Effect of Water and Acid Pre-treatment on the Physicochemical Properties of Rice Husk for Silica Extraction

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Abstract. Rice husks are residue materials from rice milling. These materials are mostly discarded after obtaining the rice, however, numerous studies have found out that rice husks are an excellent renewable source of silica. Rice husks are generally turned into rice husk ash in order to extract the silica in the material. Prior to the combustion process, pre-treatment methods are usually done in order to minimize the impurities in the husks. Failure to remove these impurities lead to undesired properties of the extracted silica. As such, we investigate some common pre-treatment methods, namely water and acid (HCl) treatment, and their effects on the surface morphology and elemental composition of the husks after treatment. It was found that H₂O was more effective in removing the bromide ions Br⁻, while HCl becomes less effective at increasing concentration. Also, acid treatment was more effective in removing the sodium and potassium components compared to water treatment. However, efficiency decreases as the acid concentration increases due to interference of silica polymerization. Thus, for the removal of impurities in rice husk, lower concentration of acid pre-treatment is recommended.

1. Introduction

Silica is the most abundant material on the earth’s crust. While crystalline silica has limited uses, amorphous silica has been found to be useful as fillers, absorbents and catalyst supports [1]. Silica nanoparticles have also been explored for medical use, such as drug delivery systems and biosensors [2], [3]. The increasing demands for such materials prompt the exploration of renewable sources for silica nanoparticles, one of which is rice husk ash [4]. Rice husk ash, which can be produced via controlled rice husk combustion, is found to have high silica content (around 95 %) [5]. However, several studies also stated that presence of impurities in the rice husk affect the quality of the rice husk ash [6], [7].

Impurities such as potassium and sodium oxides affect the surface of silica particles, decreasing the surface area, reactivity, and silica crystallization temperature [6]. To remove the impurities, acid leaching was facilitated [6], [7]. Leaching is an extraction of soluble constituent away from an insoluble solid. The process may cause physical and chemical changes because aside from removal of chemical impurities, leaching may also cause surface fragmentation due to the removal of the organic layer [8].

This work aims to compare the differences in the physical and chemical properties between untreated, water leached, and acid leached rice husks. The surface morphology of the resulting husks was investigated by scanning electron microscopy. Furthermore, elemental composition was analysed.
through energy-dispersive x-ray spectroscopy and x-ray fluorescence spectroscopy. Overall, the efficacy of removing the impurities in both pre-treatment methods were investigated.

2. Methodology

2.1. Rice Husk Preparation and Pre-treatment

Rice husk (RH) samples were obtained from local farmers in Laguna, Philippines. The rice husks were washed with water to remove dirt and other impurities. The sample was air-dried. The treatments were comprised of control (non-leached), deionized H$_2$O, 0.5 M HCl, 1.0 M HCl, and 2.0 M HCl. Dried RH were soaked in the leaching agents for 48 hrs. The RH were then filtered, washed and neutralized (pH 7.0) with deionized water. The husks were then oven dried.

2.2. Determination of Surface Morphology

Scanning electron microscopy (SEM) imaging was done to determine the changes in surface morphology of the husk for untreated and different treatment methods. Rice husk was treated with ethanol to remove adsorbed water and oven-dried prior to SEM imaging [9]. The dried sample was then physically deposited onto a carbon tape and then it was coated with platinum for 30 secs using ion sputter. The sample was subjected under scanning electron microscopy (SEM) under 500 x and 1000 x magnifications at 5.0 kV accelerating voltage. The SEM equipment used for this study was Hitachi SU-8230 FE-SEM of the Department of Mining, Metallurgical, and Materials Engineering, College of Engineering, University of the Philippines, Diliman, Quezon City.

2.3. Compositional Analysis

Energy-dispersive x-ray spectroscopy (EDS) was done to determine percent composition for the underside and outer layer of the treated and untreated rice husks. It was simultaneously conducted with scanning electron microscopy at 205x magnification and 15.0 kV accelerating voltage. X-ray fluorescence (XRF) was also done to determine percent composition for treated and untreated rice husks and consequently, it was used to determine the percent removal after different treatments. The XRF gun of HDXRF-XOS at the Extractive Metallurgy Lab II of the Department of Mining, Metallurgical, and Materials Engineering was the one used for this test.

3. Results and Discussions

3.1. Variation of Surface Morphology of Rice Husk with Treatment

Untreated and treated rice husks were subjected to SEM imaging to determine the changes in surface morphology after leaching (Figure 1). Smoothening was observed on the surface of RH after water and HCl leaching (Figures 1a, 1b, 1c). On the control sample, circular planar domes were observed. Then, with H$_2$O and HCl treatment, the domes were eroded and ridges were exposed. These ridges correspond with the silica-rich portion of the rice husk outer surface [10]. The ridges were sharper in H$_2$O samples compared to HCl. This may be caused by the removal of organic layer on the outer shell of the rice husk.

SEM imaging was also performed on the RH underside, which is mostly composed of fibres. The control underside had homogeneous flat structure that showed the distinctive feature of the organic fibre layer of the rice husk [8], [10]. Etching was observed on the surface of the treated samples relative to the untreated sample (Figures 1d, 1e, 1f). Water treated samples had fibre-like structures with minimal distinct features. On other hand, acid treated samples showed individual fibres that confirm removal of organic layer on the underside of the rice husk samples. Elemental analyses were then done to determine the composition of the removed material.
Figure 1: SEM images of (1a) untreated, (1b) H$_2$O, and (1c) 2.0 M HCl treated rice husk lemma. SEM images of the rice husk underside for (1d) untreated, (1e) H$_2$O, and (1f) 2.0 M HCl treated are also shown.

3.2. Elemental Composition

Energy-dispersive x-ray spectroscopy (EDS) was done on the outer and underside part of the husks. For the outer shell of RH, it was observed that there was an increase in C percentage, but Mg and Al were undetectable after being leached with water and HCl (Table 1). Furthermore, K and Ca were completely undetected after leaching with 2.0 M HCl. The increase in the carbon content supports the SEM image that showed exposure of the RH shell.

Table 1. Energy-Dispersive X-Ray Spectroscopy Results (Outer shell)

| % Weight | C   | O   | Mg  | Al  | Si  | K  | Ca  | Cl  |
|----------|-----|-----|-----|-----|-----|----|-----|-----|
| Control  | 26.48 | 51.70 | 0.13 | 0.75 | 20.37 | 0.20 | 0.36 | —   |
| H$_2$O   | 31.97 | 48.29 | —   | —   | 19.55 | 0.09 | 0.09 | —   |
| 2.0 M HCl| 30.96 | 48.47 | —   | —   | 20.57 | —   | —   | —   |

For the underside of the RH, there was an observed decrease in C content after treating with H$_2$O and 2.0 M HCl (Table 2). Mg, Al, and K were also undetectable after treatment with water and acid. However, Cl was detected in acid treated sample that may be due to trapped acid in the rice husk fibres. After leaching with water and acid, the silica content in the underside portion was observed to increase. This may be due to the removal of the organic layer as observed in the SEM image (Figure 1).

Table 2. Energy-Dispersive X-Ray Spectroscopy Results (Underside)

| % Weight | C   | O   | Mg  | Al  | Si  | K  | Ca  | Cl  |
|----------|-----|-----|-----|-----|-----|----|-----|-----|
| Control  | 45.72 | 46.03 | 0.06 | —   | 7.98 | —  | 0.20 | —   |
| H$_2$O   | 30.80 | 48.61 | —   | —   | 20.43 | —  | 0.16 | —   |
| 2.0 M HCl| 28.07 | 46.23 | —   | —   | 25.35 | 0.14 | 0.20 | —   |
Based on the XRF data (Table 3), it was found that most of the outer surface material were impurity elements, i.e. Mg, Al, K, and Ca. After washing with water and HCl, a decrease in the concentration of these elements was observed, which led to the smoothening of the surface morphology (Figure 1).

### Table 3. X-Ray Fluorescence Spectroscopy Results

| Elements | Br | Ca | Fe | K  | Si | Sr | Mn | Rb | Zn | Ti |
|----------|----|----|----|----|----|----|----|----|----|----|
| Control  | 0.007 | 0.520 | 0.097 | 0.771 | 98.451 | 0.002 | 0.004 | 0.001 | 0.001 | — |
| H₂O      | — | 0.608 | 0.090 | 0.135 | 98.945 | 0.016 | 0.182 | — | 0.018 | — |
| 0.5 M HCl| — | 0.105 | 0.048 | 0.050 | 99.788 | 0.009 | — | — | — | — |
| 1.0 M HCl| 0.002 | 0.171 | 0.043 | 0.028 | 99.748 | 0.002 | 0.004 | 0.001 | 0.001 | — |
| 2.0 M HCl| 0.004 | 0.471 | 0.049 | 0.029 | 99.437 | 0.005 | — | — | 0.005 | — |

#### 3.3. Removal of Impurities

X-ray fluorescence spectroscopy was performed on all systems to determine percent composition of the impurity elements (Table 3). The percent removal relative to the control was calculated by the formula,

\[
\%_{\text{removed}} = \left( \frac{C_{\text{control}} - C_{\text{treated}}}{C_{\text{control}}} \right) \times 100
\]

where \(C_{\text{control}}\) is the concentration of the element for the untreated system, and \(C_{\text{treated}}\) is the concentration of the element for a specific treatment.

![Figure 2. Percentage removal of impurities based on the XRF data.](image)

It was observed that trace amounts of Rb and Ti were present in the control and completely removed after water and acid treatment (Table 3 & Figure 2). It was also observed that HCl was much more favourable in removing Fe, Mn, and Zn, which were also found at trace amounts in the control.

Water was found to be ineffective in removing some of the metals. In solution, water weakly ionizes to form H⁺ and OH⁻:
Free OH ions can react with the metal impurities Ca, Fe, Zn, and Mn to form the corresponding hydroxides [11] according to the following reactions [12], [13]:

\[
\begin{align*}
\text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{OH}^- \quad (1) \\
\text{Ca}^{2+} + 2\text{OH}^- & \rightleftharpoons \text{Ca(OH)}_2 \quad (2) \\
\text{Fe}^{3+} + 3\text{OH}^- & \rightleftharpoons \text{Fe(OH)}_3 \quad (3) \\
\text{Zn}^{2+} + 2\text{OH}^- & \rightleftharpoons \text{Zn(OH)}_2 \quad (4) \\
\text{Mn}^{x+} + x\text{OH}^- & \rightleftharpoons \text{Mn(OH)}_x \quad (5)
\end{align*}
\]

These weakly soluble hydroxides are not easily removable by water. Mn can be present as Mn$^{2+}$, Mn$^{3+}$, or Mn$^{4+}$ [14], and any of these may form corresponding hydroxides which can undergo further oxidation. These may account for the low percent removal of the metal ions during water treatment. In addition to removing Br, Rb, and Ti, 0.5 M HCl was found to be more effective in removing Ca, Fe, K, Mn, and Zn. The hydrogen ion is more reactive compared to the ionic forms of these metals (e.g. Ca$^{2+}$, Fe$^{3+}$, K$^+$, Mn$^{2+}$, and Zn$^{2+}$) [11] ~ [13]. Thus, H$^+$ can displace these ions in the rice husk matrix, enabling effective leaching of these metal impurities. However, efficiency decreases as the acid concentration increases. Gorrepati et al. [15] report that the rate of silica polymerization rises exponentially with increasing pH. The formation of silica polymers may interfere with the ion-exchange mechanism between H$^+$ and the metal ions, thus lowering the amount of metal impurities removed.

Potassium is found to inhibit carbon removal during the rice husk combustion [16]. Ca$^{2+}$ and OH$^-$ can damage the Si-O bonds of amorphous silica [17]. It is desired to remove as much of these metals as possible to ensure the production of high purity silica from rice husk. Thus, from our results, 0.5 M HCl is recommended for use in rice husk pre-treatment for silica production.

4. Conclusion
Pre-treatments were able to remove impurities in the rice husk. Water washing was found to be effective in removing Br, K, Rb, and Ti, but not Ca, Fe, Mn, and Zn. HCl was effective in removing Ca, Fe, Mn, and Zn, with a higher efficiency in removing Br, K, Rb, and Ti. However, efficiency decreases as acid concentration increases. Therefore, low HCl concentration is recommended for rice husk pre-treatment.

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