Silica extraction from integrated refinery of rice straw for production of value-added products

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Abstract. Rice straw is an agricultural residue from rice production, which can be a potential lignocellulosic feedstock for various value-added products. In this study, silica was extracted from the rice straw. The biomass was pre-treated with ethanol and was cooked with 18% w/w sodium hydroxide to extract lignin and silica. The silica was precipitated from the alkaline solution using 30% sulfuric acid to pH 11.5 and was recovered through centrifugation. The obtained solid was washed and then combusted at 575 °C for 6 hours. The obtained ash was dissolved in sodium hydroxide solution at pH 8.0 and then re-precipitated by sulfuric acid to form silica powder, which obtained a yield of about 6.7% w/w dry rice straw. The characteristics of amorphous disk-formed silica, determined using XRD, SEM, EDS, and FT-IR.

1. Introduction
Rice straws used to be burned in the field for having no known use, which causes environmental pollution. This spurred interests to utilize them in the production of biofuels, chemicals, and new materials. In many rice-producing countries, rice straw is burned for energy production, which when combined can provide 14% of the world’s energy [2,19,20]. In this study, extraction of the high-value added product, silica, from rice straw is achieved.

Rice straw has a high content of inorganic substances, ranging between 10-17% w/w dry material. Several chemical analyses of rice straw and rice husk from different rice varieties grown in Vietnam and other countries have confirmed the abundant presence of amorphous silica, which has several applications [4,18,21]. Compared with other agricultural residues such as bamboo and sugarcane bagasse, rice straw cellulose has higher silica content. The ash produced from the combustion of rice straw contains about 75% silicon [1].

Extraction of the bio-silica involves burning followed by alkaline and acid treatment [5-7, 13-18]. However, methods for silica recovery from the biomass has major limitations and drawbacks [8], such as low extraction efficiency and low purity because other organic compounds are extracted as well. Furthermore, bio-treatment of rice straw for enhanced silicon recovery requires complex pre-treatment [9], which may not be financially viable for large-scale production due to high costs and use of uncommon microorganisms.

Rice straw has a high content of waxes [10], which interferes with silica recovery, but has a high value and market. Therefore, an integrated production of silica, waxes, lignin, and cellulose can be applied to boost the feasibility of rice straw processing, compared with the method of Prehydrolysis-Kraft Pulping [11].
The study utilized the whole rice straw biomass by integrated refining of all its components. The products obtained were cellulose, lignin, extractives, and organic silica. Without pre-treatment, alkaline extraction of silica was more difficult. The study showed that removal of waxes using ethanol, prior alkaline extraction, resulted in higher silica recovery efficiency.

2. Materials and methods

2.1. Material

*Oryza sativa* L. rice straw, harvested on October 2017 from the Red River Delta of Vietnam, was used for the experiments. The dry rice straw was grinded and screened to prepare the suitable sample that was retained on 24 mesh screen for experiments. The suitable particle sizes for rice straw pretreatment should be smaller than 0.7 cm and bigger than 0.07 cm. The prepared biomass was stored in plastic bags at room temperature. It was not washed before ethanol extraction and alkaline treatment.

Rice straw was prepared by TAPPI method T264 cm-97 for analysis of chemical composition, which was determined as follows: cellulose content 39.7% (TAPPI T17 wd-70); lignin content 17.2% (TAPPI T222 om-98); pentosane 24.3% (TAPPI T223); extractives in ethanol 4.2% (TAPPI T204); ash 13.5% (TAPPI T211 om-93); and 1% sodium hydroxide solubility of Wood and Pulp (TAPPI T212) and hot water solubility 18.3% (TAPPI T207).

2.2. Ethanol extraction of Rice Straw

For each experiment, about 300 grams of prepared rice straw was extracted by ethanol at 50°C for 120 minutes, with a solid/liquid ratio of 1/12 (w/v). It was done in a 5-L stainless reactor, which was heated in a water tank. Pre-extracted rice straw was washed, dried, and used for silica preparation by alkaline treatment.

2.3. Silica preparation from extracted Rice Straw

Fifty grams of ethanol-extracted rice straw was treated with sodium hydroxide solution with a solid/liquid ratio of 1/10 in a 1-L stainless steel tank which was heated in a glycerine tank. Sodium hydroxide dosage, temperature, and processing time were adjusted according to the aims of each experiment. Alkaline-treated rice straw was pulped for 5 minutes and then filtered to collect the black liquor (alkaline solution) and cellulose.

The alkaline solution was then treated with 30% sulfuric acid to pH 11.5 for silica precipitation, and then to pH 3.0 for lignin precipitation. The precipitates were then filtered, washed, dried, and analyzed. The silica powder recovered was burned at 575°C to obtain the ash, which was then dissolved using sodium hydroxide solution to pH 8 under heat, and filtered to remove the insoluble components. The filtered solution was diluted using sulfuric acid to precipitate silica. Silica suspension was centrifuged, and the pellet was washed and dried for the determination of yield and analysis of product properties.

Amorphous structure of silica dioxide was determined using XRD and FT-IR. The chemical composition of silica powder was determined by EDS. A form of silica particles was studied by FE-SEM JEOL JSM-7600F.

3. Results and Discussion

As known, rice straws are covered by a layer of lipophilic extractives [10], such as waxes, which are insoluble in water. During chemical processing, these hydrophobic layers make it hard for alkaline or acidic solutions to penetrate inside the plant cell walls. Meanwhile, silica compounds can glue with these compounds, forming a layer on the surface of the straw. Therefore, the compounds of straw are hard to separate. These properties were key to the separation of these compounds. To improve the efficiency of silica recovery, the rice straw was pre-treated with ethanol prior extraction. Besides being able to obtain extractives, the cell walls were easier to penetrate, improving silica removal from straw. It is a new method, different from the previous studies.
The objective of this study is to determine the appropriate conditions for separation and purification of silica dioxide from straw. The extractives and cellulose are valuable by-products of the process.

3.1. Alkaline treatment of Rice Straw

The pre-treated rice straw was treated with 5-25% w/w sodium hydroxide solution at 60°C for 180 minutes. Residual solid was washed, dried, and combusted, and the ash was collected for analysis. The alkaline solutions were treated with H₂SO₄ 30% to pH 11.0 to obtain the inorganic substances.

The determination of the ash content of alkaline-treated rice straw showed that to significantly separate the inorganic matter from the straw, the sodium hydroxide solution must be more than 15% w/w (Figure 1). The maximum yield for extracted inorganic substances was achieved using an alkaline concentration of 18% (w/w), obtaining 82% of ash. The residual solid collected in this setup was 48.3% w/w, which indicated that lignin and carbohydrate were dissolved in the alkaline solution. Compositional analysis of the residual solid showed that 72.4% were lignin and 26.6% were carbohydrates.

![Figure 1. Effect of alkaline dosage on the yield of dissolved inorganic substances. Conditions: treatment time of 180 min and treatment temperature of 60°C](image)

The effect of temperature on the yield of inorganic substances indicated that with the same time span and alkaline concentration, treatments at temperatures greater than 60°C were ineffective (Figure 2). On the other hand, treatments at temperatures less than 60°C gave a lower yield of inorganic substances. For instance, samples subjected to 50°C and 40°C only yielded 40% and 30% inorganic substances, respectively. This showed the significant effect of temperature on the degradation and dissolution of components during alkaline treatment.
Fig. 2. Effect of temperature on the yield of dissolved inorganic substances. Conditions: NaOH dosage of 18% (w/w), treatment time of 180 min.

Dissolution of inorganic substances and other organic components from rice straw into the alkaline solution requires some time. However, longer treatment time does not always translate to being more effective. From the experiments, it was observed that within the first 90 minutes, 40% of the total inorganic substances was dissolved. This amount doubled in the next 60 minutes before it reached the “threshold” (Fig. 3). Sufficient treatment time is required to swell the straw, for the alkaline solution to seep through the cell walls via osmosis, and for the inorganic substances to diffuse outwards through the cell wall.

Fig. 3. Effect of treatment time on yield of dissolved inorganic substances. Conditions: NaOH dosage of 18% (w/w), temperature of 60°C.

The suitable conditions of alkaline treatment for the extraction of silica, containing some inorganic substances, from rice straw were fixed using a solid/liquid ratio of 1:10, sodium hydroxide concentration of 18% w/w dry rice straw, temperature of 60°C, and treatment time of 150 mins.
3.2. Silica Preparation
For silica preparation, 1.0 kg of ethanol-pre-extracted rice straw was treated with sodium hydroxide at suitable conditions to obtain about 7.2 liters of silica containing alkaline liquor. Afterward, it was treated with sulfuric acid 30% at 60°C to pH 11.5-11.6. At this pH value, lignin has not precipitated yet. These conditions are required for the effective preparation of silica. The precipitate was then filtered, washed, dried and burned at 575°C for 3 hours. The grey-white ash produced was dissolved in sodium hydroxide solution at 100°C for 3 hours, then treated by sulfuric acid 25% at pH 6.0. The solution was centrifuged, and the pellet produced was dried to obtain the amorphous silica. These conditions for silica preparation have been optimized by a series of experiments.

Preparation of silica from non-pre-extracted rice straw has been carried out following the same method, except pre-treatment. A higher yield of 6.7% w/w was obtained with the ethanol-pre-treated rice straw compared to the 2.2% of the non-pre-treated samples.

The X-ray diffraction of silica (Figure 4) showed a broad peak between 20° and 30°, centered at 22.5°, typical of the amorphous silica [12]. EDS and XRD data gave clear evidence of the high purity of the collected amorphous silica, which was extracted from pre-treated rice straw.

EDS analysis confirmed that the as-derived product contained Si and O at a (52%:38%) mass ratio. These amorphous mesoporous silica disks have great potential to be prepared and utilized as molecular sieves, catalyst preparation, absorbents, etc.

![Figure 4. Characterization of silica powder: XRD (A), EDS (B), and FTIR (C)](image-url)
Scanning Electronic Microscopy (Figure 5) showed that the silica powder agglomerates were of the size 6-8 micrometer. Due to the nonconductive nature of silica, the charges quickly accumulate on the powder surfaces, even with gold sputtering, showing visible artifacts and limiting resolution.

Figure 5. SEM micrographs of silica from pre-extracted rice straw

Figure 6 shows the flow chart of the overall process of isolation of cellulose and by-products from the rice straw integrated refinery.

The ethanol-dissoluble extractives are interesting compounds, which can be used as a preservative for wood and other applications. Unbleached cellulose is used for bioethanol and nanocellulose production. Lignin can be precipitated by sulfuric acid after silica.

Compared to other methods, this scheme of refinery allows for maximum utilization of all the components of rice straw.
4. Conclusion
The modern method of lignocellulosic refineries strives to tackle the problem of agricultural wastes by the effective utilization of all the components. This study has identified ethanol pre-extraction as the best method for the removal of inorganic substances in rice straw cell walls, improving the recovery of silica, through sodium hydroxide treatment.

The sequential extraction method in alkaline solution is an efficient process for the isolation and purification of silica and lignin from rice straw.

Recovery of silica from the black liquor obtained from rice straw alkaline pulping can be considered as one of the achievements in the field of agricultural residues refining. The successful extraction of purified silica confirmed the viability of the method presented herewith in obtaining this value-added product for the rice straw refinery.

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