCO₃ or 2: 5: 1: 1: 1 composition). This aggregate is capable of absorbing Mn contents from 16.2 to 0.41 ppm (97.6%).

Aggregate	[Fe ³⁺] initial (ppm)	[Fe ³⁺] final (ppm)	% Absorption of Fe	[Mn ²⁺] initial (ppm)	[Mn ²⁺] final (ppm)	% Absorption of Mn
А	0.76	0.19	75.0	16.2	0.41	97.5
В		0.15	80.3		11.1	31.5
С		0.22	71.1		10.2	37.0
D		0.35	56.6		5.88	63.7
E		0.18	76.3		7.35	54.6

Table 3. The ability of aggregates for absorbing of Fe and Mn contents in well water

3.2. Characterization of Aggregates A and B using SEM-EDAX

The aggregates of A and B were selected from PCM due to the highest absorbed of Fe and Mn ions. We characterized their topography and morphology using SEM-EDAX. The SEM photograph of aggregate A and B and their corresponding elemental analysis is shown in Figure 2a and 2b. Figure 2 shows that aggregates A and B had a large number of granular material sizes, which distributed uniformly. Based on the pores size, aggregate B seemed the smaller pores comparing with those in aggregate A indicates the suitable material for absorbing of Fe³⁺ ions. It clearly stated in Table 3 that the aggregate B can absorb maximal of Fe³⁺ ion up to 82.5% due to the smaller ionic radius size (0.60 Å) than that for Mn²⁺ ion (0.80 Å). In case of pore size of distributions in aggregate A, which is more effective to absorb Mn²⁺ (0.80 Å) or Mn³⁺ (0.62 Å) ions having an ionic radius greater than Fe³⁺ (0.60 Å) or Fe²⁺ (0.75 Å) (Figure 2). We suggest that the characteristic of physical and chemical properties in the morphology aggregates depending on the ratio of fine and bulk manganese zeolite greensand. In addition, some researchers confirm that the ionic radii play a central role in specific areas in the chemistry, such as geochemistry, solid-state physics, and biophysics associated with their capability to absorb of the metals [15,16].

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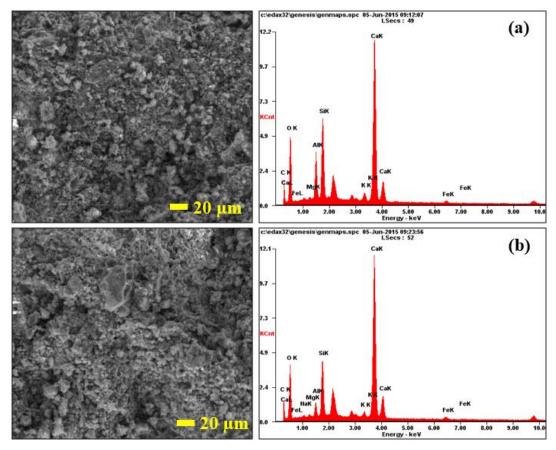


Figure 2. SEM photograph and elemental analysis of (a) aggregate A and (b) aggregate B

Figure 2a and 2b show the large quantities of Si, C, O, Mg, Al, Si, K, Ca, and Fe in the aggregate A and B. It indicates that metal contents were influenced by filler composition of CaCO₃, CaO, and white cement. The component of manganese zeolite greensand K_2Z .MnO.Mn₂O₇ were also distributed as the spherical granule and then spread across in PCM mixed with the filler containing Si, Al and Ca elements. They have an active site for ion exchange when Fe and Mn ions from the well water sample enters in PCM. In addition, K and O elements were also recorded in the spectrum and their functions as the oxidator to exchange electrons in Fe and Mn ions into an insoluble form (iron/ manganese oxide) in the aggregate. In the process of absorption of Fe and Mn ions in the form of Fe(HCO₃)₂ and Mn(HCO₃)₂ compounds in well water samples, the possibility of chemical reactions can be written, as follows:

$$\begin{split} &K_2Z.MnO.Mn_2O_7 + 4Fe(HCO_3)_2 ===>K_2Z + 3MnO_2 + 2Fe_2O_3 + 8CO_2 + 4H_2O\\ &K_2Z.MnO.Mn_2O_7 + 2Mn(HCO_3)_2 ===>K_2Z + 5MnO_2 + 4CO_2 + 2H_2O \end{split}$$

4. Conclusion

The aggregate has been successfully produced with the composition of fine manganese zeolite greensand, bulk manganese zeolite greensand, CaCO₃, CaO and white cement. The mass ratio of aggregate with their compositions (2: 5: 1: 1: 1) had the ability to absorb maximum until 97.5% of Mn^{2+} ion and aggregate (3: 4: 1: 1: 1) which was able to absorb up to 80.3% in well water sample from Pesawahan areas that most affected by Lapindo mud. The characterization of morphological form and topography granular of both aggregates showed their photography and spectrum of SEM-EDAX profiles depending on the fine or bulk manganese zeolite greensand compositions. That aggregates interacted with the filler of CaO, CaCO₃, CaO and white cement indicating that materials have an active site for ion exchanges.

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