Removal of iron in rice husk via oxalic acid leaching process

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Abstract. Rice husk (RH), an agricultural waste which has been used as an alternative source for silica (SiO₂). In order to produce high purity amorphous SiO₂ from RH, acid leaching pre-treatment was required to remove the metallic impurities, followed by calcination at 800 °C to obtain the ashes. This research was studied about using oxalic acid as the leaching agent to remove iron (Fe) content in RH. The experimental parameters used in this study were acid concentration, reaction temperature, and leaching time. Based on the chemical composition analysis, the highest SiO₂ content of 99.30% and the lowest Fe₂O₃ content of 0.43% were to be found in RHA which had treated under optimum parameters of 1.0 M of oxalic acid concentration, 90 °C of reaction temperature and 3 hours of leaching time. In addition, the particles of TRHA were observed with a tubular porous structure and irregular shape due to the leaching effect. Phase analysis by x-ray diffraction show that the amorphous SiO₂ was confirmed as a broad diffused peak. It’s been found in the 2θ angle range of 18° to 30° with no crystalline peak observed.

1 Introduction

Rice husk was the by-product from paddy field and it was yielded about 20% from the rice production [1]. Although the rice production industry was started for the past centuries, the problems of rice husk overproduction remain unsolved. In particular, the disposal of rice husk and rice husk ash (RHA) were to give risen to the environmental pollution and human health issues [2]. In the past decades, the researchers found out this agriculture wastes could be utilised into useful application. The most common application to be found was replacing the conventional silica (SiO₂) source [1].

As an alternative silica source, the purity of SiO₂ in RHA is crucial factor in order to produce high quality of ceramic-based end product. The metal impurities to be found in the rice husk may contaminate the end product. In particular, iron (Fe) affects the degree of transparency, purity, and functionality of glass based and ceramic-based end products due to its oxidation state nature [3]. Different oxidation states give different colours to the iron

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compounds. Among the industries, acid leaching process is the most common technique to remove metal impurities.

Several researchers had studied the usage of strong inorganic acids to remove the metal impurities in agricultural wastes by using acid leaching process in order to extract high purity of SiO2. However, these strong acids were difficult to dispose and destructive to the human health and environment [4]. Weak organic acids are having moderate acidity, less processing cost, and remarkable leaching effect which are suitable to replace the strong inorganic acids [5]. In this study, the effect of oxalic acid in removing Fe content and yielding high purity of SiO2 in rice husk was determined by manipulating the parameters which are acid concentration, reaction temperature, and leaching time. The chemical composition, surface morphology, and phase identification of RHA were characterised as well.

2 Experimental

2.1 Material used and sample preparation

The raw RHs used in this study were originated from the disposing field in Kuala Kedah, Kedah, Malaysia. It washed with tap water to remove dusts and contaminants followed by drying under the hot sun for a day. Next, the dried husks were pulverised into powder by using ring milling machine. The coarse powder was later sieved into fine powder (< 63μm) using sieve shaker to increase leaching efficiency.

2.2 Leaching process

All the experiments were conducted under ambient condition. Oxalic acid dehydrate powders were dissolved in distilled water to prepare oxalic acid solution. 10 g of RHs was put into a beaker filled with 250 ml of oxalic acid solution. The chosen experimental parameters were acid concentration, reaction temperature, and leaching time. Acid concentration was carried out with 0.1 M, 0.5 M, and 1.0 M; reaction temperature was selected with 70 ºC, 80 ºC, and 90 ºC; three leaching durations (1 hour- 3 hours) were chosen. The mixture was put on a hot plate magnetic stirrer with variation among the parameters. After leaching process, the leached RHs were filtered and rinsed with distilled water to remove excess oxalic acid until the filtered water turned clear. The materials were then dried in the oven at 100 ºC for 3 hours.

2.3 Calcination process

The dried RHs were calcined in the muffle furnace at controlled temperature of 800 ºC for 3 hours. This calcination process allowed the RHs undergone chemical reaction to become RHA with high purity amorphous SiO2.

2.4 Characterisation analysis

The chemical composition of untreated rice husk ash (URHA) and treated rice husk ash (TRHA) were analysed by X-ray fluorescence spectrometer (XRF). Scanning electron microscopy (SEM) was used to study the morphology of URHA and TRHA. Since the RHAs are non-conductive materials, they were sputter coated a layer of platinum to enhance the analysis. For phase identification analysis in both URHA and TRHA, X-ray diffractometer (XRD) was employed. The diffraction angle, 2θ was scanned from 10º to 80º over the samples with 0.2º step size and 2º/ min scan rate.
3 Results and discussion

3.1 Material used and sample preparation

The results of chemical composition of URHA and TRHA obtained from XRF analysis were tabulated as shown in Table 1, Table 2, and Table 3 according to the manipulation of acid concentration, reaction temperature, and leaching time, respectively.

3.1.1 Oxalic acid concentration

The effect of oxalic acid concentration was studied by conducting experiment at constant 90 °C and 3 hours of leaching time. As Table 1 shown, the SiO₂ content increased whereas the Fe₂O₃ content decreased as the acid concentration used increased. The SiO₂ was obtained with the highest amount of 99.30 % while the Fe₂O₃ was obtained with the lowest amount of 0.43 % when 1.0 M of acid concentration used in leaching rice husk. It was also observed the metal oxide impurities such as K₂O and CaO were significantly decreased as the acid concentration increased.

The complete elimination of CaO occurred at 1.0 M of acid concentration used. It happened the same on K₂O with acid concentration of 0.5 M and above was used. It has proven that the chelating reaction between carboxylic (-COOH) groups and the metal elements was the driving force to remove metal elements in rice husk by forming the metal complexes [6]. The relative amount of SiO₂ was increased due to the reduction of carbonaceous elements and thermal decomposition of organic matters in rice husk during the calcination process [7]. The optimum acid concentration was 1.0 M and it was constraint for the next parameter.

| Oxalic Acid Concentration (M) | Chemical Compound (wt %) |
|-------------------------------|--------------------------|
|                               | SiO₂         Fe₂O₃    K₂O         CaO     Others |
| URHA 1.0                     | 99.30        0.43   -             -       0.27 |
| URHA 0.5                     | 98.00        1.40   -             0.04    0.56 |
| URHA 0.1                     | 96.60        1.94   0.18          0.20    1.08 |

3.1.2 Reaction temperature

Table 2 showed the chemical composition of URHA and TRHA at 80 °C and 90 °C under controlled variables which are 1.0 M of acid concentration and 3 hours of leaching time. Based on the chemical compounds content in both TRHA, the leaching performance at 90 °C was better than at 80 °C as the SiO₂ content in RHA was increased from 92.40% to 99.30% and the Fe₂O₃ content was decreased from 2.26% to 0.43% at 90 °C. The acid molecules gained extra kinetic energy from the raised temperature, the movement of molecules greatly increased results in chelating rate increased. In addition, the particle size of husk powder also contributed in increasing leaching rate as the smaller the particle size, the more the surface area exposed, the easier the heat and mass transfer to the rice husk [8]. Temperature and particle size were able to enhance leaching effect.
Table 2. Chemical composition of URHA and TRHA with different oxalic acid concentration.

| Reaction Temperature (°C) | Chemical Compound (wt %) |
|---------------------------|--------------------------|
|                           | SiO₂ | Fe₂O₃ | K₂O | CaO | Others |
| URHA                      | 92.40 | 2.26 | 2.06 | 1.96 | 1.32   |
| 90                        | 99.30 | 0.43 | -   | -   | 0.27   |
| 80                        | 97.40 | 1.67 | -   | 0.03 | 0.90   |

3.1.3 Leaching time

The leaching time had the least effect in this experiment while the acid concentration and the reaction temperature were controlled at optimum condition (1.0 M, and 90 °C, respectively). Based on Table 3, it showed that the highest SiO₂ content (99.30%) yielded in RHA was obtained at 3 hours of leaching time as well as the lowest Fe₂O₃ content (0.43%). In contrast, the experiment conducted for 2 hours was not effective in removing the metal impurities, especially Fe. There was a small amount of Fe content removed from rice husk as there was 2.02% of Fe₂O₃ remained in RHA after leaching. In general, the leaching effect is better with longer leaching time with the addition of other variable.

Table 3. Chemical composition of URHA and TRHA with different leaching time.

| Leaching Time (hours) | Chemical Compound (wt %) |
|-----------------------|--------------------------|
|                       | SiO₂ | Fe₂O₃ | K₂O | CaO | Others |
| URHA                  | 92.40 | 2.26 | 2.06 | 1.96 | 1.32   |
| 3                     | 99.30 | 0.43 | -   | -   | 0.27   |
| 2                     | 96.50 | 2.02 | 0.28 | 0.12 | 1.08   |

3.2 Surface morphology analysis of RHA

In URHA, the particles were irregular size and shapes and distributed evenly as shown in Figure 1(a). This might cause by the grinding action on the RH to obtain a mean particle size of 63μm for better leaching efficiency. However, there were some agglomeration observed (showed by the yellow circles) and it showed a clearer in Figure 1(b) whereby the particles were not decomposed but agglomerated together instead. This phenomena might be happened due to the sample was not undergoing acid leaching treatment [4]. On the other hand, the particles in TRHA were decomposed but they were remained in irregular size and tubular shape as shown in Figure 1(c). In Figure 1(d), the surface condition on the TRHA particle was clearly observed with the porous structure due to the leaching effect and calcination on organic matters [9].
3.3. Phase Identification Analysis of RHA

The crystallinity of SiO$_2$ in RHA was strongly affected by the combustion temperature and time [4]. Both URHA and TRHA were undergone calcination at 800 °C for 3 hours and showed the same broad diffused pattern at the 2θ angles range of 18º to 30º as shown in Figure 2. This phase analysis was similar to other researcher’s result whereby the broad diffused peak was indicating SiO$_2$. No sharp peak was observed. As a result, the identification of amorphous SiO$_2$ was confirmed in RHA [10].
Fig. 2. XRD results of URHA and TRHA with various experimental parameters.

4 Conclusion

Acid leaching using oxalic acid was effective and efficient in removing metal elements especially iron (Fe) in rice husk. Removal of metal impurities in rice husk was greatly enhanced the purification of silica (SiO$_2$) yielded after calcination at 800 °C. The optimum parameters in leaching rice husk were 1.0 M of oxalic acid concentration, 90 °C of reaction temperature, and 3 hours of leaching time. Particles of TRHA showed porous structure due to elimination of organic matters whereas particles of URHA were not decomposed but agglomerated under morphology analysis. Phase identification analysis between both URHA and TRHA was showing a broad diffused peak at 20 angles range of 18° to 30°, amorphous SiO$_2$ observed.

The authors would like to thank the Center of Excellence Geopolymer & Green Technology and School of Materials Engineering, Universiti Malaysia Perlis Malaysian Government for giving us facilities to run this research project.
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