



Effect of $C_6H_8O_7$ Concentration on Silica Extraction of Rice Husk, Rice Husk Ash and Mixture of Rice Husk With Rice Husk Ash Via Acid Leaching Process

Noratiqah Syahirah Mohd Zarib*, Shahrulazam Abdullah

Faculty of Mechanical Engineering, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia

*Corresponding author Email: eiqasyahirah@gmail.com

Abstract

Rice husk and rice husk ash are wastes found in agricultural industry. Rice husk contains over 70% of organic silica. Silica is used in industries such as functional filler for paints, plastics, rubber while silica sand is used in water filtration and agriculture. The organic silica could be extracted through various methods such as sol-gel method, purification and hydrothermal heat carrier. The focus of this paper is to analyse the effect of acid treatment of silica extraction of rice husk and rice husk ash. Parameters such as concentration of acid and weight percentage used in the mixture of rice husk and rice husk ash during organic leaching method were also compared. In this paper, citric acid ($C_6H_8O_7$) was used for production of silica from rice husk and rice husk ash. Samples were characterized using Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Energy Dispersive X-Ray Spectroscopy (EDX). The result indicates that highest percentage silica of rice husk, rice husk ash and mixture between rice husk and rice husk ash after leaching has an amorphous structure.

Keywords: silica; rice husk; rice husk ash; inorganic acid; agriculture waste

1. Introduction

Silica (SiO_2) was discovered from Berzelius in 1824. Prior to that, the Romans used silicon dioxide in the form of sand to increase the strength of concrete. Silica is a white or transparent, odorless solid and crystalline substance. It belongs to group IV of the chemical family called metal oxides. It is a very stable compound, and only reacts with hydrofluoric acid. Silica is an acidic oxide due to the production of hydrogen ions when it is in water. Silica conveys visible and ultraviolet light. Silica comes in many several geometrical patterns [1]. Because of its lignin content and high silica, rice husk is tough, woody and abrasive in nature with low nutritive properties and resistance to weathering [2-3].

Leaching treatment is a convenient track to extract the silica. Citric acid ($C_6H_8O_7$) solution which is an organic acid is regularly used in leaching treatment to prepare the silica material. By using the citric acid in leaching treatment it may overcome the extraction of silica from rice husk and rice husk ash that are dangerous for environmental and human health. The objectives of this paper are to investigate the effect of acid concentration in extraction of silica from rice husk, rice husk ash and mixture with rice husk and rice husk ash by characterization using citric acid.

Rice husk is a potential material, which is amenable for value addition. The usage of rice husk either in its raw form or in ash form is numerous [3]. Most of the husk from the milling is either burnt or dumped as waste in open fields and a small amount is used as fuel for boilers, electricity generation, bulking agents for composting of animal manure and the exterior of rice husk are composed of dentate rectangular elements, which themselves are

composed mostly of silica coated with a thick cuticle and surface hairs. The mid region and inner epidermis contain little silica [4]. The major constituents of rice husks are cellulose, hemicellulose, lignin and ash. The ash consists mainly of silica (SiO_2) and some alkali metal impurities.

2. Materials and Methods

Raw materials used in this experiment are rice husk and rice husk ash. Rice husk and rice husk ash was supplied by the Universiti Teknologi MARA (UiTM) laboratory. In this research, silica is obtained from the rice husk and cogon grass. Firstly, 20 grams of rice husk needs to be prepared to become powder through the process of milling for 30 minutes to produce fine powder while for rice husk ash, the dried rice husk was placed in a crucible in an electrical furnace at $600^\circ C$ for 5 hours to get black ash. The ash was then ground for 30 minutes to become powder. Next, rice husk was ground by using a Sieving machine for 10 minutes to become fine powder before the acid leaching process. Then, rice husk ash powder with a mean particle size of $45 \mu m$ was put into a 500 ml of citric acid solution into the beaker.

The concentrations of 0.1 mol and 0.5 mol were used for this research. The beaker was placed on a hot plate magnetic stirrer at a constant temperature of $60^\circ C$. After the acid leaching process, the water rinsing treatment of the rice husk was carried out with the distilled water at room temperature to eliminate the citric acid content from the ash and husk. The samples were dried for 60 minutes at $110^\circ C$ in the furnace. Silica powder obtained from the process of extraction underwent characterization technique. The



overall steps were repeated by replacing rice husk with rice husk ash.

The Hitachi SU3500 instrument was used. Sample specimens with a diameter of 15mm each were aluminum coated in an aluminum sputter coater for 60 seconds at 15mA current output. The aluminum coating was necessary to ensure a conducting surface was obtained for electron bombardment and characterization. This step is crucial to do as the test specimens were non-conductive. To eliminate the electron charging effects the SEM was operated at 3kV and a working distance of 15mm. The selected areas of interest were focused and micrographs were taken. Software of Smart Insight EDAX was used for EDX analysis. Rigaku Ultima IV Diffractometer with PANdata software package was used to analyze the structures of rice husk and rice husk ash samples. An Aluminum-glass composite sample holder with a rectangular slot measuring 2cm x 1 cm x 0.2 cm was filled with the powdered sample using front loading method. The samples were analyzed using a $\text{CuK}\alpha$ radiation with a nickel filter. Finally, XRD patterns were recorded in the range of $2\theta = 10^\circ\text{--}80^\circ$ with the scanning speed of $2^\circ/\text{min}$.

3. Result and Discussion

3.1 Phase Analysis of Untreated Rice Husk (RH) and Rice Husk Ash (RHA)

Fig. 1(a) shows the XRD diffraction pattern of untreated rice husk (RH). The major reflection or peaks of SiO_2 occur at Bragg's 2θ angles of 22.27° for untreated rice husk (RH). Fig. 1(b) shows the XRD diffraction pattern of untreated rice husk ash (RHA). The y-axis shows the intensities of the peak and x-axis is the range of phase 2θ . The major reflection or peaks of SiO_2 occur at Bragg's 2θ angles of 21.26° . Silicon carbide (SiC) was present at the intensity of untreated rice husk ash (RHA) and occurred at peak of 35° . SiC was found at the intensity of untreated rice husk ash (RHA) because burning of rice husk release more carbon. Peak differences could be used to evaluate phase analysis between untreated rice husk and rice husk ash. The intensity of untreated rice husk (RH) is higher compared with untreated rice husk ash (RHA), due to carbon release from untreated rice husk (RH) is less than untreated rice husk ash (RHA). A rather broad peak spanning 2θ angle for both Fig. 1(a) and (b) of amorphous structures was observed.

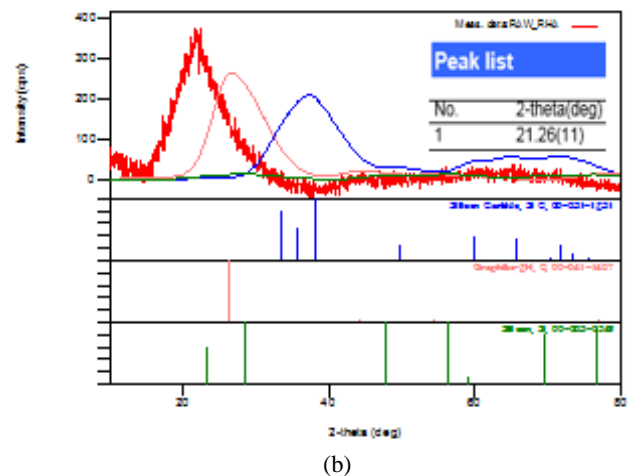
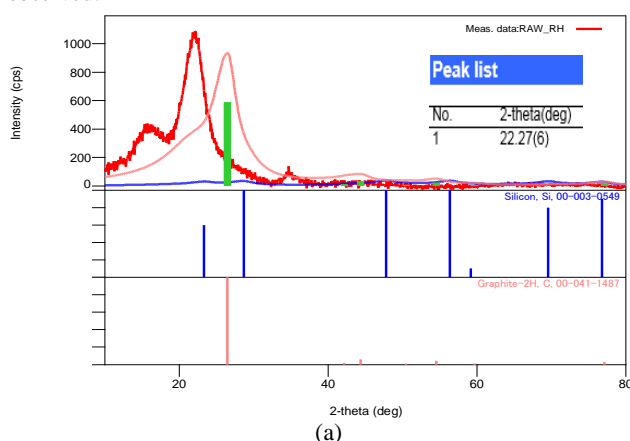


Fig. 1: XRD pattern of (a) untreated rice husk (RH) and XRD pattern of (b) untreated rice ash (RHA)

3.2. Morphology Surface of Untreated Rice Husk (RH) and Rice Husk Ash (RHA)

Fig. 2(a) shows the image of untreated rice husk powder at a magnification of 2000x. It shows that the surface is smooth and not decomposed because the sample is not treated with any chemical. The silica and organic impurities distribution of untreated rice husk particle were analyzed by using EDX and the result is presented in Fig. 2(a). It showed that SiO_2 is most concentrated in weight percentage about 90.5 wt % compared with other impurities. This is due to the bonding of two oxygen (O) atoms and one silicon (Si) atom.

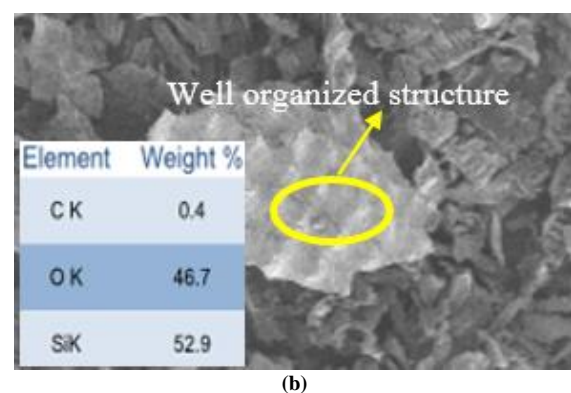
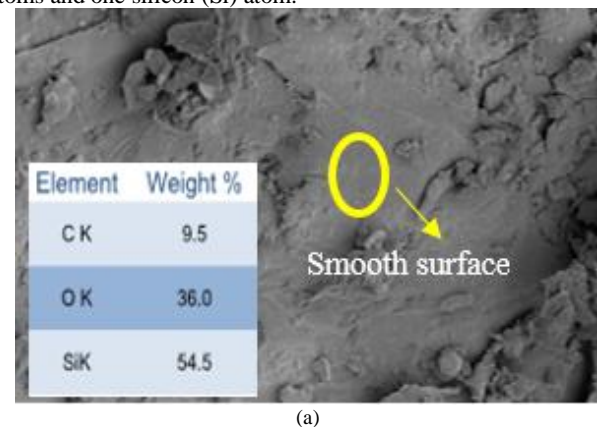


Fig. 2: SEM image of (a) untreated rice husk (RH), (b) untreated treated rice husk ash (RHA) at magnification of 2000X.

Fig. 2(b) shows the SEM image of untreated rice husk ash (RHA) powder at a magnification of 2000x. It shows that the morphological features of outer untreated rice husk ash are well organized in structure that resembles rolling hills. This figure shows that the particles are not decomposed because the sample is not treated with any chemical or any treatment. The rice husk was

burned at 600°C to become ash. The silica and inorganic impurities distribution of untreated rice husk ash particle were analyzed by using EDX and the result is presented in Fig. 2(b). It was detected that SiO₂ is most concentrated in weight percent which is 99.6 wt % than other impurities. This is due to the bonding of oxygen (O) and silica (Si). In the SEM image, rolling hills particles ash are in polygonal shape. Strong intensity of Si and O₂ in the EDX spectrum confirmed the silicon dioxide (SiO₂) is at a higher weight percentage compared with EDX spectrum of untreated rice husk (RH) as shown in Fig. 2(a) before.

3.3. Phase analysis of treated Rice Husk (RH), Rice Husk Ash (RHA), Mixture 30% Rice Husk (RH) and 30% Rice Husk Ash (RHA) after leaching treatment

The XRD patterns of the samples with different citric acid concentration are presented in Fig. 3.

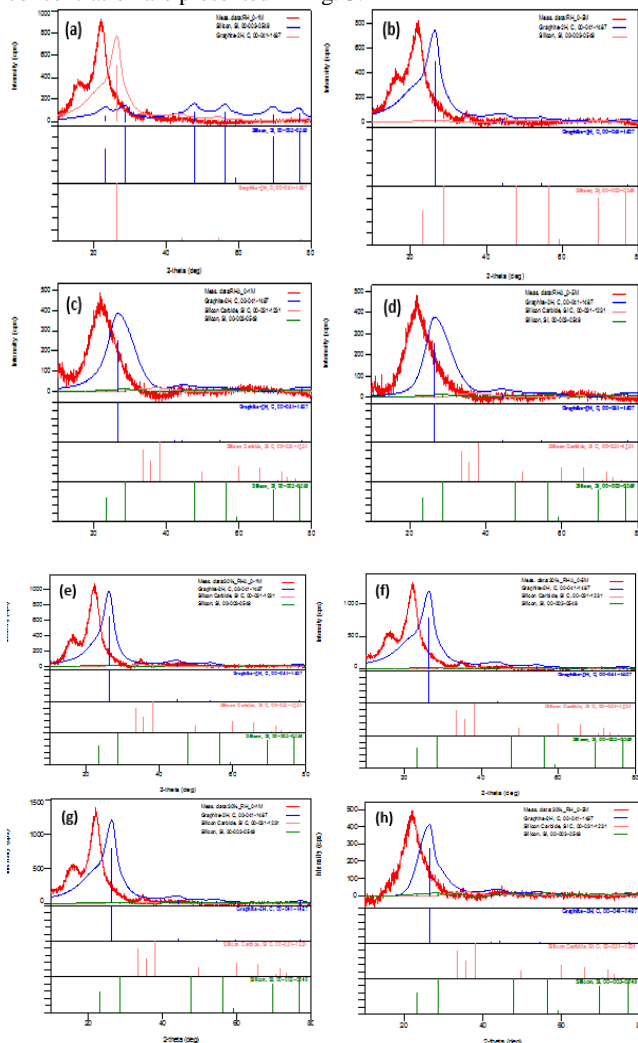


Fig. 3: XRD pattern of (a) 0.1M treated rice husk, (b) 0.5M treated rice husk, (c) 0.1M treated rice husk ash, (d) 0.5M treated rice husk ash, (e) 0.1M 30% rice husk + 70% rice husk ash, (f) 0.5M 30% rice husk + 70% rice husk ash, (g) 0.1M 30% rice husk ash + 70% rice husk, (h) 0.5M 30% rice husk ash + 70% rice husk.

The phase clearly shows that the presence of Si (DB card number: 00-003-0549) for this figure is in amorphous phase due to no sharp peak occurrence. Fig 3(a) and (b) is referred in Table 1, Fig 3(c) and (d) is referred in Table 2, Fig 3(e) and (f) is referred in Table 3 and Fig 3(g) and (h) is referred in Table 4. Table 1 indicates the value peak of 2θ angles of treated rice husk within different concentrations of citric acid.

Table 1: Different concentrations of treated rice husk (RH) by Bragg's 2θ angles (°) for XRD peaks

Samples	Bragg's 2θ angles (°) of Si
0.1M treated rice husk	22.14 Å
0.5M treated rice husk	22.29 Å

Table 2 shows the value peak of 2θ angles of treated rice husk ash, while Table 3 indicates the value peak of 2θ angles of treated 30% rice husk + 70% rice husk ash. Table 4 shows the value peak of 2θ angles of treated 30% rice husk ash + 70% rice husk within different concentrations of citric acid.

Table 2: Different concentrations of treated rice husk ash (RHA) by Bragg's 2θ angles (°) for XRD peaks

Samples	Bragg's 2θ angles (°) of Si
0.1M treated rice husk ash	21.29 Å
0.5M treated rice husk ash	21.46 Å

Table 3: Different concentrations of 30% rice husk + 70% rice husk ash by Bragg's 2θ angles (°) for XRD peaks

Samples	Bragg's 2θ angles (°) of Si
0.1M 30% rice husk + 70% rice husk ash	21.33 Å
0.5M 30% rice husk + 70% rice husk ash	22.33 Å

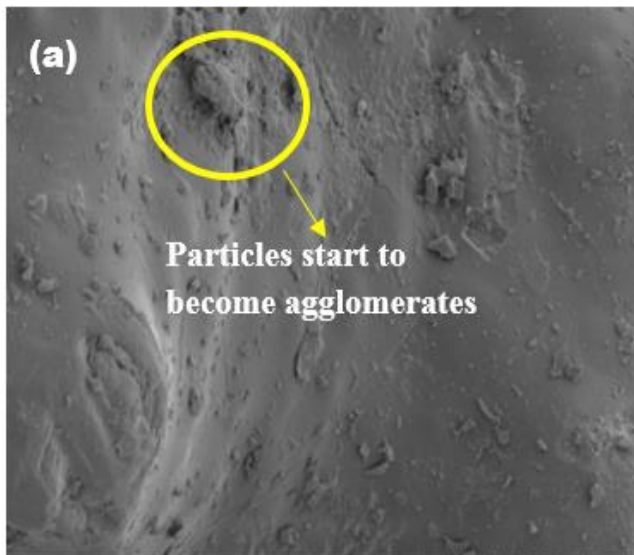
Table 4: Different concentrations of 30% rice husk ash + 70% rice husk by Bragg's 2θ angles (°) for XRD peaks

Samples	Bragg's 2θ angles (°) of Si
0.1M 30% rice husk ash + 70% rice husk	22.32 Å & 34.84 Å
0.5M 30% rice husk ash + 70% rice husk	22.33 Å & 46.6 Å

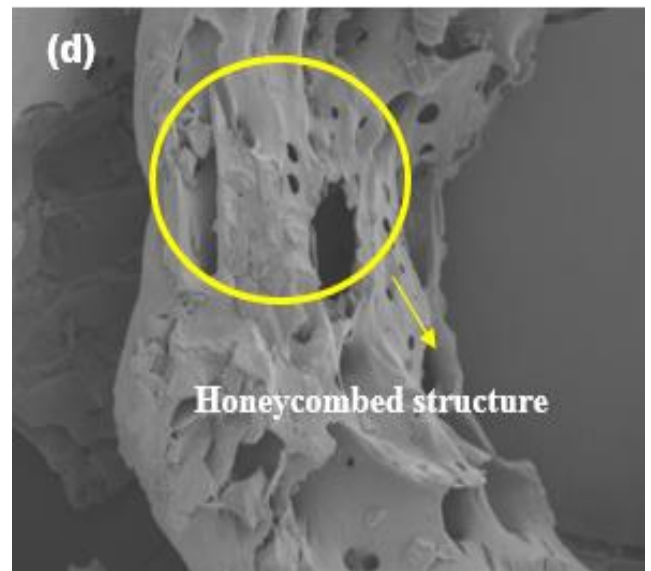
These four tables show the angles detected increased by increasing the concentration of citric acid solution. This is because the content of metal oxide impurities in rice husk and rice husk ash decreased when concentration of citric acid solution was increased. Thus, it is shown in these figures that citric acid leaching treatment is significantly useful and effective to remove impurities and increased the purity of silica in rice husk and rice husk ash. Organic acids such as citric acid have carboxyl groups and act as chelating agents [5]. These carboxyl groups, tend to donate protons (H⁺), resulting in the negatively charged carboxyl group that is capable of forming stable complexes with several metal ions. The impurities were removed from the ash via chelate reaction between carboxyl groups (-COOH) and the metal elements. Therefore it is possible that these negatively charged carboxyl groups are able to form stable complexes resulting in their removal especially from rice husk ash.

3.4. Morphology surface analysis of treated Rice Husk (RH), Rice Husk Ash (RHA), Mixture 30% Rice Husk (RH) and 30% Rice Husk Ash (RHA) after leaching treatment.

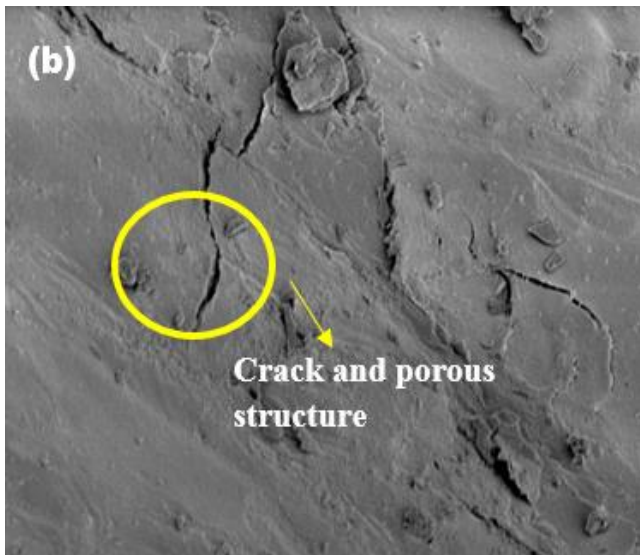
The morphology characteristic of rice husk, rice husk ash and modified rice husk was observed by Scanning Electron Microscope (SEM) and EDX analysis. Fig. 4 shows the SEM image of (a) 0.1M treated rice husk, (b) 0.5M treated rice husk, (c) 0.1M treated rice husk ash, (d) 0.5M treated rice husk ash, (e) 0.1M 30% rice husk with 70% rice husk ash, (f) 0.5M 30% rice husk with 70% rice husk ash, (g) 0.1M 30% rice husk ash with 70% rice husk, (h) 0.5M 30% rice husk ash with 70% rice husk at magnification of 2000x.



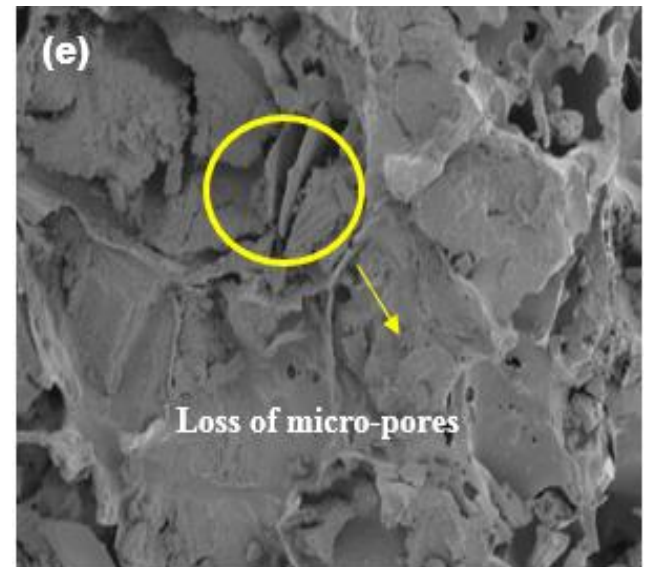
(a)



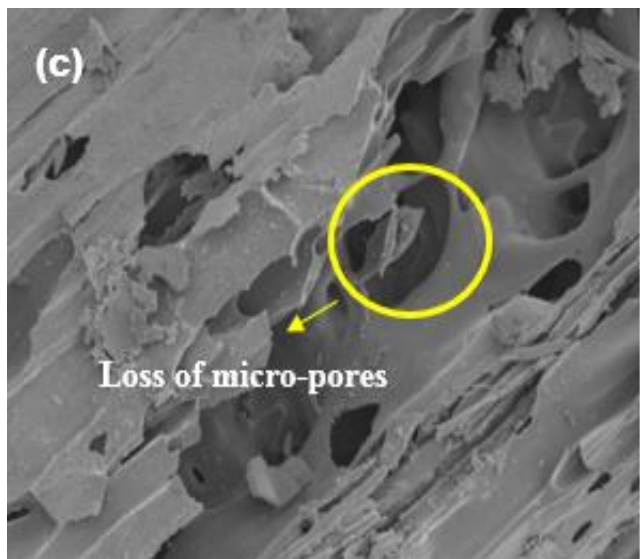
(d)



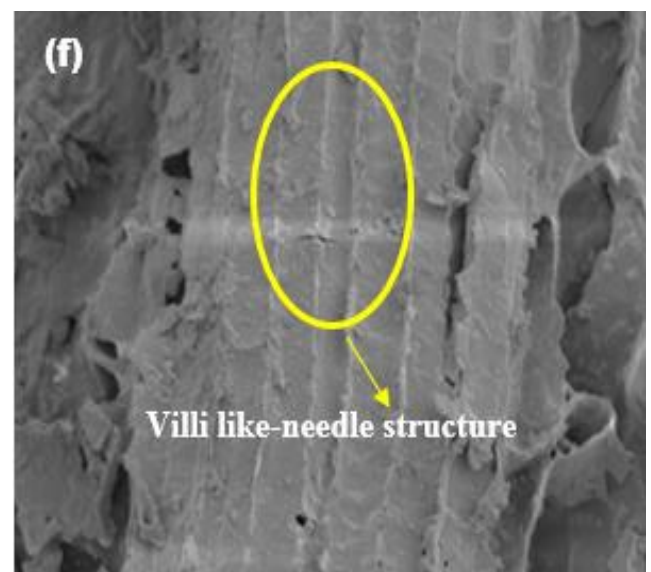
(b)



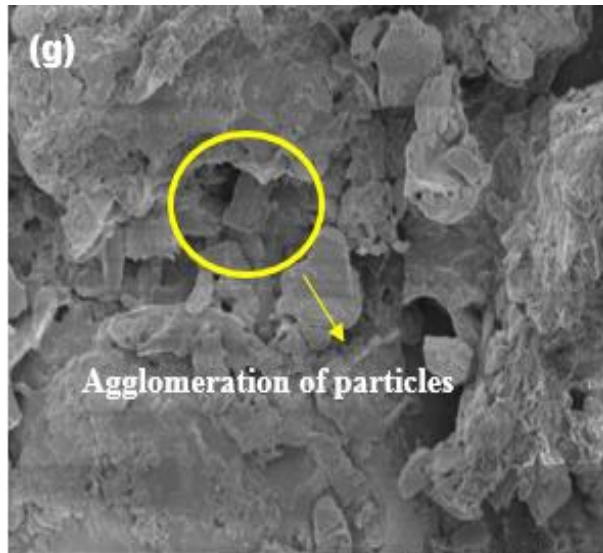
(e)



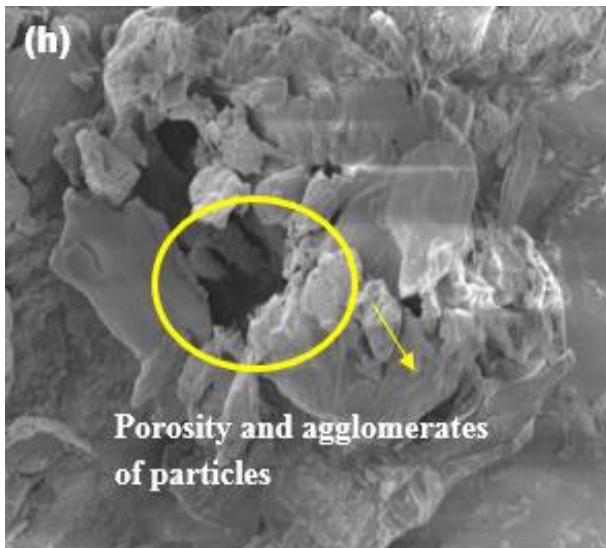
(c)



(f)



(g)



(h)

Fig. 4: SEM image of (a) 0.1M treated rice husk and (b) 0.5M treated rice husk at magnification of 2000x, (c) 0.1M treated rice husk ash and (d) 0.5M treated rice husk ash at magnification of 2000x, (e) 0.1M 30% rice husk + 70% rice husk ash and (f) 0.5M 30% rice husk + 70% rice husk ash at magnification of 2000x, (g) 0.1M 30% rice husk ash + 70% rice husk and (h) 0.5M 30% rice husk ash + 70% rice husk at magnification of 2000x

Fig. 4(a) indicates that the particles start to become agglomerates while Fig. 6(b) shows the inner and outer epidermis of rice husk (RH) starting to crack and has porous structures. Both images of Fig. 4(a) and (b) occur due to chemical reaction of leaching treatment that presents the silica. Fig. 4(c) and (d) show the morphology of rice husk ash combust at 600°C respectively. The SEM photomicrograph reveals the silica nature of the ash as shown in Fig. 4(c) and (d) which is also confirmed by the presence of amorphous in the XRD. The combustion at a temperature of 600°C shows the loss of micro-pores which is possibly attributed to pores collapse. The porous nature of RHA and its honeycombed structure is responsible for its high specific surface and makes it suitable for making insulating brick.

At 2000x magnification electron microscope, some regular and criss-cross framework construction can be seen on the surface of the native mixture rice husk and rice husk ash in Fig. 4(e) and the irregular surface and porous structure are observed. After the combination of rice husk and rice husk ash had been leached with citric acid the particles became smaller with irregular and crushed shapes. There were many embossments approximated epidermal

villi-like needles between these lines of framework as observed in Fig. 4(f). It is because the citric acid reaction decomposed silica dioxide into finer particles. Thus, the materials were beneficial to the extraction of silica and removed impurities of carbon.

Fig. 4(g) and (h) show that when the process of leaching treatment occur with citric acid solution, the silica reacted with citric acid showing increasing porosity and agglomerations compared to the untreated of rice husk and rice husk ash. Non-activated samples with citric acid generally have low specific surface area and micro-pores area than activated extract. Fig. 4(g) and (h) also affirm that the weak acid somewhat affected the surface area development and pore structure evolution.

The elemental compositions of different concentration on treated rice husk and treated rice husk ash using Energy Dispersive X-ray analysis are shown in Fig. 5. The different elements have the characteristic X-ray peak of different wavelengths. And the dispersive intensity of each spectral line is related to the element concentration. The EDX spectrometer was used to analyze the elemental composition of extraction. Results showed that concentration of 0.5M of each sample have increase in the relative of silica (SiO_2) and Silicon dioxide (SiC) compared to 0.1M of each samples. The content of graphite (C) impurities in rice husk and rice husk ash also reduced when concentration of solution was increased. Thus, it is shown in these figures that citric acid leaching treatment is significantly useful and effective to remove impurities and increased the purity of silica in rice husk and rice husk ash.

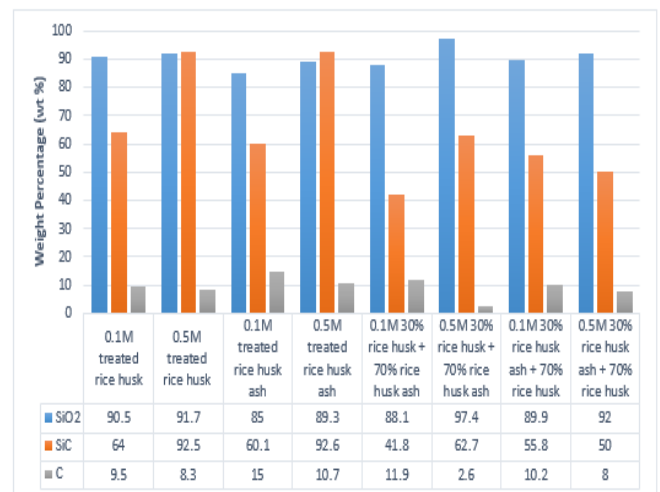


Fig. 5: Effect of leaching treatment on impurity elements on treated rice husk, rice husk ash and mixture of rice husk and rice husk ash at different concentration of citric acid by EDX analysis

4. Conclusion

The properties of silica dioxide (SiO_2) produced via acid leaching treatment process has been studied. The extraction of silica is obtained by grinding the rice husk and rice husk ash through powder. Then the samples were stirred with 0.1 M and 0.5M of citric acid for 60 minutes. In this research, for characterization techniques, 10 samples were analyzed using EDX and it is proven that highest silica content of rice husk increased from 83.9% to 97.4% by 0.5 M 30% RH + 70% RHA of citric acid and 0.1M rice husk ash slightly decreased from 99.6 % to 85% at stirring time 60 minutes after leaching treatment. These samples can be used as alternate material for silica source. The silica extraction and its morphological research are done by using SEM. Amorphous silica is observed. The recycling of major disposal product of rice husk was developed. Hence, untreated rice husk and rice husk ash showed that SiO_2 consist of smooth surface and for sample of 1.0 M citric acid showed the surface is rough and particulates. Sample mixture of 30% rice husk with 70% rice husk ash and 70% rice husk with 30% rice husk ash 0.5 M of citric acid both showed the

most concentrated of weight percent of silica compared to 0.1M. Through XRD, it has been proven that all these samples are in an amorphous phase. There are high demands for SiO₂ nowadays. SiO₂ has high potential to be the one of the commercialize products. In this research, SiO₂ is termed as a green product; it is made of rice husk. There are many applications by using the SiO₂ such as making glass, manufacturing in tires and act as filler material in electronic circuits. Through the recycle techniques of waste glass from waste materials, it has the potential in reducing the waste and improves the environment quality. Hence, in term of cost, by using the waste materials such as rice husk, SiO₂ may be produced with lower costs. Lastly, the temperature of drying time is lowered. This indirectly saves the time and production of cost.

Acknowledgement

The authors would like to thank Universiti Teknologi MARA (UiTM) for financial support [Project Grant No: 600-IRMI/PERDANA 5/3 BESTARI (051/2018)].

References

- [1] A. M. Marwa., R. A. Ibrahim and K.N. Abdalla. (May 2012). Current Transport in SiO₂ Films Grown by Thermal Oxidation for Metal-Oxide Semiconductor. *Engineering Science, Technology and Innovation*. 1(2), pp.25-32.
- [2] Q. Feng., Q. Lin and F. Gong. (October 2004). Adsorption of Lead and Mercury by Rice Husk Ash. *Colloid Interface Science*. 278, pp. 1-8.
- [3] S. I. Gritsada, and N. Maku. . (August 2015). Utilization of Coal-And Biomass-Fired Ash in the Production of Self-Consolidating Concrete. *Cleaner Production*.100, pp.59 -76.
- [4] J. Hadipramana and A.M.A Zaidi. (December 2016). Pozzolanic Characterization of Waste Rice Husk Ash (RHA) From Muar, Malaysia. *Journal of Materials Science and Engineering*. 160.
- [5] A. Dongmin and A. Wang. (August 2010). A Green Route to Preparation of Silica Powders with Rice Husk Ash and Waste Gas. *Journal Chemical Engineering*. 162, pp. 509-514.
- [6] S. Khushboo., S. Niharika and D. Vijay. (July 2013). Pure Silica Extraction from Perlite: Its Characterization and Affecting Factors. *Innovative Research in Science, Engineering and Technology*.2 (7), pp. 2936-2941.