Effect of leaching treatment on extraction of silica from combination of rice husk and rice husk ash

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Abstract. Rice husk and rice husk ash are one type of agricultural wastes that can easily be found around the world. A rice husk contains over 70% of organic silica. The focus of this paper is to analyse the effect of acid treatment of silica extraction of rice husk and rice husk ash due to silica as a raw material that can be apply in industrial. Parameters such as concentration of acid and weight percentage used in mixture of rice husk and rice husk ash during organic leaching method were also compared. In this paper, citric acid (C$_6$H$_8$O$_7$) was used for production of silica from rice husk. Samples were characterized using Scanning Electron microscopy (SEM), X-ray diffraction (XRD) and Energy Dispersive X-Ray Spectroscopy (EDEX). The result indicates that highest percentage silica of rice husk, rice husk ash and mixture between rice husk and rice husk ash after leaching was on 1.0M and has an amorphous structure.

1. Research Background
Rice husk (RH) is an important agricultural residue. RH has a relatively high content of inorganic compounds, representing approximately 20% of the dry weight of the husk. Silica represents 94% of the total while the remaining 6% are K$_2$O, CaO, MgO, Al$_2$O$_3$, and P$_2$O$_5$ in decreasing concentrations [1]. Most of RH will be burnt as fuel to produce energy resulting in the waste product which is rice husk ash (RHA). If these RHA are not utilized, it will result in massive waste generation, energy loss and environmental pollution. Therefore, it is very important to find ways to utilize RHA thoroughly [2]. This residual ash obtained from the combustion can contain over 60% of silica and some amount of metallic impurities. Depending on the burning process, RHA can contain silica in the amorphous form; therefore, this residue can be considered as a new economically viable raw material to produce silica or to be used as silica resource [3].

Leaching treatment is a convenient track to extract the silica. Organic acid which is Citric acid (C$_6$H$_8$O$_7$) solution is regularly used in leaching treatment to prepare the silica material. Hence, by using the citric acid in leaching treatment may overcome the extraction of silica from rice husk and rice husk ash that are dangerous for environmental and human’s health. The objectives of this paper were to investigate the effect 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.

2. Materials and Method
Raw materials used in this experiment are rice husk and rice husk ash. Rice husk and rice husk ash was supplied by BERNAS Company. In this research, silica is obtained from the rice husk and rice
husk ash. 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°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 μm was put into a 500 ml of citric acid solution into the beaker. The concentrations of 1.0 mol is used for this research. The beaker was placed on a hot plate magnetic stirrer at a constant temperature of 60°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°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 and mixture between rice husk and rice husk ash.

The Hitachi SU3500 instrument was used. Sample specimens with a diameter of 15mm each were aluminium coated in an aluminium sputter coater for 60 seconds at 15mA current output. The aluminium coating was necessary to ensure a conducting surface was obtained for electron bombardment and characterization [4]. 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 PAN-data software package was used to analyse the structures of rice husk and rice husk ash samples. An Aluminium-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 analysed using a Cu Kα radiation with a nickel filter. Finally, XRD patterns were recorded in the range of 2θ range of 10°-80° with the scanning speed of 2°/ min and the structural pattern was recorded.

3. Results and Discussion

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

Figure 1(a) show the XRD diffraction pattern of untreated rice husk (RH). The major reflection or peaks of SiO₂ occur at Bragg’s 2θ angles of 22.27° for untreated rice husk (RH). Figure 2(b) show the XRD diffraction pattern of untreated rice husk ash (RHA). At y-axis, it shows the intensities of the peak and x-axis is the range of phase 2θ. The silica powder obtained was also similar to other commercial silica in terms of functional group, physical nature, and also amorphous nature [5]. The major reflection or peaks of SiO₂ occur at Bragg’s 2θ angles of 21.26°. Silicon carbide (SiC) was present at the intensity of untreated rice husk ash (RHA) and occur at peak of 35°. SiC was found at the intensity of untreated rice husk ash (RHA) because of burning of rice husk due to release of more carbon during burning to become an ash [6]. In order to compare the phase analysis between untreated rice husk (RH) and untreated rice husk ash (RHA) is the different of peaks. The intensity of untreated rice husk (RH) is higher in peaks which is increase 1° 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 20 angle for both Figure 1(a) and (b) are characterize of amorphous structures is observed.
3.2 Phase Morphology Analysis of Untreated Rice Husk (RH) and Untreated Rice Husk Ash (RHA)

Figure 2(a) shows the image of untreated rice husk powder respectively at magnification of 2000x. It show 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 analysed by using EDX and result is presented in Figure 2(a). It was showed that SiO$_2$ is the most concentrated in weight percent which is 90.5 wt % than other impurities. This is due to the bonding of two oxygen (O) and silicon (Si). Figure 2(b) shows the SEM image of untreated rice husk ash (RHA) powder respectively at magnification of 2000x. It shows the morphological features of outer untreated rice husk ash which well organized in structure that resembles with rolling hills [7]. This figure show that the particles is not decomposed because the sample is not treated with any chemical or any treatment. The rice husk was burn at 600°C become an ash. The silica and inorganic impurities distribution of untreated rice husk ash particle were analysed by using EDX and result is presented in Figure 2(b). It was detected that SiO$_2$ is the 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 and strong intensity of Si and O$_2$ in the EDX spectrum is confirmed the silicon dioxide (SiO$_2$) is at higher weight percentage compared with EDX spectrum of untreated rice husk (RH) at Figure 2(a) shown before.

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

According to these XRD diffractograms figures, the optimum rate for parameter of silica is 1.0M compared to other concentration. Figure 3(a) is a diffractogram of 1.0 M rice husk (RH) via citric acid leaching treatment. The major reflection or peaks of silica (Si) occur at Bragg 2θ angles for 1.0 M of rice husk is 22.65°. While Figure 3(b) represents of 1.0 M rice husk ash (RHA) via citric acid leaching treatment. For rice husk ash (RHA), there were two major elements presents at this phase which is silica, Si and Silicon Carbide (SiC). The major reflection or peaks of silica (Si) occur at Bragg 2θ angles for 1.0 M of rice husk ash is 21.59° while for silicon carbide occur range at 20°~40°.

Mixtures of rice husk and rice husk ash is one of the concentration parameter through this process of leaching treatment to identify the effect of molarity acid treatment in extraction of silica. Figure 3(c) shows the XRD diffraction pattern of 1.0 M 30% rice husk (RH) via citric acid leaching treatment. The major reflection or peaks of silica (Si) occur at Bragg 2θ angles for 1.0 M of 30% rice husk is 22.57°. While Figure 3(d) is a diffractogram of 1.0 M 70% rice husk (RH). The major reflection or peaks of silica (Si) occur at Bragg 2θ angles for 1.0 M of rice husk is 22.41°. As the evident from the diffractograms, the all the samples in these four figures are amorphous phase. The most intense extraction peaks can be ascribed to the presence of silica which is Si–O–Si is stretching and bending vibrations [8]. To obtain amorphous silica from rice husk, the processing temperature should not exceed 700°C and combustion temperature above 900°C, the silica rice husk ash consisted of crystalline of cristobalite and a small amount of tridymite.

Figure 3: XRD pattern of the (a) rice husk (RH), (b) rice husk (RHA), (c) 30% rice husk (RH) and (d) 30% rice husk ash (RHA) obtained by the leaching treatment
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.

As can be seen from Figure 4(a), it can be showed a flaky shape of SiO$_2$ particles and rough in surface. Citric acid is an organic acid give an organized distribution and flake-like structure of rice husk powder to fine and become agglomerate. It can be observed that smaller particles in the submicron range aggregated to form particle sizes in range of several microns. Hence, powders adhere together and agglomerated due to the leaching treatment. However, after the combustion and citric acid leaching treatment, Figure 4(b) shows that the surface characteristics on extraction were significantly change from smooth surface into a fish-bone shape and formation of pores were observed. The rice husk was combus at 600°C become an ash. It is clear that silica particles exhibit non spherical and irregular fiber-like structures. The pores are evolve from the disintegration of rice husk structure as the cellulose-lignin matrix burned away and leaving porous silica with large pores of different sizes.

Mixtures of rice husk and rice husk ash is one of the concentration parameter through this process of leaching treatment to identify the effect of molarity acid treatment in extraction of silica. Figure 4(c) and Figure 4(d) shows the SEM image of 1.0M of 30% rice husk and 70% rice husk ash and 1.0M of 30% rice husk ash and 70% rice husk after leaching treatment. Figure 4(c) indicates the surface particles of silica in mixture of rice husk and rice husk ash for formation of well structure having a small pores as compared with Figure 4(d) due to pore collapse by heat. It clearly seems that particles of silica in this mixtures are in agglomeration. As shown in Figure 4(d), the crack in the sample was found. Silica starts to form smaller particles solitary. These figures can be explained that silica can be extracted more or absorbed by increase the concentration of citric acid. This is due to leaching with higher concentration of citric acid can dissolve inorganic impurities contained in rice husk up to enlarge the pores [9]. When the pores is increased, the surface area of the material increased as well. Thus it can be seen that the morphology of 1.0 M of citric acid concentration of rice husk and rice husk ash can change apparently with the change of concentration during the leaching treatment. Thus, confirmed that the highest concentration of silica in the rice husk is in the outer surface of the husk in the amorphous form.

![Figure 4: SEM images of (a) rice husk (RH), (b) rice husk (RHA), (c) 30% rice husk (RH) and (d) 30% rice husk ash (RHA) after leaching treatment at magnification of 2000X](image-url)
In order to access the efficiency of the leaching step and to determine the best leaching condition, the weight percentage (wt %) of impurities in the leached sample is ratio to the impurities in as untreated rice husk (RH) and rice husk ash (RHA). Figure 5 shows the effect of the leaching treatment under parameter of 1.0M leached with citric acid for major impurity elements of interest. The result of the impurities reduction is evident where the purity of the silica in the 1.0M rice husk and 1.0M of 30% rice husk ash with 70% rice husk were increased from 90.5% to slightly over 94.9wt% and 99.2wt%, while for 1.0M rice husk ash and 1.0M of 30% rice husk with 70% rice husk ash have general decrease from 99.6wt% to 98.9wt% and 97.4wt%.

**Figure 5**: Effect of leaching treatment on impurity elements on untreated and treated rice husk and rice husk ash

It can be seen from Figure 5 that carbon (C) in the treated RH and RHA is removed equally well by all leaching conditions considered in this experiments. This suggest that carbon in treated RH and RHA is possibly exist as amorphous oxide. The leaching treatment at 60°C for one hour however, more effective in removal of carbon. It is seen that there is a significant decrease in the carbon content of treated RH and RHA. Carbon has a low adsorption of X-rays and neutrons making it a particularly useful material in nuclear applications. Carbon is chemically inert to almost all chemicals. It burns completely when heated in oxygen to form carbon dioxide. However, it fails to burn in air, even if it is heated to high temperatures.

4. **Conclusion**

The effect of leaching treatment through rice husk (RH) and Rice Husk Ash (RHA) produced by extraction of silica (SiO$_2$) has been prepared. EDX showed highest silica content of rice husk increased from 83.9% to 90.5% by 1.0 M of citric acid and rice husk ash slightly decreased from 99.6% to 98.9% by 1.0 M of citric acid at stirring time 60 minutes after leaching treatment. These samples can be used as alternated material for silica source. Amorphous silica is observed by SEM. Sample mixture of 30% rice husk with 70% rice husk ash and 70% rice husk with 30% rice husk ash 1.0 M of citric acid both showed the most concentrated of weight percent of silica compared to 0.1M and 0.5M. XRD showed these samples are in an amorphous phase. In the future, it is suggested that the concentration to produce SiO$_2$ need to be considered at optimum concentration by increasing the formation of SiO$_2$ and heating rate to dried the samples should be higher than 60 °C because the samples are not dried fully if below than 60 °C. Some parameters of leaching treatment which has
been set can be modified in term of various parts such as type of waste materials, type of chemical in organic material and inorganic materials and ratio of stirring time to be longer. A variety of results can be obtained by manipulating the parameters. The researcher will have series of results and analysis which can be commercialized.

References
[1] Mohammed N, Ismail AR, and Ismail AR 2012. A simple Method of Obtaining Spehrical Nanosilica from Rice Husk. International Journal on Advanced Science Engineering Information Technology, 2, pp. 28-30.
[2] Yan L, Yupeng G, Dongmin A, & Zichen W 2011. A Sustainable Route for Preparation of Activated Carbon and Silica form Rice Husk ash High-Purity Amorphous Silica from Rice Husk. Journal Hazard Master, 186, pp. 1314-1319
[3] Ana M 2009. Silica Sol Obtained from Rice Husk Ash. Purify Chemistry and Technology. 3, pp. 1-4.
[4] Faizul CP and Noorina HJ 2014. Extraction of Silica from Palm Ash Using Organic Acid Leaching Treatment. Engineering Materials, 795, pp. 701-706.
[5] Feldman LC and Gusev EP 2012. Current Transport in SiO2 Films Grown by Thermal Oxidation for Metal-Oxide Semiconductor. Engineering Science, Technology and Innovation, 1(2), pp. 25-32.
[6] Gritsada SI and Maku N 2015. Utilization of Coal- And Biomass-Fired Ash in the Production of Self-Consolidating Concrete. Cleaner Production, 100, pp. 59 -76.
[7] Hadipramana J, Riza FV, Adnan SH and Zaidi AMA 2016. Pozzolanic Characterization of Waste Rice Husk Ash (RHA) from Muar, Malaysia. Journal of Materials Science and Engineering, 160.
[8] Khushboo S, Niharika S and Vijay D 2014. Pure Silica Extraction from Perlite: Its Characterization and Affecting Factors. Innovative Research in Science, Engineering and Technology, 2(7), pp. 2936-2941
[9] Selvakumar KV 2013. Extraction of silica from burnt paddy husk: International Journal of Chemtech Research, 6(9), pp. 4455-4459.

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