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Performance of Silica Membranes from Fly Ash Coal of PT Semen Baturaja in Reducing Metal Content in Mine Acid Water

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Abstract

Mine acid water has a high level of acidity as a result of oxidation of rocks containing pyrite and sulfide minerals from the remains of rocks exposed to oxygen in the water, which usually contain high metal content. One way to reduce the metal content in acid mine water is to use a silica membrane. In the study, silica membranes were made by extracting silica from fly ash by using two types of solvents or extractors, namely HCl and HNO_3. The adsorption time are 100 min, 120 min, and 140 min with the aim to find out which extractors can produce membranes with performance good and optimum time in the absorption of metal content from acid mine drainage. SEM analysis shows that there is no pore formed on the membrane. The membrane with HCl extractor works better in reducing metal content. The optimum adsorption time in the 120th min is 18.9 mg/L. Acid mine drainage also experienced a decrease in flux from 14.9283 L/m^2 hours to 6.8244 L/m^{2}h for the membrane with HCl extractor and for HNO_3 membrane decreased from 11.9427 L/m^{2}h to 7.6774 L/m^{2}h.

Keywords: Silica Membranes, Fly Ash Coal, Metal Content, Mine Acid Water, extractor

Abstrak (Indonesian)

Air asam tambang memiliki tingkat keasaman yang tinggi akibat dari oksidasi batuan yang mengandung pirit dan mineral sulfida yang terpapar oleh oksigen yang berada di dalam air dan mengandung kadar logam yang tinggi. Salah satu cara untuk mengurangi kadar logam dalam air asam tambang adalah dengan menggunakan membran silika. Pada penelitian ini, membran silika dibuat dengan mengekstraksi silika dari *fly ash* dengan menggunakan dua jenis pelarut yaitu HCl dan HNO_3. Waktu adsorbsi yaitu 100 menit, 120 menit, dan 140 menit dengan tujuan untuk mengetahui pengekstrak yang dapat menghasilkan membran dengan kinerja yang baik dan waktu optimum dalam penyerapan kadar logam air asam tambang. Analisa SEM menunjukkan tidak adanya pori yang terbentuk pada membran. Berdasarkan hasil analisa dari penelitian yang dilakukan, dapat diketahui bahwa membran dengan pengekstrak HCl bekerja lebih baik dalam menurunkan kadar logam dengan waktu adsorbsi optimum pada menit ke-120 yaitu 18,9 mg/L. Air asam tambang juga mengalami penurunan fluks dari 14,9283 L/m^{2}jam menjadi 6,8244 L/m^{2}jam untuk membran dengan pengekstrak HCl dan untuk membran HNO_3 menurun dari 11,9427 L/m^{2}jam menjadi 7,6774 L/m^{2}jam.

Kata Kunci: Membran Silika, Abu Terbang Batubar, Kandungan Logam, Air Asam Tambang, Ekstraktor

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INTRODUCTION

South Sumatra is one of the provinces in Indonesia that has many industries, including the coal mining industry. Coal is one of the mining materials used for PLTU. The process of burning coal to produce power in the industry will produce the remaining combustion called fly ash and bottom ash which, if not utilized properly, can disrupt human health and the environment.

The number of industries that use coal as fuel leaves a number of serious problems because the fly ash produced contains significant amounts of heavy metals. The release of residual burning ash in the

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form of both fly ash and bottom ash will have a bad impact on the environment, so there needs to be special handling to overcome these impacts, one of them is by utilizing waste into new material that has economic value [1].

Fly Ash is ash that results from the transformation, melting or gasification of inorganic materials contained in coal. In one coal combustion process, fly ash is produced around 80% and the rest is bottom ash which is around 20%. According to data from the Ministry of Environment, the resulting fly ash waste reaches 85 tons / day and bottom ash waste reaches 48 tons / day [2]. Meanwhile according to regulations [3], fly ash and bottom ash waste can be categorized as B3 waste (toxic and dangerous material). The main components of coal fly ash derived from power plants are silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3), the rest are carbon, calcium, magnesium, and sulfur. Coal production in South Sumatra in 2013 amounted to 200 tons which was partly used as fuel for mine power plants. Increasing coal demand has led to increased coal exploration. Coal exploration by means of mining will produce mine waste water. Mining wastewater consists mainly of acid mine drainage and mud. Coal mine wastewater contains residues, causing acidity, and contains iron and manganese which, if disposed directly into the environment, will cause environmental damage, namely the pollution of rivers around the mining area.

Silica is one of the most dominant components of fly ash which is around 30-36%. Silica is widely used in vegetable oil refining, pharmaceutical products, detergents, adhesive materials, packaging column chromatography, and ceramics [4,5,6,7). Many studies have been carried out on silica from fly ash, including Eka Suprihatin [5] used fly ash as an ingredient to make silica membranes, which was used to reduce BOD and COD levels in palm oil waste, using fly ash as an ingredient to make membranes as well. It carried out by Citria Afrianty [6], where fly ash is used to make ceramic membranes which are then used to treat acid mine drainage. Acid mine drainage has a Mn content of 16.8 mg/L in it [6], therefore the treatment of acid mine drainage is deemed necessary to reduce the negative impacts and hazards that can be caused from the presence of this metal in the water.

Based on the uses and research that has been done [6] it can be seen that fly ash can not only be used as an additional material in the manufacture of cement or concrete, but also can be used as a raw material for making membranes that can benefit the environment, where silica from the fly ash has the ability to absorb heavy metals from industrial waste. Therefore, this study is intended to reduce metal content in acid mine drainage by using silica membranes.

MATERIALS AND METHODS

Materials

In this study, experiments were carried out using fly ash which was made into a silica membrane. The stages of the process are: extraction of silica (SiO_2) from fly ash, then making Poly Vinyl Alcohol (PVA) mixture and continue to make silica solid membranes and finally to test the performance of silica membranes.

To analyze of membrane performance in mine acid water we did some steps : cut around membrane according to the diameter of the column, insert the silica membrane into a simple deposition column, then flow 150 ml of acid mine water into a column containing silica membrane and collect results with a time variation of 100, 120 and 140 min s. We still have to test the decrease in Mn in the product with Atomic Absorption Spectrophotometry (AAS).

Methods

The process of making silica membranes with coal fly ash is carried out by the extraction process of silica from fly ash, where prior to the extraction process, firstly the fly ash is soaked in hot water for 2 (two) hours which aims to remove the remaining impurities or unwanted disturbing elements that are still on the fly ash so that it does not interfere with the extraction process. Silica extraction is carried out by dissolving fly ash in HCl and HNO_3 solutions while heated and stirredd with a magnetic stirrer. The acid solution is chosen as a silica extracter because basically silica purification from fly ash can be done by dissolving the metal content in fly ash using acid solvents [7]. Extraction using acids can produce pure silica, because other elements which are considered to be irritants can dissolve in acids, while silica cannot dissolve in acids. Acid solvents commonly used for dissolving metal elements in fly ash are HCl and HNO_3 [8].

In the extraction, heating and stirring process is carried out until the mixture between the extracting solution and fly ash boils, where in the research fly ash soaked with HCl takes longer. This is caused by the boiling point of HCl which is higher when compared to the boiling point of HNO_3, which is 110^{o}C so that it takes time to warm up longer than the HNO_3 solution. The precipitate formed after the heating process shows that HCl produces a turbid green solution, while HNO_3 produces a slightly turbid and yellowish solution. The color formed in the solution shows the presence of metal dissolved in it. The more turbid HCl solution shows that HCl solution dissolves more metal than HNO_3 solution which only slightly becomes cloudy. In the process of forming silica, the pH is maintained in the range of 6.5 - 7.

The process of silica gel deposition is at pH 6.5-7 because the pH is too acidic or too low silica will experience protonation or silica will be positively charged. Silica must not be positively charged because it will cause difficulty in absorbing metals that are also positively charged, therefore the pH is set in neutral conditions with the aim that silica is deprotonated, where silica will be negatively charged so that it can absorb metals that are positively charged. In the research conducted, the amount of silica obtained using HCl solvent was 11.53 grams while the amount of silica with HNO_3 solvent was 15.04 grams from 7 times the extraction process. This is related to the effect of acidity on the amount of silica that can be formed, where in more acidic conditions not all solutions can form silica gel, so that when the pH between HCl and HNO_3 solution has reached 7 when added NaOH, the solution using HCl produces more silica little because of the more acidic nature of HCl compared to HNO_3. This is shown when checking the pH before adding NaOH, the solution using HCl has a lower pH of 0 on pH paper, while the solution using HNO_3 has a pH in the range 1-2.

Silica powder obtained after the oven process was brown, where the silica powder extracted using HNO_3 was darker or more brown than the silica powder extracted using HCl. This color change from the time of adding the first NaOH, which is white to brown, is due to the dissolution or extraction process of silica by using acids that are not perfect in separating silica from other metals, where there are still certain metal elements that are still included or trapped in silica. The presence of metals in the silica deposit causes the silica precipitate to be filtered and the oxidation process occurs between silica containing iron and air, so that the silica which is initially white turns brownish along with the length of time it is filtered. The silica extracted with HNO_3 solution looks darker or browner than the silica extracted with HCl, indicating the metal content in HNO_3 silica is more than that of silica HCl. This is consistent with the color of the solution produced during the extraction process, where the solution produced from HCl extract is more turbid which shows more metal dissolved in it.

HCl has a better ability to dissolve metals because of the higher acidity of HCl compared to HNO_3. As is well known, metals will dissolve more easily in acidic solutions, so the more acidic the solvent, the more metals will be successfully separated from the fly ash and the more pure the silica will be obtained. Membrane preparation was done by mixing silica powder with PVA and PEG solution, where PVA will function as an adhesive agent between silica powders; this is in accordance with the nature of PVA, which has good chemical elasticity and stability. PVA solution obtained in the form of clear liquid is very thick, this is in accordance with the function of PVA solution in the manufacture of membranes, which functions as an adhesive between silica powders to be able to fuse and form a solid membrane. Poly Ethylene Glycol (PEG) will function as an emulsifier between PVA solution and silica powder, where PEG as an emulsifier will increase the regularity of the pore shape on a silica solid membrane [9].

RESULT AND DISCUSSION

In this study, the manucfacture of silica membranes from coal fly ash was carried out, where silica was obtained by extracting from fly ash using HCl and HNO_3 solutions at the same concentration ie 1 M.

The amount of silica obtained using HCl solvent is 11.53 grams and the amount of silica with HNO_3 solvent is 15.04 grams. After silica is obtained, then proceed with the process of making silica solid membranes using PEG and PVA solutions. After the membrane is formed, the membrane performance test is carried out by channeling acid mine water through the membrane, which results are then tested using the Atomic Absorption Spectrophotometry (AAS) method to determine whether there is a decrease in metal content (Mn) from acid mine drainage as listed in Table 1.

Table 1. Atomic Absorption Spectrophotometry Analysis Results

Time (min s)	Mn levels (mg/L)	
	HCl Extractor	HNO_3 Extractor
0	16.8	16.8
100	20.9	21.7
120	19.1	18.9
140	18.3	20.4

Besides being tested with AAS, the membrane was also analyzed using the Scanning Electron Microscopy (SEM) method to determine the morphology or structure of the membrane obtained. The results of SEM analysis can be seen in figure below :

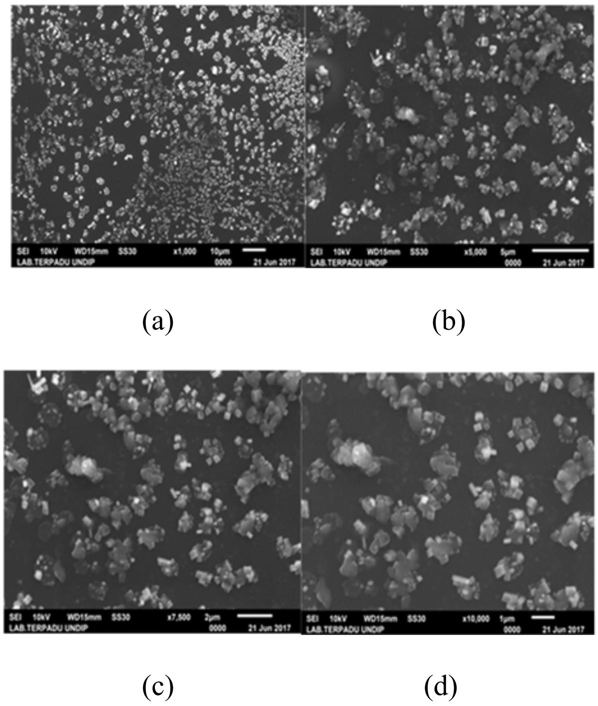

Figure 1. The results of SEM analysis on silica membrane with HCl extract at magnification , (a) 1000x; (b) 5000 x; (c) 7500 x; and (d) 10,000x

Whereas the results of SEM analysis on silica membranes with HNO_3 extractor are shown on Figure 2.

In the Figure 2, it can be seen that there was a decrease in metal content in acid mine drainage after passing through the membrane, but in acidic mine water first had an Mn content of 16.8 mg/L, whereas when passed through the membrane exactly at the 100th min Mn in acid mine drainage actually increased to 20.9 mg/L.

As for the changes in Mn metal content in the membrane extracted with HNO_3 solution can be seen in Figure 4. The acid mine water sample was initially 16.8 mg/L, when it was flowed to the membrane extracted with HNO_3 solution.

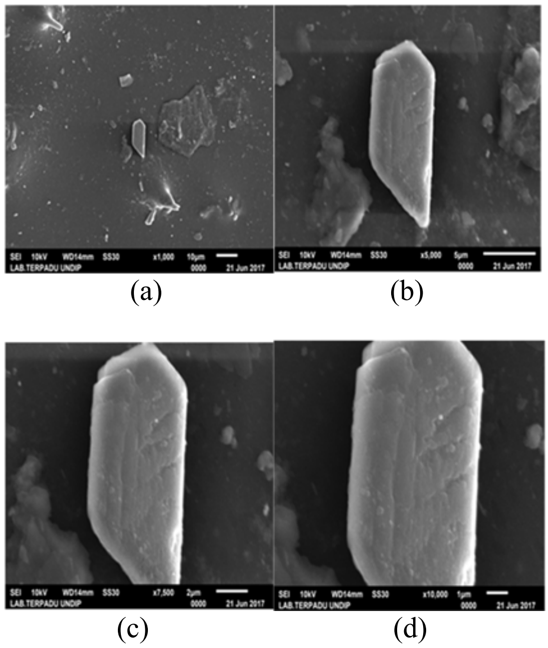

Figure 2. Results of SEM analysis on the membrane with HNO_3 extract at magnification,
(a) 1000x; (b) 5000x; (c) 7500x; and (d) 10000x.

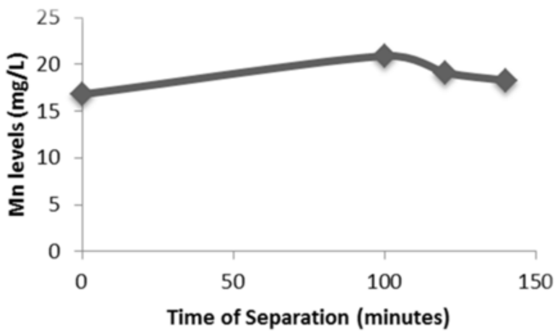

Figure 3. The changing of Mn metal content in the membrane with extract HCl at each time of separation

An increase of Mn levels in the 100th min was detected which became 21.7 mg/L, then dropped back to 18.9 mg/L at 120 min s. Mn concentration increased again in the 140th min to 20.4 mg/L. The changing of Mn values can be seen in the figure 4.

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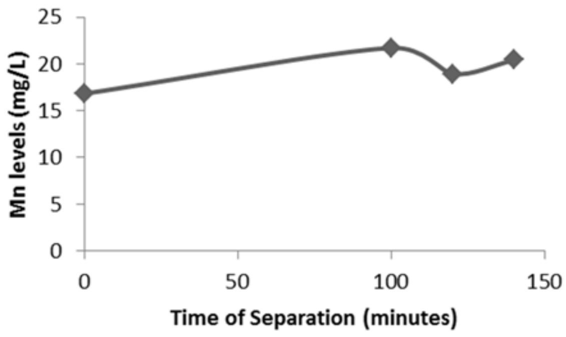

Figure 4. The changing of Mn metal content in the membrane by extractor HNO_3 at each time of separation

Based on the results of AAS, it can be seen that the performance of the membrane cannot produce a stable decrease in metal content, wherein there is an increase in the metal content in acid mine drainage after being flowed into the membrane compared to the initial metal content. This can be caused by a membrane that still contains metal in it due to a less than perfect extraction process, so that when acidic mine water is flowed into the membrane the metal content in the membrane is dissolved along with acid mine drainage, this is supported based on SEM analysis there are still metals which is trapped together with silica inside the membrane which causes an increase in metal content after it has flowed into the membrane.

Based on the data obtained, it can be seen that the decrease in Mn content with the membrane extracted with HCl is better than the membrane extracted with HNO_3, wherein the HNO_3 membrane increased Mn levels quite rapidly in the 100th min to 21.7 mg/L and decreased in the 120th min it became 18.9 mg/L, but then rose again in the 140th min to 20.4 mg/L. Basically, fly ash itself has Mn content in it, where the Mn content in the fly ash is 0.60%, while in the oxide element (MnO) the level is 0.49%. The incomplete extraction process results in Mn levels being trapped together with the extracted silica, therefore when acid mine drainage is passed through the membrane for a long time, the Mn content in the silica will dissolve along with the permeate which will cause an increase in Mn levels inside permeate produced [10]. This is consistent with the previous explanation that the silica membrane obtained by extracting HNO_3 still contains more metal in it, so that the membrane obtained cannot reduce the metal content properly. From the results obtained, it can be seen that the silica membrane extracted with HCl can work better in reducing Mn levels compared to silica membrane extracted with HNO_3.

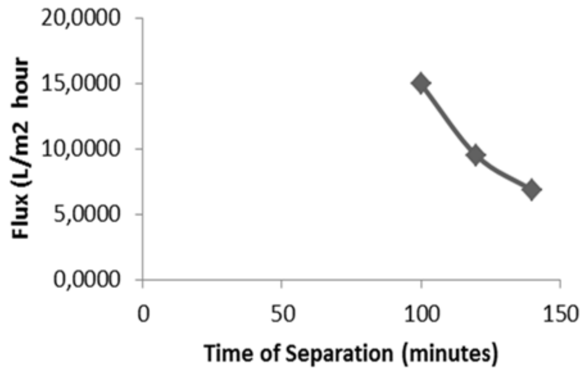

Figure 5. The decreasing flux in the membrane by extracting HCl

Figure 5 shows that in the membrane with HCl extract there is a decrease in flux value, where for the 100 min the flux value is 14.9283 L/m^2 h, then in the 120t min it decreases to 9.4546 L/m^2 h, and at the 140 min the flux value is reduced to 6.8244 L/m2 h. Just like the membrane with HCl extractor, the membrane with HNO_3 extract also decreased the flux value, where in the 100 min the flux value was 11.9427 L/m2 h, then it dropped in the 120 min to 9.4546 L/m^2 .jam, and down again in the 140 min to 7.6774 L/m2 h. The decrease in flux in the membrane with HNO_3 extract can be seen in the following figure:

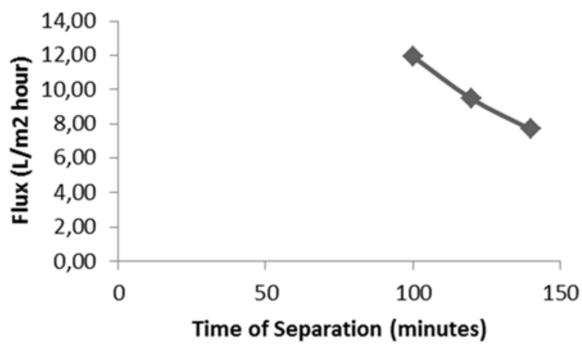

Figure 6. The decrease of flux in the membrane by HNO_3 extraction

The graph shows that the performance of the membrane is still fairly good, because as is known that the value of flux is a parameter to determine the good and bad performance of a membrane [11].

CONCLUSION

Silica can be obtained by extracting fly ash using acidic solutions, namely HNO_3 and HCl with pH maintained in the range 6.5 - 7. The amount of silica used in making the membrane will affect the morphology of the membrane produced. Flux will decrease along with the increase of adsorption time caused by increasing fouling as time increases which causes the membrane pore to be closed, so that the resulting permeate will be less. The silica membrane produced from the HCl extractor can work better in reducing the metal content compared to the silica membrane produced by extracting HNO_3.

REFERENCES

[1] Agustin R., Extraction and Determination of Silica Content (SiO_2) "*Extraction Results from Fly Ash (Fly Ash) Coal*". Jember: Final Project of the Department of Chemistry, State University of Jember, 2013.

[2] Bandung District Environmental Office, Opening Speech at the "*Socialization of Coal Waste Management*", Bandung March 3, 2008.

[3] Ministry of Environment, "*Utilization of Fly Ash and Bottom Ash as Alternative Management of The Environment*", 2008.

[4] Brinker CJ and Scherer GW, Applications. In: Sol-Gel Science, "*The Physics and Chemistry of Sol-Gel Processing*". Academic Press, San Diego, CA, pp. 839-880, 1990.

[5] Suprihatin E, Zaharani TA and Dewi TK., "Making Silica Membrane from Fly Ash and Its Application to Reduce COD and BOD Levels of Palm Oil Liquid Waste," *Journal of Chemistry*, vol. 4, no. 3, pp. 48-53, 2012.

[6] Afrianty C, Gustin L and Dewi TK., "Processing of Acid Mine Water Waste using Ceramic Membrane Technology," *Journal of Chemical Engineering*, 18 (3), pp. 16-25, 2012.

[7] Kheloufi A, Berbar Y, Kefaifi A, Medjahed, SA, and Kerkar F., "Improvement of Impurities Removal from Silica Sand by Leaching Process. Algeria": Silicon Technology Development Unit, 2009.

[8] Denida MA., "Silica Purification in fly ash from Power Plants in Paiton with Dissolution of Acid Chloride and Aqua Regia," MIPA ITS, 2016.

[9] Rini AP, Hastuti R, and Gunawan, "The Effect of Poly Ethylene Glycol (PEG) Composition in Silica Solid Membrane Synthesis from Rice Husk and Its Application for Decolorization of Batik Liquid Waste," Essay. Faculty of Mathematics and Natural Sciences, Department of Chemistry, Diponegoro University, 2008.

[10] Amalina YN, Salimin Z and Sudarno, "Effect of pH and Processing Time on the Removal of Cr, Fe, Zn, Cu, Mn, and Ni Heavy Metals in Wastewater Electroplating Industry with Biochemical Oxidation Process," *Journal of Environmental Engineering*, 4 (3), pp. 1-9, 2015.

[11] Ardiansyah and Kusuma AB., "Characteristics of Flux Reduction in Humic Acid Solution Filtration with Microfiltration," *Journal of Chemical Technology*. Vol. 2, no. 2, pp. 267-274, 2013.