Citric acid leaching process for removal of iron (Fe) from rice husk

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Abstract. Rice husk containing the highest amount composition of silica (SiO₂) compared with other agricultural waste. With such a large availability of rice husk, it becomes economical to industrial by the implementation concept of sustainability beside decompose the rice rusk into ash. The extraction of silica and elimination of metallic element, such as iron (Fe) from rice husk (RH) was treated by leaching process. With this, the RH can be utilized to produce various types of useful renewable resources such as silica (SiO₂). Using the organic acid as leaching solution is more eco-friendly instead using the inorganic acid that classified as very dangerous chemical due to the high level of hazard. The treated and untreated rice husk ash characterizes using scanning electron microscopy and X-ray diffraction spectroscopy. The morphology of treated rice husk shows the tubular aggregate due to the presence of alkaline earth metal such as Ca and Mg.

Under the optimum condition with 90 ºC solution temperature, 60 minutes stirring time, 3% of citric acid and calcination temperature of 800 ºC for 3 hours, amorphous silica with more than 78% was prepared via citric acid leaching treatment and combustion process.

1 Introduction

Rice husk (RH) can be utilized to produce a various type of useful renewable resources such as high-purity silica (SiO₂) [1]. With such a large availability of rice husk, it becomes economical to industrial applications.

The presence of iron (Fe) in the rice husk should be treated because the presence small amount of iron in industrial application of silica is harmful, as it impairs the transmission in optical fibres and the transparency of glasses, it discolours ceramic products and lowers the melting point of refractory materials [2].

The iron content can be reduced by a number of methods such as leaching process. The process of leaching is used to extract or remove the substances from the solids. This method involves leaching of the mineral with inorganic or organic acids. The most used organic acids are citric, acetic and oxalic, and inorganic acids are sulphuric, hydrofluoric and hydrochloric acid [2].

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2 Materials and methods

2.1 Rice husk

Rice husk (RH) contains a high concentration of silica in amorphous and crystalline (quartz) forms. Table 1 shows the typical composition of the rice husk where the silica oxide \( \text{SiO}_2 \) is the main compound which contribute 94.48% [3].

| Composition (Wt%) | \( \text{SiO}_2 \) | CaO | MgO | \( \text{Fe}_2\text{O}_3 \) | Na\textsubscript{2}O | K\textsubscript{2}O | TiO\textsubscript{2} | MnO | SO\textsubscript{3} | P\textsubscript{2}O\textsubscript{5} |
|------------------|------------------|-----|-----|------------------|----------|--------|----------|-----|--------|----------|
|                  | 94.48            | 0.36| 0.32| 0.05             | 0.04     | 1.40   | 0.003    | 0.32| 0.15   | 0.45     |

2.2 Purification of silica

Rice husk obtained from local paddy mill was grind until formed fine powder rice husk (<75μm). Grounded rice husk then dispersed with citric acid solution with a variation of acid solution (1 - 3 %), stirring time (30 - 90 minutes) and solution temperature (70 - 90 °C). The solids were separated by filtration and washed with distilled water after every reaction condition in order to remove all traces of excess acid. Then, the treated rice husk dried for overnight in the oven at temperature of 60 °C.

Treated rice husk undergoes calcination process in order to eliminate moisture in the rice husk. The calcination process has been performed in front loading box furnace with controlled temperature (800 °C) and soaking time (3 hours). Finally, the untreated rice husk ash (URHA) and treated rice husk ash (TRHA) were characterized using XRD and SEM-EDX.

3 Results and discussions

3.1 Characterization of RHA

Pre-purification of thermal (800 °C) treated rice husk accelerating the hydrolysis of hemicellulose and cellulose contained in rice husk and removing most of the metallic impurities. As shown in Table 2 and Fig. 1, the optimum leaching condition of treated rice husk ash (TRHA) and untreated rice husk ash (URHA) with silicon (Si) content was 77.97 and 57.76% while for iron (Fe) content were 0 and 11.19% respectively. The leaching conditions (citric acid solution concentration, solution temperature and stirring) were influencing the Si and removal of Fe from the rice husk.
Table 2. SEM-EDX result of element content (%) in treated and untreated rice husk ash

| Sample | Parameter | Element     | Percentage (%) |
|--------|-----------|-------------|----------------|
| TRHA   | Temperature : 90 ºC | Silicon (Si) | 77.97          |
|        | Time : 60 min | Iron (Fe)   | 0              |
|        | Concentration : 3% | Oxygen (O)  | 11.80          |
|        |               | Platinum (Pt) | 10.23        |
| URHA   |           | Silicon (Si) | 57.76          |
|        |              | Iron (Fe)    | 11.19          |
|        |              | Oxygen (O)   | 15.51          |
|        |              | Platinum (Pt) | 15.54        |

Fig. 1. SEM images and EDX result by 5000x magnification and size particle 30μm a) URHA, b) TRHA (Temperature: 90ºC, Time: 60 min, Acid Concentration: 3%)

3.2 Effect of acid concentration

In leaching treatment process, acid concentration is one of the crucial parameters in order to obtain the best result. Generally, the content of silica will rise with the increasing of acid concentration, but when it reaches a certain level, it will remain almost constant.

Table 3 shows the solution temperature of acid citric and stirring time was 90 ºC and 60 minutes, respectively. The Si content dramatically increased from just 57.76% in URHA up to 77.97% after undergoes leaching treatment. RHA undergoes leaching treatment with 3% citric acid concentration result in Si content was 77.97%, while for 1% was 75.69%. Moreover, the metallic element especially Fe was fully eliminated with 1% and 3% of citric acid solution where the temperature and stirring time fixed. Thus, it is shown that citric acid leaching treatment is significantly useful and effective in removal of Fe from rice husk ash.
Table 3. Mass element (%) by energy dispersion x-ray (EDX) of rice husk ash with different citric acid concentration.

| Citric Acid Concentration | Mass Element (%) | Si     | Fe    | O     | Pt    |
|---------------------------|------------------|--------|-------|-------|-------|
| 3%                        |                  | 77.97  | 0     | 11.80 | 10.23 |
| 1%                        |                  | 75.69  | 0     | 14.80 | 9.51  |
| URHA                      |                  | 57.76  | 11.19 | 15.51 | 15.54 |

3.3 Effect of stirring time

The stirring time was varied from 30 minutes to 90 minutes, while fixing the solution temperature (90 ºC) and acid concentration (3%). Table 4 shows that the Si content increased with the increasing of stirring time. The Si content slightly increased from 74.67% to 77.97% when the stirring time increased from 30 minutes to 60 minutes. However, no significant increase in silica content was observed at a longer stirring time more than 60 minutes, so 60 minutes was confirmed to be the optimal stirring time.

Table 4. Stirring time (minutes) effect on the mass element content by fixing the solution temperature and acid concentration.

| Stirring Time (min) | Mass Element (%) | Si     | Fe    | O     | Pt    |
|---------------------|------------------|--------|-------|-------|-------|
| 30                  |                  | 74.67  | 0.21  | 15.27 | 9.85  |
| 60                  |                  | 77.97  | 0     | 11.80 | 10.23 |
| 90                  |                  | 77.97  | 0     | 11.80 | 10.23 |
| URHA                |                  | 57.76  | 11.19 | 15.51 | 15.54 |

3.4 Effect of solution temperature

Table 5 shows the chemical composition of rice husk ash via citric acid solution treatment under different solution temperature. The solution of citric acid concentration of 3% and reaction time of 60 minutes were used.

The use of high temperatures can lead to an increase in the leaching performance as shown in Table 5, but the use of high temperatures was seen to be limited with organic acids due to their low boiling temperatures and decompositions [4]. Table 5 shows that with increase in the temperature, the content of Fe was decreased from 11.19% to 0.14% and Si content increased from 57.76% to 77.78% took place via the citric acid solution leaching at 70 ºC while at 90 ºC was 77.97% with elimination of Fe. It can be concluded that using higher temperature in the process will improve the leaching result.

Table 5: Effect of various solution temperature.

| Solution Temperature (ºC) | Mass Element (%) | Si     | Fe    | O     | Pt    |
|---------------------------|------------------|--------|-------|-------|-------|
| 70                        |                  | 77.78  | 0.14  | 9.68  | 12.40 |
| 90                        |                  | 77.97  | 0     | 11.80 | 10.23 |
| URHA                      |                  | 57.76  | 11.19 | 15.51 | 15.54 |
3.4.1 Phase analysis

Fig. 2 illustrates the XRD patterns of untreated and treated rice husk ash. As seen from XRD peaks, Fe$_2$O$_3$ peak was disappeared in treated rice husk ash samples. It is shown that citric acid leaching process can be used in removal of Fe from rice husk ash.

By calcination temperature of 800°C all rice husk ash having a monoclinic crystal system and amorphous phase with peak intensity of broad smooth hump at the 2θ angle of 15º to 25º on Fig. 2. The feature of amorphous material, indicating that pyrolysis converted the crystalline cellulose structure to amorphous, random, disordered structure and potentially capable of adsorption [6]. This phase analysis result was similar to other researcher’s result whereby the broad hump peak was indicating presence of SiO$_2$. No sharp peak was observed. As a result, the identification of amorphous SiO$_2$ was confirmed in rice husk ash.

![XRD result](image)

**Fig. 2.** XRD result with 2θ degree indicated sample a) solution temperature: 90 ºC, stirring time 90 min and 1% citric acid solution, b) solution temperature: 90 ºC, stirring time 60 min and 3% citric acid solution and c) solution temperature: 90 ºC, stirring time 90 min and 3% citric acid solution

4 Conclusion

This study had shown that it is practicable to remove iron (Fe) from rice husk using organic acid leaching process. Citric acid leaching process are reliable and efficient. The mass of Si element can reach up to 77.97% with optimum leaching conditions which were 3% citric acid solution, 90 ºC solution temperature and 60 minutes of stirring time.

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