

SHORT, NON-REFEREED PAPER

## ORGANIC ACID TREATMENT OF SUGARCANE RESIDUES FOR THE PRODUCTION OF BIOGENIC SILICA

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### Abstract

Biogenic silica was extracted from sugarcane leaves through an organic acid thermo-chemical treatment method. Two sugarcane leaves batches were investigated: one batch with a midrib and the other without the midrib. Both produced amorphous silica with high purity (> 90 % (m/m) silica) but their textural properties were distinctly different. The sugarcane leaves were leached with 7 % (m/m) citric acid at 80 °C for two hours prior to being washed, dried in the oven for 24 hours and burned using a four step programme ranging from room temperature to 873 K in a furnace. The characterisation of the final products was performed by X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), nitrogen sorption and Elemental Analysis (CHN). The produced white ash had an insignificant amount of carbon and the pore structure was mainly formed by mesopores.

*Keywords:* sugarcane, sugarcane leaves, biogenic silica, amorphous silica, mesoporous, thermo-chemical treatment.

### Introduction

Plants are classified as either silica accumulators or silica non-accumulators. Sugarcane and other types of *Gramineae* (grasses) are considered silica accumulators (Le Blond *et al.*, 2010). While silica is present in plants in an amorphous state, isolated silica can be either amorphous or crystalline, depending on several factors like the temperature, pressure and the rate of cooling. Crystalline silica has three most stable varieties: cristobalite, tridymite and quartz (Parks *et al.*, 1999). Amorphous silica in sugarcane has been reported to be partially converted to crystalline silica at 1283 K, therefore the burning temperature was a crucial factor. Amorphous silica was used in a variety of organometallic and inorganic materials as a major precursor. This work focuses on the use of sugarcane leaves for the production of amorphous biogenic silica using citric acid. Citric acid is an organic acid and more environmentally friendly, economical and ecological compared to inorganic acids.

### Materials and Methods

Sugarcane farmers in Durban, South Africa supplied the sugarcane leaves. Upon collection, the leaves were dried in the oven overnight. The leaves were then separated into two batches: one batch had the midrib removed (the vein in the middle of the leaf blade) and was labelled LWOMR. The other batch was used with the midrib still attached and was labelled LWMR. Each batch of leaves was cut down into small pieces prior to any treatment. In separate

experiments, the batches of cut sugarcane leaves were each leached with 7 % (m/m) citric acid at 353 K for two hours. After the hot citric acid leaching, the leaves were rinsed with deionised water to remove excess acid. The leaves were then dried in the oven at 323 K for 24 hours.

After 24 hours, the dried leaves were subjected to sequential burning in a furnace. The burning programme consisted of different temperatures and holding times, as follows: 30 minutes at 583 K, 60 minutes at 723 K, 210 minutes at 783 K and, lastly, 30 minutes at 873 K. After the burning and cooling of the ash, the resulting samples were labelled LWOMRA-CA and LWMRA-CA for leaves with and without midrib, respectively.

### **Characterisation**

A Vario EL micro analyser system (Heraeus, Hanau, Germany) was used for an elemental analysis. The elemental composition of the samples was determined using an X-ray fluorescence (XRF), Bruker S4 Explorer WDRFA, Germany. For this purpose, 0.75 g of the sample was mixed with 0.25 g of a wax powder. The mixture was ground to form a fine powder prior to being pressed with a hydraulic press (PerkinElmer, Germany) at 10 tons for two minutes to produce a cylindrical pellet with 20 mm diameter.

The phase identification was carried out using a Seifert XRD 7 apparatus that was equipped with Ni-filtered, Cu -K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The surface morphology was studied by scanning electron microscopy (SEM) using an Ultra 55 (Zeiss, Jena, Germany) that was operated at 5 keV. Nitrogen sorption analysis was used to determine the textural properties of the biomass samples. This was carried out using an ASAP 2010, Micromeritics, Norcross, GA, USA, where the Brunauer-Emmett-Teller (BET) model in the relative pressure of the range of (P/P<sub>0</sub>) between 0.05 and 0.25 was used to evaluate the specific surface area and the value of 0.162 nm<sup>2</sup> was used for a cross section of a nitrogen molecule (Brunauer *et al.*, 1938). The desorption branch of the isotherm was used to determine the pore size distribution by using the Barret-Joyner-Halenda (BJH) method (Barrett *et al.*, 1951).

## **Results and Discussion**

### **Elemental, chemical and phase analysis of sugarcane leaves ash samples**

The chemical analysis results from XRF analysis are shown in the Table. The pre-treatment of both batches of leaves resulted in a white ash that was high in silica and a significant reduction of the total content of the other metal oxides (potassium oxide, calcium oxide, magnesium oxide, ferric oxide, aluminium oxide, and potassium oxide) and chlorine, which are regarded as impurities. These impurities were removed from the sugarcane leaves via the chelating reaction between metal cations and carboxyl groups (-COOH) of the citric acid (Alyosef *et al.*, 2013). It can be observed from the Table that the silica content in both the leaves samples increased to 95 % (m/m) and 95.4 % (m/m) for leaves with and without the midrib, respectively. Chlorine was almost completely removed from both samples while the other impurities were significantly reduced. The organic materials in the biomass such as cellulose and hemicellulose are hydrolised by the citric acid and this enabled the carboxyl groups of the leaching agent to pass through the monosaccharides to chelate the metallic impurities (Umeda and Kondoh, 2010).

An XRD analysis was used to identify the two different phases of the produced biogenic silica. The x-ray diffraction pattern of both sugarcane leaves confirmed that the silica formed was amorphous with almost no traces of crystalline phases.

**Table 1: Chemical analysis of the inorganic components of sugarcane leaves samples determined by xrf.**

Constituent	LWMRA-Raw [mass%]	LWMRA-CA [mass%]	LWOMRA-Raw [mass%]	LWOMRA-CA [mass%]
SiO <sub>2</sub>	62.7±0.4	95.0±0.3	63.8±0.5	95.4±0.3
P <sub>2</sub> O <sub>5</sub>	1.1±0.1	0.7±0.0	1.4±0.1	0.4±0.0
K <sub>2</sub> O	3.4±0.1	0.40.0	3.8±0.1	0.2±0.0
CaO	15.3±0.1	1.7±0.0	14.9±0.1	2.6±0.0
MgO	1.7±0.1	0.6±0.0	1.5±0.1	0.4±0.0
SO <sub>3</sub>	4.8±0.1	0.8±0.0	4.5±0.1	0.8±0.0
Fe <sub>2</sub> O <sub>3</sub>	2.7±0.0	0.1±0.0	2.3±0.0	0.1±0.0
Al <sub>2</sub> O <sub>3</sub>	3.6±0.1	0.5±0.0	3.1±0.1	0.1±0.0
Cl	1.8±0.1	0.0±0.0	1.7±0.1	0.0±0.0
Others*	2.9±0.0	0.2±0.0	3.0±0.0	0.0±0.0

\*Other measured inorganic oxides

### **Textural properties**

The leaves without the midrib had the largest BET surface area of 323 m<sup>2</sup>g<sup>-1</sup> compared to 238 m<sup>2</sup>g<sup>-1</sup> for the leaves that did not have the midrib removed. The average pore diameter (measured through a BJH method) of the biogenic silica produced from sugarcane leaves that had the midrib removed was 5 nm and this material also possessed the largest pore volume of 0.41 cm<sup>3</sup>g<sup>-1</sup>.

The pore size distribution of the biomass ash samples was also determined using nitrogen sorption. The biogenic silica from both sugarcane leaves has a pore size distribution that is mostly in the mesoporous range.

The surface structure of the produced biogenic silica was examined by SEM analysis. The ash samples from both leaves resulted in similar SEM images which indicated that the morphological structures of an ash produced from sugarcane leaves has a backbone or stem shape with varying diameters.

### **Conclusions**

Pre-treatment of South African sugarcane leaves with citric acid has been demonstrated to be an effective method of removing the inorganic impurities while increasing the silica content in the ash. White ash with a purity more than 95 % (m/m) SiO<sub>2</sub> (or porous amorphous silica) can be successfully obtained from South African sugarcane leaves. The biogenic silica obtained from South African sugarcane leaves has a narrow size distribution of 2 – 10 nm in the mesopore range. Biogenic silica of the leaves without the midrib resulted in a higher BET surface area of 323 m<sup>2</sup>g<sup>-1</sup> as compared to 238 m<sup>2</sup>g<sup>-1</sup> for the leaves with the midrib. The obtained ash from the South African sugarcane leaves was purely amorphous with no traces of crystalline silica.

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