

EXTRACTION OF SILICA FROM SUGARCANE LEAVES FOR SYNTHESIS OF ZEOLITE AS ETHYLENE ADSORBENT TO PRESERVE FRESH FRUIT

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Abstract

Sugarcane is widely grown in the Northeastern region of Thailand. The sugarcane leaves are usually eliminated before harvesting by burning, producing PM 2.5 as air pollutant. Here, we explore an approach to produce high-purity silica from the sugarcane leaves by leaching with hydrochloric acid (2.0 M) and subsequent calcination at 500°C for 4 h. The obtained silica is in an amorphous phase. The silica purity is 83.4 ± 0.9 wt.%, better than the product without acid leaching (18.5 ± 0.2 wt.%). Then, the silica was used in the synthesis of zeolite by hydrothermal method. The obtained zeolite has LTA as a major phase, zeolite NaX and SOD as minor phases. The zeolite has a high ethylene-adsorbed volume of $5.26 \text{ cm}^3/\text{g}$, comparable to the reported value in the literature. Consequently, the zeolite synthesized from the sugarcane leaves silica is a promising adsorbent to preserve fresh fruit.

Keywords: Ethylene adsorption; Silica; Sugarcane leaves; Zeolite LTA; Zeolite NaX

Introduction

Sugarcane (*Saccharum Officinarum*) is one of the most important crops in Thailand. The stalks are valuable for sugar production, whereas the leaves have low value. Farmers usually remove the leaves before the harvest by burning them, producing PM 2.5, which is currently a serious pollution problem in Thailand. Consequently, finding ways to use sugarcane leaves is considered to lessen the problem.

One inorganic component in sugarcane leaves is silicon (Si) (Tsai *et al.*, 2000). Typically, the

silicon from bio-resources could be extracted by acid leaching and calcination to produce silicon dioxide or silica (SiO_2) (Bunmai *et al.*, 2018). Silica has been utilized in many products and applications such as semiconductor materials, personal care, pharmaceutical, food and zeolite synthesis (Kow *et al.*, 2014). High purity silica can be employed as a silicate precursor in zeolite synthesis. An example is zeolite X in sodium form (NaX) with Si/Al ratio around 1.0-1.5, which is employed as a catalyst and adsorbent because it has a large surface area and

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uniform pore size, thermal stability and moderate acido acid-base property (Manadee *et al.*, 2017; Rongchapo *et al.*, 2018). Such outstanding properties make zeolite a potential adsorbent for gases including carbon dioxide (CO₂), propane (C₃H₈), ethane (C₂H₆) and ethylene (C₂H₄) (Moises *et al.*, 2013). The interest of this work is to adsorb ethylene which is naturally produced by plant hormones and accelerates fruit ripening (Coloma *et al.*, 2014). The adsorption of ethylene could slow down the ripening and prolong the shelf-life of the fruits. Besides, the presence of aluminium in the framework of zeolite NaX results in a net negative charge which requires charge balancing cation such as Na⁺. The charge is beneficial for ethylene adsorption because it could interact with π electron of ethylene (Sue-aok *et al.*, 2010). Moreover, the CH groups could interact with the framework oxygen of zeolite.

The goal of this work is to extract silica from sugarcane leaves and utilize it for the synthesis of zeolite for ethylene adsorption. The synthesis is performed with the gel of NaX. Then, the ethylene adsorption capacity of zeolite from sugarcane leaves is compared to that of commercial zeolite.

Materials and Methods

Materials

Fresh sugarcane leaves were collected from a sugarcane field around Suranaree University of Technology. Chemicals utilized in this work were sodium aluminate (NaAlO₂, 95%, Sigma-Aldrich), sodium hydroxide (NaOH, 97%, Carlo Erba), and hydrochloric acid (HCl, 37%, Merck).

Silica Extraction

The extraction of silica from sugarcane leaves was adapted from the literature (Bunmai *et al.*, 2018). Briefly, the fresh sugarcane leaves were dried at room temperature for a week, cut into small pieces, approximately 3-5 mm and dried in a hot-air oven at 80°C for 12 h. After that, 30 g of dried sugarcane leaves were refluxed in 400 mL of HCl (2.0 M) at 90°C for 3 h, cooled down, filtered and washed with deionized (DI) water until the filtrate was neutral. The refluxed leaves were dried at 90°C for 12 h and calcined at 500°C for 4 h. The powder yield was calculated by equation (1)

$$\text{Powder yield} = \frac{\text{weight of calcined sugarcane leaves}}{\text{weight of dried sugarcane leaves}} \times 100 \quad (1)$$

Synthesis of zeolite by using silica from sugarcane leaves

Zeolite from sugarcane leaves was synthesized from the gel composition of NaX, with the molar

ratio of NaAlO₂: 4SiO₂: 16NaOH: 120H₂O modified from the literature (Jantarit *et al.*, 2020). The first step was the preparation of a Na₂SiO₃ solution. A solution containing 14.62 g of Na₂SiO₃ was prepared by mixing of 4.10 g the silica, 1.61 g NaOH pellet and 8.92 g DI water (deionized water) together in a 250 mL polypropylene bottle. Then, the mixture solution was vigorously stirred for 18 h to produce a clear solution. Next, 9.08 g of NaOH pellet and 1.36 g of NaAlO₂ as an aluminum source were added into 87.95 g of DI water and the mixture was stirred for 30 min. Then, the Na₂SiO₃ solution and the mixture of NaAlO₂ were mixed together and further stirred for 1 h. Finally, the reaction gel was crystallized at 90°C for 24 h under a static condition. The resultant products were washed with DI water and separated by centrifugation. The washing process was carried on until the measured pH of the supernatant is about 7. After the washing, the samples were dried at 110°C for 24 h.

Characterization of silica and zeolite from sugarcane leaves

Elemental compositions of the calcined product from sugarcane leaves, with or without acid leaching, were determined by energy dispersive X-ray fluorescence spectroscopy (ED-XRF) on Horiba (model XGT 5200) (Osakoo *et al.*, 2020). Each sample (0.35 g) powder was pressed on a sample holder to produce a smooth outer surface. The measurement was achieved by using the Rh X-ray tube operated with a current of 1 mA and a voltage of 30 kV, and equipped with the Peltier-cooled silicon drift detector (SDD). Phases of calcined product from acid-leached sugarcane leaves and zeolite were studied by X-ray diffraction (XRD, Bruker D2 ADVANCE) using Cu K α X-ray generated with a current of 30 mA and a potential of 30 kV.

The chemical composition of the zeolite sample was determined by inductively coupled plasma with optical emission spectroscopy (ICP-OES) on a Perkin Elmer, Optima 8000. The samples were prepared by acid digestion method and then diluted to a final volume of 100 mL (Rongchapo *et al.*, 2018).

Ethylene Adsorption

The ethylene amount was determined by temperature-programmed desorption of ethylene (C₂H₄-TPD) in a Belcat-B equipped with a thermal conductivity detector. An adsorbent weight of 50 mg was packed in a tubular U-shaped quartz cell, pre-treated at 300°C under a flowing of He gas (50 mL/min) for 3 h and cooled to 50°C. Then, a constant flow of 50 mL/min of C₂H₄/Ar gas mixture was introduced for 30 min to saturate the



Figure 1. Texture appearance of sugarcane leaves: (a) after leaching with 2.0 M HCl; (b) after calcination and (c) XRD pattern of solid powder after acid leaching and calcination

adsorbent. Afterward, it was purged with He for 3 h to remove the excess amount. Finally, the C_2H_4 -TPD measurement was performed from 50 to 500°C with a heating rate of 10°C/min with He as a carrier gas. The adsorbed volume of ethylene was calculated by integrating the peak area of ethylene desorption from 50°C to 800°C compared with the calibration of the actual amount of ethylene against the area of TCD response (Manadee *et al.*, 2017).

Results and Discussions

Silica from sugarcane leaves

The texture appearance of the dried sugarcane leaves after leaching with HCl and calcination is displayed in Figures 1a and 1b, respectively. The color of sugarcane leaves after leaching is dark brown due to the decomposition of hydrocarbon compounds (Chindaprasirt and Rattanasak, 2020). The product after the calcination is white, the typical color of silica powder. The result implies that carbon compounds in the sugarcane leaves are mostly removed.

The XRD pattern of the white powder after acid leaching and calcination is shown in Figure 1c. The pattern shows a broad peak at 22°, corresponding to amorphous silica (Kow *et al.*, 2014). This result agrees with Bunmai *et al.* (2018) that the extracted silica from a bio-silica source is mainly in an amorphous phase. This amorphous silica is suitable for zeolite synthesis because it can be dissolved easily in NaOH solution to produce a silicate precursor for zeolite synthesis. Furthermore, the solid yield from sugarcane leaves in this work is around 1 wt.%, similar to Le Blond *et al.* (2010). The silica yield of 0.45 to 1.8 wt% was obtained from the raw leaf samples. The difference in silica contents results from their natural biological composition (Kow *et al.*, 2014).

Silica purity

The chemical compositions in oxide forms of the calcined sugarcane leaves, with and without refluxing determined by ED-XRF, are demonstrated

Table 1. Chemical composition determined by ED-XRF of calcined sugarcane leaves

Component	Without refluxed mass (wt.%)	Refluxed mass (wt. %)
SiO ₂	18.5 ± 0.2	83.4 ± 0.9
CaO	24.7 ± 0.6	11.5 ± 0.2
K ₂ O	49.3 ± 0.5	4.6 ± 0.3
MnO ₂	3.4 ± 0.06	0.5 ± 0.1
Cl	2.1 ± 0.2	nd
Fe ₂ O ₃	0.9 ± 0.05	nd
SrO	0.5 ± 0.05	0.1 ± 0.01
Rb ₂ O	0.2 ± 0.01	nd
ZnO	0.3 ± 0.01	nd

Table 2. Comparison of silica purity in the present work to literature

Sample	Extraction method	Silica purity (wt.%)	Reference
Sugarcane leaves ash	Alkali fusion method	77.8	Arumugam and Ponnusami, 2015
Sugarcane bagasse ash	Leached in HCl (2.5 M) at 25°C for 2 h	66.3	Chindaprasirt and Rattanasak, 2020
Sugarcane leaves (not refluxed)	Calcined at 500°C	18.5 ± 0.2	This work
Sugarcane leaves (refluxed)	Leached in HCl (2.0 M) at 90°C for 3 h and calcined at 500°C	83.4 ± 0.9	This work

in Table 1. The unrefluxed sample contains K₂O, CaO and SiO₂ as the main components with a small amount of other inorganic oxides, including MnO₂, Fe₂O₃, ZnO, Rb₂O and SrO. On the other hand, the refluxed sample has a silica purity of 83.4% and the other contents are significantly decreased. Thus, acid leaching improves the silica purity because metal oxides are dissolved easily in the HCl solution with the formation of chloride salt solutions (Chindaprasirt and Rattanasak, 2020). In addition, the purity of silica from sugarcane leaves in the present work is higher than that in the literature (77.75 and 66.3 wt.%) (see Table 2.) (Arumugam and Ponnusami, 2015; Chindaprasirt and Rattanasak, 2020). Although it is treated in HCl (2.0 M), trace amounts of other components such as

CaO and K₂O are still observed, indicating a moderate efficiency of acid leaching with HCl (2.0 M). Thus, the silica purity may be improved by either leaching with a higher HCl concentration or prolonged leaching time.

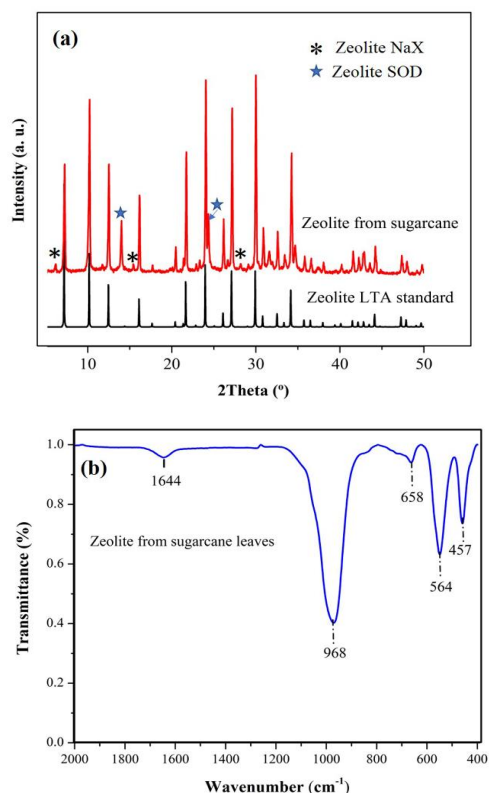


Figure 2. XRD pattern (a) and FTIR spectrum (b) of zeolite from sugarcane leaves

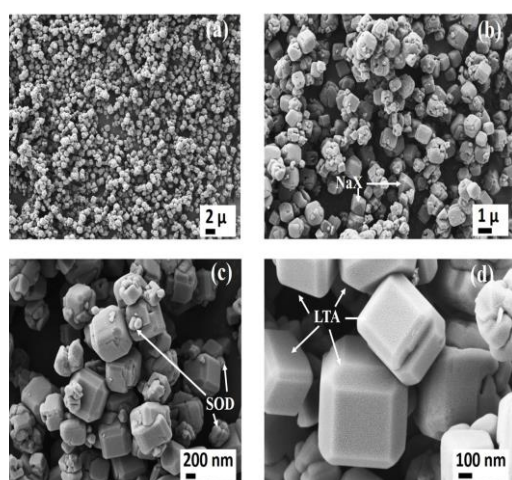


Figure 3. SEM images of zeolite from sugarcane leaves with various magnifications: (a) 1K, (b) 5K, (c) 10K and (d) 30K

Zeolite from Sugarcane leaves

The XRD pattern and FTIR spectrum of the zeolite synthesized with silica from sugarcane leaves are presented in Figures 2a and 2b, respectively. The XRD pattern has peak positions similar to those of zeolite LTA standard with strong intensities. However, there were peaks with low intensities corresponding to zeolite NaX and SOD.

Thus, we can conclude that zeolites from acid-leached and calcined sugarcane leaves have LTA zeolite as the major phase and NaX and SOD zeolites as the minor phases (Li *et al.*, 2016; Jantarit *et al.*, 2020). The existence of mixed phases could result from impurities such as CaO in the silica source in the synthesis. This remark agrees well with the report from Zhang *et al.* (2011). They suggested that a small amount of CaO residue presented in the mixture of the gel NaX behaves as an inhibitor in the synthesis of zeolite NaX. The calcium ion could compete with sodium cation to occupy the cationic sites of the zeolite. The consequence promotes the formation of LTA and SOD zeolites.

The FTIR spectrum in Figure 2b consists of the bands at 968, 658 and 457 cm⁻¹, attributing to asymmetric stretching of internal tetrahedral, symmetric stretching and bending mode of T–O–T bonds in TO₄ tetrahedra (T = Si or Al) in zeolite structure, respectively. Moreover, the band at 546 cm⁻¹ is assigned to D4R vibration, the main secondary building unit in LTA zeolite (Li *et al.*, 2016). The band at 1644 cm⁻¹ contributes to the vibration of OH groups from adsorbed water. The FTIR spectrum confirms that the dominant phase of the zeolite is LTA, consistent with the XRD result.

The Si/Al ratio of commercial NaA and zeolite from sugarcane leaves, determined by ICP-OES, is 1.00 and 1.51. The larger value in zeolite from sugarcane leaves is caused by the presence of mixed phases of NaX, LTA and SOD zeolites, respectively.

The SEM images with various magnifications are exhibited in Figures 3a-3d. The zeolite morphology comprises mainly cubes with cut edges (octadecahedron) and size around 800 nm, consistent with the sharp edges of ideal LTA zeolite (Ballabh *et al.*, 2006). Notably, there are small spherical particles corresponding to the morphology of SOD zeolite decorated on LTA particles (Figures 3b and 3c). Moreover, the trace amounts of octahedral shape particles, attributing to the morphology of NaX zeolite are observed (Figure 3b) (Janrarit *et al.*, 2020). Hence, the SEM result confirms that zeolite from sugarcane leaves has mixed phases of LTA as the major phase, NaX and SOD as minor phases, in good agreement with the XRD result.

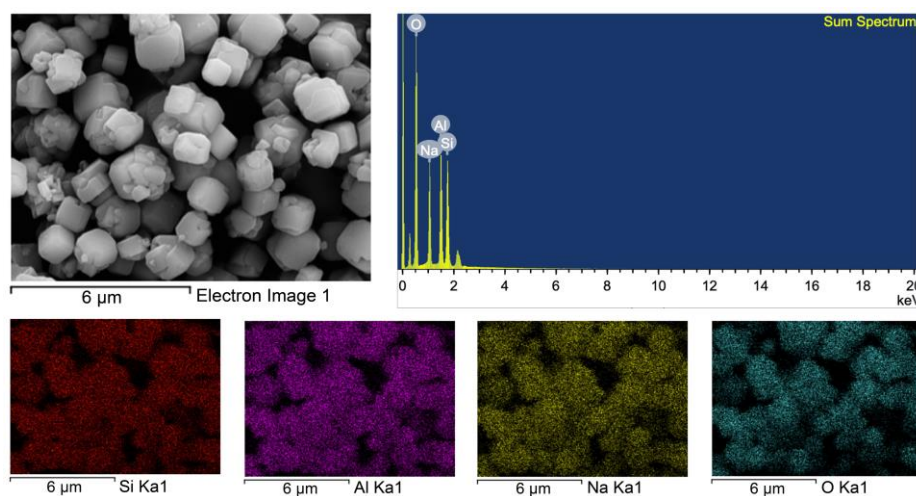


Figure 4. SEM-EDS mapping-images and EDX spectra of zeolite from sugarcane leaves

SEM-EDS mapping images and EDX spectra of elemental compositions in zeolite from sugarcane leaves are demonstrated in Figure 4. Si, Al, O, and Na atoms dispersed homogeneously throughout the particles of zeolite. This result suggests that these elements are indeed inside the structure of zeolite from sugarcane leaves. One should realize that Ca and K species remaining in the silica source after refluxing in HCl (2.0 M) were not observed in the structure of the zeolite. This result is not surprising because these species could be in the form of metal silicate hydrate, inactive species in the zeolite synthesis (Li *et al.*, 2022). Subsequently, they could be removed by washing with water after the zeolite synthesis.

Ethylene adsorption by zeolite NaA from sugarcane leaves silica

The final part is the application of zeolite in the field related to food and agricultural industries. The commercial NaA and zeolite from sugarcane leaves were further tested for ethylene adsorption. Their adsorbed volumes are $5.71 \text{ cm}^3/\text{g}$, and $5.26 \text{ cm}^3/\text{g}$, respectively. The smaller adsorbed volume of zeolite from sugarcane leaves could result from the higher Si/Al ratio. However, the adsorbed volume of zeolite from sugarcane leaves is greater than that of clinoptilolite zeolite (33 wt%) /chitosan composite in the literature ($0.524 \text{ cm}^3/\text{g}$ adsorbent) (Sousa *et al.*, 2020). This result demonstrates that the zeolite from sugarcane leaves is a potential adsorbent for ethylene released from plant hormones in fruits. The ripening of fruits such as bananas can be slowed down when the concentration of ethylene is less than $0.01 \text{ } \mu\text{L/L}$ (Hayama *et al.*, 2006).

Conclusions

Silica yield obtained from sugarcane leaves after leaching in 2.0 M HCl and calcination was $83.4 \pm 0.9 \text{ wt.}\%$, higher than the sample without leaching ($18.5 \pm 0.2 \text{ wt.}\%$). The silica was further used in the zeolite synthesis from the initial gel of NaX. The obtained zeolite has mixed phases of LTA as the dominant phase and NaX and SOD zeolites as minor phases. The presence of CaO impurity in the silica source might be an inhibitor in the synthesis of zeolite NaX. The ethylene-adsorbed volume of zeolite from sugarcane leaves was $5.26 \text{ cm}^3/\text{g}$, slightly lower than that of commercial zeolite NaA ($5.71 \text{ cm}^3/\text{g}$). Based on a promising adsorption capacity, the zeolite from sugarcane leaves could be an alternative adsorbent for ethylene to prolong fruit ripening.

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