INNSPUB

International Journal of Biosciences | IJB |
ISSN: 2220-6655 (Print) 2222-5234 (Online)
http://www.innspub.net
Vol. 18, No. 6, p. 228-232, 2021

RESEARCH PAPER OPEN ACCESS

# Silica and other nutrient contents of agricultural wastes at different pre-extraction methods

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**Key words:** Boiler ash, Carbonized rice hull, Extraction methods, Rice hull ash

http://dx.doi.org/10.12692/ijb/18.6.228-232 Article published on June 30, 2021

## Abstract

This study was conducted to determine the potential of agricultural wastes such as rice straw, rice hull and boiler ash as a source of silica and other nutrients for crop production and determine the best extraction technique to form a liquid fertilizer from the wastes. Laboratory study on the most efficient silica extraction technique was conducted. It was laid out in a factorial Completely Randomized Design (CRD) with two factors and four replications. First factor includes the different agricultural wastes; rice straw, carbonized rice hull (CRH), rice hull ash (RHA) and boiler ash and the second factor includes extraction techniques such as yeast fermentation (control), acid, and enzyme and acid pre-treatments combined. In terms of silica extraction, acid pre-treatment and fermentation is shown to be the most efficient and CRH has the highest silica content and acceptable pH level; hence, further study on the efficiency of this technique and the CRH liquid extract was recommended.

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## Introduction

Silica ($SiO_2$) is one of the valuable inorganic multipurpose chemical compounds and the most abandon material on the earth's crust (Todkar *et al.*, 2016). However, various extraction or industrial processes involving raw materials in the manufacture of pure silica require high temperature facilities (more than 700°C), thus energy intensive. This study explored simple chemical processes for extraction of silica that use non-conventional raw materials such as agricultural wastes e.g. rice straw, boiler ash and rice hull that poses disposal problems in the long term. These materials can be used for the production of silica especially rice hull and boiler ash. As for rice hull, it is rich in silica (about 60%) and can be an economically variable material for the production of silica gels and powders (Thuadaij and Nuntiya, 2008). Rice straw is also one of the potential silica sources containing approximately 13.1% silica (De Souza *et al.*, 2002). The potential production of silica from these agricultural wastes could be of importance in the future if further studied. Furthermore, methods of silica extraction is now being considered and studied worldwide and some of the results revealed that acid pre-treatment of samples is the most efficient in silica extraction (Dawan & Medrano, 2020).

Although silicon is not considered as an essential element for plant growth, its beneficial effects on the growth, development, yield and disease resistance have been observed in a wide variety of plant species (Ma, 2002). This study therefore ought to prove that silicon is present from the extract of different agricultural wastes. The study generally aimed to extract silica from different agricultural wastes and utilize these materials for silica-rich liquid fertilizer development. Specifically, it aimed to; determine silicon available in different agricultural wastes and identify the best treatment and pre-treatment techniques in silicon extraction.

## Materials and methods

### *Sample collection and preparation*

The rice hull and straw samples were collected in a commercial rice mill and rice paddy, respectively in Cagumitan, Tuao West, Cagayan. While the boiler ash samples were collected at Cagayan Sugar Mill Corporation (CARSUMCO) in Sto. Domingo, Piat, Cagayan. The different agricultural waste samples were collected (dried during collection) and air-dried for two weeks in a room temperature. Rice straw was chopped into 2-3cm length and dry-blended using osteorizer. The rice hull was subjected to carbonization and ashing through complete combustion more than 700°C by the use of furnace. After complete combustion, rice hull ash and the other samples were prepared for pre-treatment extraction and fermentation.

### *Experimental design and treatments*

The study was laid out in a factorial completely randomized design (CRD) with two factors such as four agricultural wastes (rice straw, rice hull ash, carbonized rice hull and boiler ash) and three extraction techniques [yeast fermentation (control), acid pre-treatment and acid pre-treatment & fermentation]. In treatment 1, the samples had undergone yeast fermentation. In treatment 2, the samples were pre-treated with 75% sulfuric acid and neutralized using 25% NaOH (Zhang *et al.*, 2006). For treatment 3, the samples were first pre-treated with 75% sulfuric acid and neutralized using 25% NaOH and subjected to fermentation (Frantz *et al.*, 2008). Each fermented samples was pasteurized at 60°C for 30 minutes. The samples were subjected to laboratory analyses for the determination of macro and micronutrient contents.

### *Laboratory analysis*

All the chemical analysis of the actual agricultural waste samples and the produced liquid extracts such as pH, total macronutrients (N, P, & K) and total micronutrients (Zn, Cu, Mn & Fe) was carried out at the Analytical Services Laboratory (ASL) of the Department of Agriculture - Cagayan Valley Integrated Analytical Laboratory (DA-CVIAL), Tuguegarao City, Cagayan, except for the silica ($SiO_2$) content analysis. Standard methods for chemical laboratory analyses were followed. Samples for silica content analysis were submitted to ChemPro Laboratory in Pasig City following the standard protocol on sample preparation and submission.

*Statistical analysis*

The data were analyzed using STAR (Statistical Tool for Agricultural Research) to determine the difference between treatment means at 5% level of significance by least significant difference (LSD).

## Results and discussion

*Macro- and micro-nutrient contents of the agricultural wastes*

Chemical properties of the agricultural wastes before they were subjected to different extraction techniques are shown in Table 1. As presented, the major composition of rice straw is Zn as compared with the other wastes under study. Rice hull ash, carbonized rice hull and boiler ash are composed mainly of $SiO_2$ (90.5, 92.4 and 40.6%, respectively). These results revealed that $SiO_2$ is the main compound expected to be present in the liquid extracts (Table 2). Moreover, there is a notable amount of total Fe in boiler ash (178.6g•kg$^{-1}$) and total Zn in rice straw (31.0g•kg$^{-1}$). However, these values were not reflected in the composition of the liquid extracts (Table 2). These could be attributed to the sources of these agricultural wastes.

**Table 1.** Chemical composition of the agricultural wastes (g kg$^{-1}$).

| Chemical Properties | Agricultural waste samples | | | |
|---|---|---|---|---|
| | Rice straw | Rice hull ash | Carbonized rice hull | Boiler ash |
| Total N | 1.05 | 0.22 | 0.44 | 0.22 |
| Total P | 0.05 | 0.51 | 0.18 | 0.60 |
| Total K | 1.73 | 0.71 | 0.63 | 1.43 |
| Total Zn | 31.0 | 0.21 | 2.65 | 1.05 |
| Total Cu | 13.0 | 0.60 | 0.03 | 0.44 |
| Total Mn | - | 1.71 | 0.94 | 0.64 |
| Total Fe | - | 7.60 | 0.64 | 178.6 |
| $SiO_2$ (%) | 13.0 | 90.50 | 92.40 | 40.60 |

*Chemical composition of the liquid extracts from agricultural wastes*

*Macronutrient content*

Macro-nutrient contents of the extracts from agricultural wastes as affected by the different extraction techniques are shown in Table 2. Based on the results, no significant differences were observed among the treatments in terms of macronutrient contents (N, P and K). Total N values were generally low with 0.22% except for rice straw extracted using combined acid pre-treatment and fermentation (0.44%). Total P ranged from 0.09 to 0.21% and did not meet the minimum standard for total macronutrient of 2%. Moreover, very low total K levels ranged from 0.03 to 0.33%.

*Liquid extracts' pH*

In terms of pH (Table 2), the extracts that can be utilized for crop production are those derived from rice straw using the three extraction techniques; yeast fermentation, acid pre-treatment, and acid pre-treatment with fermentation (7.31, 6.76 and 7.30, respectively), extracts from rice hull ash using acid pre-treatment and fermentation (6.95), and extracts from carbonized rice hull using acid pre-treatment (7.64) and combination of acid pre-treatment and fermentation (7.01).

*Micronutrient content*

Also shown in Table 2 are the micronutrient and $SiO_2$ contents of the liquid extracts. No significant differences were observed among the treatments in terms of micronutrient contents (Zn, Cu, Mn and Fe). Very low total Cu (0.01% generally) and total Zn content (0.01 to 0.02%) was noted for all the samples tested. Relatively higher total Mn content was noted in rice straw extracts using the three methods tested. Total Fe was also noted to be relatively higher in rice hull ash under yeast fermentation and acid pre-treatment although values are not significant.

*$SiO_2$ content*

In terms of $SiO_2$ content (Table 2 con...), significant effect of acid pre-treatment was noted. For rice straw sample extracts, acid pre-treatment showed significantly highest $SiO_2$ of 7.93%. However, this is comparable with the analysis of rice hull ash and carbonized rice hull extracts using acid pre-treatment (6.65%) and combined acid pre-treatment and fermentation, respectively (7.73%). Based on standard percentage required by plants, total silica content optimum level should at least be 5% (Fernandez *et al.*, 2013). In this study, it was found out that acid pre-treated rice hull ash and combined acid pre-treated and fermented carbonized rice hull extracts can be a good source of silica. However, based on the level of pH, only carbonized rice hull (CRH) extract (pH = 7.01) can be used for growing crops compared with the other extracts.

**Table 2.** Chemical composition of the liquid extracts from agricultural wastes as influenced by the extraction techniques.

| Treatment | Chemical composition | | | | |
|---|---|---|---|---|---|
| | pH | Total N,% | Total P,% | Total K,% | Total Zn,% |
| *Rice Straw* | | | | | |
| Yeast fermentation | 7.31 b | 0.22 a | 0.10 a | 0.22 a | 0.02 a |
| Acid pre-treatment | 6.76 b | 0.22 a | 0.10 a | 0.33 a | 0.02 a |
| Acid pre-treatment and fermentation | 7.30 b | 0.44 a | 0.11 a | 0.03 a | 0.01 a |
| *Rice Hull Ash* | | | | | |
| Yeast fermentation | 8.23 ab | 0.22 a | 0.16 a | 0.03 a | 0.02 a |
| Acid pre-treatment | 9.08 a | 0.22 a | 0.11 a | 0.06 a | 0.02 a |
| Acid pre-treatment and fermentation | 6.95 b | 0.22 a | 0.14 a | 0.03 a | 0.02 a |
| *Carbonized Rice Hull* | | | | | |
| Yeast fermentation | 8.13 ab | 0.22 a | 0.09 a | 0.06 a | 0.03 a |
| Acid pre-treatment | 7.64 b | 0.22 a | 0.13 a | 0.06 a | 0.02 a |
| Acid pre-treatment and fermentation | 7.01 b | 0.22 a | 0.21 a | 0.33 a | 0.02 a |
| *Boiler Ash* | | | | | |
| Yeast fermentation | 8.08 ab | 0.22 a | 0.11 a | 0.11 a | 0.01 a |
| Acid pre-treatment | 8.79 ab | 0.22 a | 0.13 a | 0.14 a | 0.01 a |
| Acid pre-treatment and fermentation | 8.59 ab | 0.22 a | 0.15 a | 0.14 a | 0.02 a |

In a column for each property measured, means followed by the same letter are not significantly different at 5% level of significance.

**Table 2** continued.

| Treatment | Chemical composition | | | |
|---|---|---|---|---|
| | Total Cu,% | Total Mn,% | Total Fe,% | $SiO_2$,% |
| *Rice Straw* | | | | |
| Yeast fermentation | 0.01 a | 0.16 a | 0.14 a | 3.47 b |
| Acid pre-treatment | 0.01 a | 0.29 a | 0.13 a | 1.95 b |
| Acid pre-treatment and fermentation | 0.01 a | 0.30 a | 0.08 a | 7.93 a |
| *Rice Hull Ash* | | | | |
| Yeast fermentation | 0.01 a | 0.01 a | 0.25 a | 1.22 b |
| Acid pre-treatment | 0.01 a | 0.01 a | 0.25 a | 6.65 a |
| Acid pre-treatment and fermentation | 0.01 a | 0.01 a | 0.07 a | 3.68 b |
| *Carbonized Rice Hull* | | | | |
| Yeast fermentation | 0.01 a | 0.01 a | 0.07 a | 1.99 b |
| Acid pre-treatment | 0.01 a | 0.02 a | 0.08 a | 2.49 b |
| Acid pre-treatment and fermentation | 0.01 a | 0.01 a | 0.06 a | 7.33 a |
| *Boiler Ash* | | | | |
| Yeast fermentation | 0.01 a | 0.02 a | 0.06 a | 2.71 b |
| Acid pre-treatment | 0.01 a | 0.01 a | 0.06 a | 2.56 b |
| Acid pre-treatment and fermentation | 0.01 a | 0.01 a | 0.06 a | 2.45 b |

In a column for each property measured, means followed by the same letter are not significantly different at 5% level of significance.

## Conclusion

The use of acid pre-treatment and fermentation in silica extraction was found to be effective for agricultural waste such as carbonized rice hull; however, other macro- and micronutrients are recommended to be supplemented in addition to these extracts when tested to field crops to evaluate its potential effects.


## Acknowledgement

The authors would like to thank Cagayan State University (CSU) for providing financial support in the conduct of this research, and also to the tireless efforts of CSU Piat research office personnel namely: Maurine Bayubay and Roselene Layugan.

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