A Study on the Effect of Using Different Type of Organic Acid on the Pretreatment of Extraction Silica from Rice Husk Ash (RHA)

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***Abstract*-Rice husk is an abundant agricultural by-product, which contain high amount of silica which is about 60% and can be made into raw materials that can produce silica gel and powders. There are abundant uses of silica which are for the glass production, adsorbent, cleansing agent and others. Synthesis was done by using different acids namely, acetic acid, citric acid, and formic acid. The sample was collected from rice mill that located in Sabah. The proximate analysis of the sample was determined the moisture content, volatile matter, fixed carbon and ash by using the thermobalance TGA/SDRA51e according to ASTM D5142-02a. The percentage of the silica being extracted was being compared to the previous research. The characterization of the silica obtained determined by the Fourier Transform Infrared Spectrograph (FTIR) and the surface area were analyzed by using BET surface area instrument. In this research, the variation concentration of organic acid that was used for the pre-treatment of the RHA was not being concerned. It was found that, using inorganic acid at the pre-treatment will give higher yield of silica from RHA. The percentage of silica that was extracted with the pre-treatment of acetic acid, formic acid, and oxalic acid are 38.97 %, 36.14 % and 37.27 % respectively.**

Keywords-Rice husk ash, Silica gel, Surface area

I. INTRODUCTION

Rice husk are the hard component that covering the grains of rice and the ash from rice husk is able to be one of the source of amorphous reactive silica, which can be applied in many applications in component science. The Silicon dioxide (SiO_2) which is also known as Silica can be applied in many industries for the production of Portland cement [1], production of glass for windows, drinking glasses, beverage bottles, optical fibers for telecommunication and so much more. In the past two decades, the demand of rice has grows as the population increasing. Therefore the by-product from the rice milling which is the rice husk being disposed at landfill site will contribute to air and water pollution [2]Rice husk ash (RHA) is very rich in silica content and it is as agricultural by-product that is plentiful available in rice producing countries in Asia [3].

Rice husk act as fuel and it content high amount of ash. The ash that been produce by combustion of rice husk in air contain high amount of silica. Besides, by using rice husk as materials to obtain silica will give high quality and economical effective compared to existing technology of manufacturing Silica from quartz [4]. From the previous study, the uses of mineral acid (HCL, H_2SO_4 and HNO_3) in pre-acid wash treatment had yield 85% of silica from the RHA. This research was conducted to study the effect of using three types of organic acids, which are acetic acid, citric acid and formic acid on the pre-treatment of silica extraction. The characterization of silica was analyzed by using Fourier Transform Infrared Spectrograph (FTIR) and BET surface area instrument.

II. METHODOLOGY

A. Proximate analysis

From the proximate analysis, the moisture content, volatile content and ashes in the rice husk were determined. The moisture content, volatile matter, fixed carbon content and ash in the rice husk sample were determined using the Thermogravimetric Analyzer (TGA). The proximate analysis was conducted by following to ASTM [5] using thermobalance TGA/SDRA51e which were manufactured by Mettler Toledo that is located in Instrument Laboratory Faculty of Chemical Engineering UiTM Shah Alam.

B. Material preparation

The rice husks were collected from rice milling that is located in Sipitang Sabah. This pollution-carrying remaining part was used to be the material in this research. Four samples of rice husk, which are 10 gram each, were prepared for this experiment. All of the samples were carbonized in furnace at 600 ˚C for 4 hours to increase the respective amount of silicon dioxide (SiO_2) by the decrease of carbonaceous materials that available in the samples and to remove out other undesirable components.

C. Acid pre-treatment

The main objective of the acid pre-treatment is to remove impurities so that the purity of silica that were

obtained from rice husk can be improved. By doing so, the metallic impurities can be remove thus white colour of silica can be produced. The step were managed in the following manner. Ten grams of RHA samples were spread in 100 mL of distilled water and the pH of dispersion was being adjusted to 7 by using 6M organic acids which are Acetic acid, Citric acid and Formic acid. These solutions were being stirred for 2 hours using magnetic stirrer. After stirring, the dispersions were being filtered by filter paper. Distilled water was used in this experiment to wash the sample.

D. Extraction of silica

The residues that were obtained from the pre-acid treatment were being dispersed in 1N portion of NaOH. After that, the solution was boiled in 250 ml Erlenmeyer flasks for 1 hours with constant stirring. By mixing the NaOH with the sample, sodium silicate was formed. The solutions are then were filtered by filter paper and were allowed to cool down until it has reached room temperature. The filtrate from the filtration was then being titrated with 1M of hydrochloric acid until it reaches pH of 7 with constant stirring. At pH of 7, silica gel was formed and it was being dried up in oven at 140 ˚C for 8 hours to remove all the moisture before the silica being weighed. The content of the silica that was extracted from the rice husk was calculated by the following formula:

Percentage of silica $=(m_o - m) / m_o \times 100\ \%$ [6]
Where;
m_o = weight of RHA after the organic acid pre-treatment (g).
m = weight of dry silica being extracted after extracted with 1N of NaOH (g).

E. Characterization of extracted silica

The infra-red spectrum of the extracted silica was characterized by using FTIR that was located in Instrument Lab in Faculty of Chemical Engineering UiTM Shah Alam. The surface area, pore volume and pore size of silica also being synthesized.

III RESULT AND DISCUSSION

A. Physical properties of the rice husk

The rice husk were evaluated for its physical properties by using the proximate analysis in accordance to the ASTM International (D3172-07a [7]). The proximate analysis of the rice husk has been conducted using Thermobalance TGA/SDRA51e (Mettler Toledo) which is located at Instrumentation Lab Faculty of Chemical Engineering, UiTM Shah Alam. The moisture content, ash content, volatile content and fixed carbon were analyzed from the result that was obtained from TGA with 20.00 ℃. min^{-1} of heating rate. The moisture content was detected when there were mass losses of sample at temperature of 146 ℃. The mass of samples decreases as the water evaporates from the sample until it reaches temperature of 146 ℃. By referring to figure 4.1, the initial weight of sample at 27.86 ℃ was 20.01 mg and the mass gradually decreases to 18.6399 mg at 146 ℃ for about 30 seconds before it losses more mass. From this data, the moisture content of the rice husk sample is 6.847 %. The significance of moisture analysis is to calculate other analytical results which are volatile matter, ash and fixed carbon from the sample according to (ASTM D3173-11 [8]).

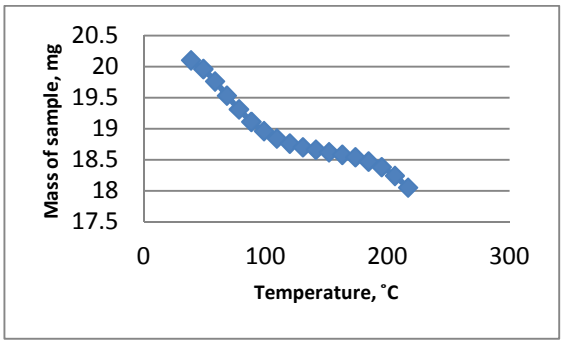

Figure 4.1 Data for moisture analysis in rice husk sample.

After determining the moisture content of the rice husk sample, it was then continue heated to 755 ℃ for determining the ash content. The objective of finding the ash content of the rice husk is to identify the inorganic residue. The most organic residue that can be found in the rice husk ash is Silicon dioxide (Silica) which is 93.1% from the total weight [9]. Form figure 4.2, the ash content that was discovered from the rice husk at temperature of 755 ℃ is 41.286 %. Therefore, it is economical to extract the Silicon dioxide from the rice husk, as the ash content is quite high.

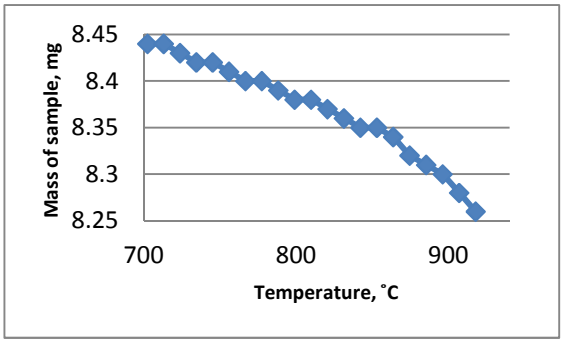

Figure 4.2 Data for ash content in rice husk sample.

According to ASTM D3175-07 [7], the sample should be heated to a final temperature of 950 ± 20 ℃ in order to obtain the final weight of sample for volatile matter content calculation. The significance of finding the volatile matter in the rice husk is to identify the amount of gaseous products in the absence of moisture. From figure 4.3, as the temperature rolling to 964.82℃, the mass of sample was slowly decreases to 8.2572 mg. By calculating the volatile matter content of sample by using the standard ASTM method, the volatile matter is 55.286 %.

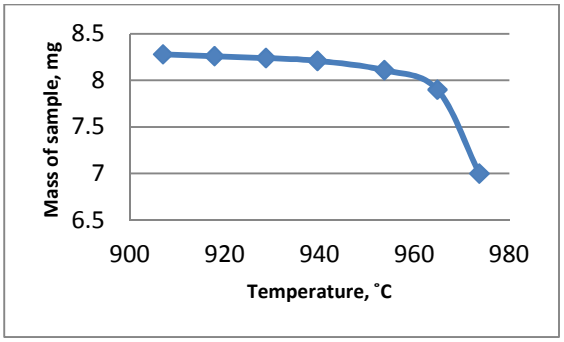

Figure 4.3 Data for volatile matter content in rice husk sample.

The fixed carbon was determined by subtracting 100 % with moisture content, volatile matter content and ash content of the silica. The percentage of fixed carbon of the rice husk is 2.76%. Low amount of fixed carbon indicates that the rice husk only require short time for combustion. High amount of fixed carbon shows that the sample is suitable for combustion or pyrolysis.

Table 4.1 Summary of proximate analysis of the rice husk.

Moisture content (%)	6.8 %
Ash content (%)	41.29 %
Volatile matter (%)	49.11%
Fixed carbon	2.76 %

B. Silica recovery from rice husk ash

For the extraction of silica, different types of organic acid were used to adjust the quality of rice husk ash before the extraction of precipitated silica. The washing of the rice husk ash at the pretreatment by using organic acid can help to dealuminate the sample by removing the iron to certain extend to adjust the raw material quantity. The type of organic acid that was used in this experiment were acetic acid, formic acid and oxalic acid. Basically, organic acid are weak acids and it does not dissociated completely in water while strong acid do dissociated completely in water. From the previous study that has been conducted by [10] inorganic acid such as hydrochloric acid, nitric acid and sulphuric acid was used at the pretreatment and the highest yield of silica which is 85% can be obtained by using hydrochloric acid. [11], has studied the effect of the yield of silica extracted from corn cob by using three types of organic acid which are citric acid, acetic acid, oxalic acid and combination of 50% concentration of citric acid and acetic acid each.

From the research that has done by Saleem, 2014 [11], it was found that the extraction by using citric acid shows the highest yield of silica, which is 35.3 %. From both research, the result that was obtained from this experiment were compared to show which acid can obtained the highest yield of silica. From this experiment, the highest percentage of silica extracted is by using acetic acid which is 38.97 %. The molecular weight of acetic acid is 60 g/mol which is the highest among the three types of organic acid which is the reason why it can give high amount of silica. The percentage of rice husk that was soaked in the oxalic acid shows the lowest value because crystals were produced because it will prevent for the removal of ash from the rice husk. However, the amount of silica that was obtained from the pretreatment of oxalic acid and formic acid were 37.27% and 36.14% respectively. Table 4.2 shows that the highest percentage of silica that can be obtained using inorganic acid which is 85% (hydrochloric acid). It was found that the yield of silica is strongly dependent to the type of acid used for washing. By referring to table 4.2, the lowest amount of silica extracted is when using organic acid at the pretreatment regardless the type of sample used. The comparison of weight percentages of extracted precipitated silica from rice husk soaked in organic acids are shown in figure 4.4. After the filtrate of washed rice husk ash being titrated with HCl, the centrifuged silica is shown in figure 4.5.

Table 4.2 Comparison percentage of silica extracted by using different type of acid at the pretreatment.

Author	**Type of acid**	**Percentage of silica extracted (%)**
Selvakumar, 2014[10] Using inorganic acid at the pretreatment extraction of silica from rice husk.	Hydrochloric acid	85%
	Nitric acid	75%
	Sulphuric acid	60%
Saleem, 2014[11] Using organic acid at the pretreatment extraction of silica from corn cob.	Citric acid	35.3%
	Acetic acid	31.5%
	Oxalic acid	20.4%
	(50% of each) citric acid and acetic acid	25.7%
	Acetic acid	38.97%
	Formic acid	36.14%
	Oxalic acid	37.27%

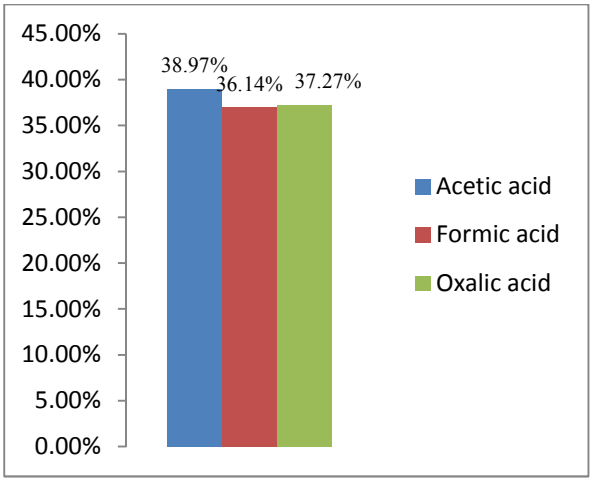

Figure 4.4 Yield of silica extracted from rice husk ash by using acetic acid, formic acid, and oxalic acid at pre-treatment washing.

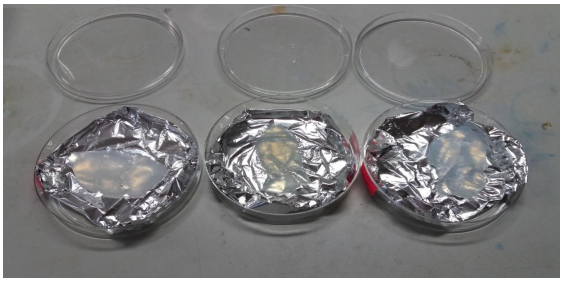

Figure 4.5 Silica gel after centrifuge.

C. Characterization of silica by using FTIR

The extracted precipitated silica from the rice husk soaked in the organic acid (Acetic acid, Formic acid, and Oxalic acid) were being identified by using FTIR spectrum and it is shown in figure 4.6, figure 4.7 and figure 4.8. According to a research that was conducted by [12] the bond stretching that was formed at a range of 791 cm^{-1} to 964 cm^{-1} is due to the Si-O-Si symmetric bond stretching vibration. For this research, the symmetric bond of Si-O-Si were formed at 798 cm^{-1}, 961.87 cm^{-1} and 959.27 cm^{-1} for the RHA washed with acetic acid, formic acid and oxalic acid respectively. The symmetric bond stretching Si-O-Si for all of the samples was fall in the range as was proposed by [12].

While, for the asymmetric bond stretching of Si-O-Si, the range are 1010 cm^{-1} to 1098 cm^{-1}. The band of the asymmetric bond stretching of silica from the samples was 1063 cm^{-1}, 1051 cm^{-1} and 1066.78 cm^{-1} for acetic acid, formic acid and oxalic acid correspondingly. For the band of the bending vibration of the water molecules, which has trapped in the matrix of silica, is between the ranges of 1635 cm^{-1} to 1645 cm^{-1}. It was found that, the bending vibration of the water molecules exists in the samples. Meanwhile, the board band at 3310 cm^{-1} to 3490 cm^{-1} is an evidence of the existing stretching vibration of the O-H bond from the silanol groups (Si-OH) and it is due to the water molecules that being absorbed on the silica surface as reported by [13].

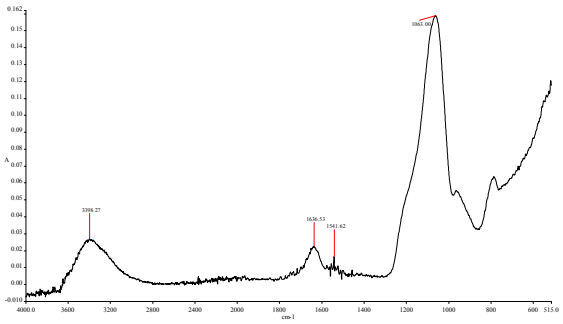

Figure 4.6 FTIR spectra of extracted precipitated silica from the rice husk soaked in acetic acid.

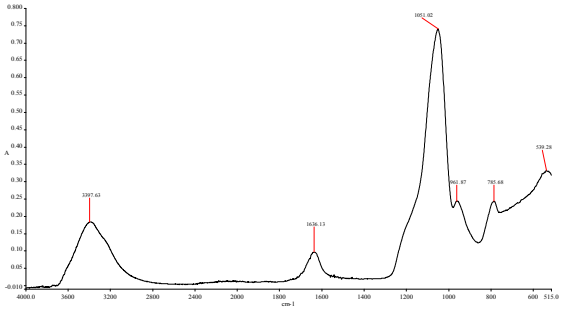

Figure 4.7 FTIR spectra of extracted precipitated silica from the rice husk soaked in formic acid.

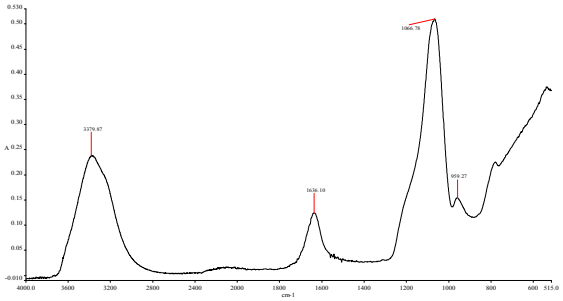

Figure 4.8 FTIR spectra of extracted precipitated silica from the rice husk soaked in oxalic acid.

D. Surface area, pore volume and pore size of the extracted silica.

The summary of the surface area, pore volume and pore size of the extracted silica was summarized in table 4.3. The highest surface area was found to be the extracted silica that was washed with formic acid at the pre-treatment which are 148.97 m^2/g for single point surface area, 164.70 m^2/g for BET surface area, and 246.82 m^2/g for the Langmuir surface area. This could be evidence that pre-treatment of the RHA by using formic acid could gives higher amount of surface area if compared to the other organic acid. However, the surface area that was recorded from this experiment was much lower that the surface area that was obtained by [14] which is 406.6 m^2/g because the sample was aged in the NaOH solution for 24 hr and without undergone inorganic acid pre-treatment.

The typical surface area of silica as proposed by [15] is 20 m^2/g (BET nitrogen adsorption). There were three

types of methods that were used to identify the surface area which are single point surface area, BET surface area, and Langmuir surface area. The surface area of silica sample that was washed by using oxalic acid was also has high surface area if compared to the silica that was washed by acetic acid during the pre-treatment.

The lowest surface area was the silica that washed with acetic acid which is only 129.02 m^2/g of single point surface area, 146.12 m^2/g of BET surface area, and 197.89 m^2/g of Langmuir surface area. The pore volume (cm^3/g) and pore size (Ă) were also shown in Table 4.3. The highest pore volume is silica that was washed with formic acid, which is 0.4450 cm3/g, and the highest pore size (Ă) is from the silica that was washed with oxalic acid. The higher surface area indicates that the silica is more porous and it is more suitable for the application as absorbent or catalyst support.

Table 4.3 Surface area, pore volume and pore size of the extracted silica.

Silica Sample	**Washed with formic acid**	**Washed with oxalic acid**	**Washed with acetic acid**
Surface area (m^2/g)			
Single point surface area	148.97	133.05	129.02
BET surface area	164.70	146.86	146.12
Langmuir surface area	246.82	188.62	197.89
Pore volume (cm^3/g)			
Single point adsorption total pore volume of pores	0.4450	0.4057	0.3782
Pore size (Ă)			
Adsorption average pore diameter	108.09	110.48	103.53

IV CONCLUSION

As a conclusion, it was found that the rice husk contain high amount of ash content, which is 41.29 %. The rice husk ash that washed by using acetic acid shows the highest percentage of silica being extracted which is 38.97 % if compared to the rice husk that was washed by formic acid and oxalic acid. While, the lowest percentage of silica that was being extracted is when the rice husk ash being washed by using formic acid, which is only 36.14 %. The rice husk ash that was washed by using acetic acid shows the highest amount of the extracted silica because of this acid has the highest molecular weight compared to formic acid and oxalic acid. The silica obtained also being analyzed by using FTIR. There were four peaks that was focused which are Si-O-Si symmetric bond, Si-O-Si asymmetric bond, water molecules and O-H bond from silanol groups. From the analysis, all the peaks were falls within the range as were proposed by previous findings. The surface area of the silica was also being analyzed by using three methods that are single point surface area, BET surface area and Langmuir surface area. It was found that the rice husk that was washed by formic acid has the highest surface area which are 148.97 m^2/g, 164.70 m^2/g and 246.82 m^2/g for single point surface area, BET surface area and Langmuir surface area respectively if compared to formic acid and oxalic acid. The pore volume of silica is directly proportional to the surface area. High surface area of silica signifies that the silica is more porous and suitable to be used as absorbent or catalyst.

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1. Flörke, O.W., et al., *Silica.* Ullmann's Encyclopedia of Industrial Chemistry, 2008.
2. Kumar, A., et al., *Recovery of value added products from rice husk ash to explore an economic way for recycle and reuse of agricultural waste.* Reviews in Environmental Science and Bio/Technology, 2016. **15**(1): p. 47-65.
3. Subbukrishna, D., et al. *Precipitated silica from rice husk ash by IPSIT process*. in *15th European Biomass Conference & Exhibition*. 2007.
4. Bajirao S. Todkar, Onkar A. Deorukhkar, and S.M. Deshmukh, *Extraction of silica from Rice Husk.* International Journal of Engineering Research and Development, 2016. **12**(3).
5. Standard, A., *D5142: Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures.* ASTM International, West Conshohocken, PA, 2004.
6. An, D., et al., *A green route to preparation of silica powders with rice husk ash and waste gas.* Chemical Engineering Journal, 2010. **162**(2): p. 509-514.
7. Standard, A., *D3175-07 in Standard Test Method for Volatile Matter in the*

Analysis Sample of Coal and Coke. West Conshohocken.
8. Standard, A., *D3173–11, 2011. Standard Test Method for Moisture in the Analysis Sample of Coal and Coke. ASTM International, West Conshohocken, PA*.
9. Haido, J.H., et al., *Dynamic response simulation for reinforced concrete slabs.* Simulation Modelling Practice and Theory, 2010. **18**(6): p. 696-711.
10. Selvakumar, K., et al., *Extraction of silica from burnt paddy husk.* International Journal of ChemTech Research, 2014. **6**(9): p. 4455-4459.
11. Saleem, M., et al., *SYNTHESIS OF PRECIPITATED SILICA FROM CORN COB BY USING ORGANIC ACIDS.* 2014.
12. Olah, G.A., et al., *Nano-structure supported solid regenerative polyamine and polyamine polyol absorbents for the separation of carbon dioxide from gas mixtures including the air*. 2010, Google Patents.
13. Javid, A., M.M. Heravi, and F.F. Bamoharram, *One-pot synthesis of 1, 8-dioxo-octahydroxanthenes utilizing silica-supported preyssler nano particles as novel and efficient reusable heterogeneous acidic catalyst.* Journal of Chemistry, 2011. **8**(2): p. 910-916.
14. Mohamed, R., I. Mkhalid, and M. Barakat, *Rice husk ash as a renewable source for the production of zeolite NaY and its characterization.* Arabian Journal of Chemistry, 2015. **8**(1): p. 48-53.
15. Chandrasekhar, S., et al., *Review processing, properties and applications of reactive silica from rice husk—an overview.* Journal of materials science, 2003. **38**(15): p. 3159-3168.