AFSSAAE

Advances in Food Science, Sustainable Agriculture and Agroindustrial Engineering 2022, 5(2), 138-143
ISSN 2622-5921

ORIGINAL RESEARCH Open Access

Eco-friendly production of silica particles and fertilizer from rice husk, rice straw, and corncob wastes

Rafiq Usdiqa Maulana[1], Sania Isma Yanti[1], Riyanti Zhafirah Makrudi[1], Tunjung Mahatmanto[1]*, Untung Murdiyatmo[2]

[1)] Department of Food Science and Biotechnology, Faculty of Agricultural Technology, Universitas Brawijaya, Malang, Indonesia
[2)] Institute for the Development of Sustainable Agriculture, Indonesia

KEYWORDS

Agroindustrial waste
Eco-friendly process
Fertilizer
Silica particles
Sol-gel method

ABSTRACT

Agroindustrial wastes represent a rich and underutilized source of valuable minerals. Because the amount of biomass wastes generated by the agroindustry is increasing and the demand for sustainability is arising, there is a growing need for improving agroindustrial waste utilization and valorization. One of the major industrial interests has been obtaining silica from biomass wastes. The synthesis of silica from agroindustrial waste materials typically involves the use of high energy input for calcination or incineration and chemicals for extraction. To reduce energy consumption and chemical waste generation, we modified a sol-gel method to yield a by-product that can be used as a fertilizer. High purity silica was obtained from rice husk (95.1%), rice straw (91.4%), and corncob (95.9%). The silica particles were amorphous and white in color. The mean diameters of the silica particles obtained from rice husk, rice straw, and corncob were 72.4, 68.1, and 52.9 µm, respectively. The acid waste generated from the process was neutralized to yield potassium chloride. This by-product had mineral contents that could be used for inorganic fertilizer. In addition to supporting sustainability, the development of agroindustrial waste utilization methods is important for the establishment of inexpensive processes that are adaptable for large-scale manufacturing.

Introduction

Agricultural industries produce large amounts of plant waste biomass that are mainly unused. It is estimated that about 2 billion tons of agricultural wastes are produced worldwide (Millati et al., 2016). The majority of agroindustrial wastes are recalcitrant to degradation and incinerated on site to generate heat and electricity. The ash produced must then be disposed of, typically in landfills, open ground, or underground. This ash waste disposal incurs huge costs to industries. In smaller settings such as local farms, agricultural wastes are typically burned in open air. These common practices are burdening the environment because the toxic residues released can contaminate the air and groundwater. To help reduce this environmental burden, it is imperative that agroindustrial wastes be handled properly. One alternative is to process the wastes in a biorefinery facility where they can be converted into high-value products. Because agricultural wastes are derived from plant materials that store minerals, their ashes typically contain silica, although in varying amounts (Cornejo et al., 2014). The silica derived from plant materials are often referred to as biogenic silica.

The extraction of silica from agricultural waste biomass can be achieved through thermal or chemical processes or their combinations (Patel et al., 2017). Thermal processes may be done by calcination or pyrolysis at high temperatures (e.g., 500–1200°C) for a period of time (e.g., 30 minutes to 19 hours) in a furnace or reactor (Espindola-Gonzales et al., 2010; Yang et al., 2015). Although the conditions can vary, thermal treatment will remove the bulk of the organic matter in the agricultural waste and may yield silica with a low carbon content. On the other hand, chemical processes may be done by acid or alkali or both, before and after the thermal

*Corresponding author
E-mail address: tjmahatmanto@ub.ac.id

Received on 9 May 2022, revised on 10 September 2022, accepted on 6 December 2022

treatment. These treatments can accelerate the hydrolysis of lignocellulosic components contained in the agricultural wastes, remove oxide impurities, and improve the microstructural properties of the ash (Alyosef et al, 2015; Shen, 2017). The selection of the method to obtain silica from agricultural wastes should not only consider the yield and quality of the silica but also the impact of the processes to the environment. Recently, a sol-gel method based on alkali extraction and acid precipitation was developed to reduce the consumption of energy and chemicals for silica synthesis from bagasse ash (Chindraprasirt and Rattanasak, 2020). However, the chemical waste generated from the process has not been dealt with. Here, we modified the sol-gel method to extract silica from three agricultural wastes, i.e., rice husk, rice straw, and corncob ash, to yield potassium silicate as a by-product for use as foliar fertilizer.

Research Methods

Materials

The biomass materials used in this study were rice husk, rice straw, and corncob. The rice husk, rice straw, and corncob were obtained from local farmers in Tuban, East Java, Indonesia. The chemicals used in this study included distilled water, hydrochloric acid (HCl) 37%, and potassium hydroxide (KOH).

Biomass Preparation and Pre-treatment

The preparation and pre-treatment of the biomass materials for silica extraction were done following a method described by Chindapraisit and Rattanasak (2020). Rice husk, rice straw, and corncob were charred using a porcelain dish on an electric stove at ~300°C. The resulting ash was passed through a 100-mesh sieve and collected before pre-treatment. Each biomass ash was weighed and mixed with HCl 1N on a magnetic stirrer for 1 hour at a ratio of 1:10 (50 g biomass ash to 500 mL HCl 1 N) and allowed to stand for 30 minutes to remove minor oxide compounds (metal compounds other than silica). Spent HCl was removed from the pre-treated biomass ash by filtration. The pre-treatment step was performed 3x until the total volume of HCl reached 1.5 L. The 3x pre-treated biomass ash was washed with 1.5 L distilled water and dried in an oven at 110°C for 5 hours. We refer to this sample as pre-treated ash. All liquid waste generated was collected for later use (described below).

Silica Particle Extraction by Sol-Gel Method

Silica was extracted from the pre-treated ash using a sol-gel method as previously described (Cornejo et al., 2014). Briefly, pre-treated ash was mixed with KOH 1 N with a ratio of 1:8 (1 g pre-treated ash to 8 mL KOH) on a magnetic stirrer by reflux method at 90°C for 1.5 hours to extract the silica. The suspension was filtered as above, and the solid residue was washed with boiling distilled water (1x volume of the filtrate) to obtain a solution of potassium silicate. The potassium silicate filtrate was then added with HCl 2.5 N until pH 7.0 and a gel was formed. The gel was aged at room temperature for 18 hours. The aged gel was then washed with boiling distilled water (5x volume of the gel) and filtered on a 200-mesh sieve until the silica gel turned white. The silica gel was dried in an oven at 110°C for 5 hours, ground in a mortar and pestle, and filtered through a 100-mesh sieve to obtain silica powder. The yield of the silica was calculated using the following equation:

$$Yield = \frac{Mass\ of\ silica\ particles}{Mass\ of\ pretreated\ ash}\ x\ 100\% \quad (1)$$

Silica Particle Characterization

Silica particles synthesized from the rice husk, rice straw, and corncob ash were characterized by X-ray diffractometer (XRD) to determine the phase and purity of the silica, X-ray fluorescence (XRF) to determine the elemental composition of the sample, field emission scanning electron microscopy (FESEM) to determine the surface morphology of the particles, and particle size analyser (PSA) to determine the size distribution of the particles.

Waste Treatment

Liquid waste from the extraction process was neutralized with KOH 5 N until pH 7.0 to obtain a by-product that can be used for potassium fertilizer. The elemental composition (K, Si, Mg, Ca, and Fe) of the neutralized waste was analysed using inductively coupled plasma (ICP).

Results and Discussion

Silica Synthesis and Characterization

In this study, silica was extracted from rice husk, rice straw, and corncob ash using KOH and precipitated using HCl. The yield, purity, phase, and size of the silica obtained from the synthesis are given in Table 1.

Table 1. The characteristics of silica obtained from rice husk, rice straw, and corncob

	Rice husk	Rice straw	Corncob
Yield (%)	27.0	26.0	11.0
Purity (%)	95.1	91.4	93.9
Phase	Amorphous	Amorphous	Amorphous
Mean diameter (nm)	72.4	68.1	52.9

Table 2. Oxide composition of silica particles obtained from rice husk, rice straw, and corncob

Compound	Concentration (%)		
	Rice husk	Rice straw	Corncob
SiO_2	95.1	91.4	93.9
K_2O	4.18	7.31	3.13
CaO	0.608	1.21	1.72
Fe_2O_3	0.039	0.042	0.949
MnO	0.030	0.010	0.023
CuO	0.026	0.025	0.032
NiO	0.005	0.012	0.009
Yb_2O_3	0.040	-	0.020
Eu_2O_3	-	0.040	-
TiO_2	-	-	0.072
Cr_2O_3	-	-	0.057
ZnO	-	-	0.023
Re_2O_7	-	-	0.050

The yields of the silica obtained in this study ranged from 11.0 to 27.0%. This variation mainly stems from the different silica content in each material. Rice husk ash contains more than 95% silica whereas rice straw ash contains around 75% and corncob ash around 35% (Cornejo et al., 2014; Nandiyanto et al., 2017). Assuming that these figures apply, this means that the silica extraction efficiency of the method was higher for rice straw (35%) than for corncob (31%) and rice husk (28%). The yields obtained in this study was low compared with the yield obtained by Chindapraisit and Rattanasak (2020), but the purity of the silica was high, all above 90%. The composition of the silica particles obtained is given in Table 2. Besides SiO_2, other metal oxides were present albeit at very low concentrations. One however, was noticeable, i.e., the K_2O. We assume that the majority of this metal oxide came from the alkali treatment that remained after washing, thus additional washing steps could be implemented to improve the silica purity. The other metal oxides detected could arise from the side reactions that occurred during the thermal and chemical treatments.

XRD analysis shows clean spectra with no significant impurities (Figure 1A). The SiO_2 was detected at 23–24° 2θ as broad peaks, indicating that the particles were amorphous. FESEM analysis shows that the microstructure of the silica particles were irregular in shape and size (Figure 1B). PSA analysis shows that the majority of the silica particles was around 120–140 μm in diameters and only fewer than 3% were in the high nanometer range (Figure 1C). Because the yield, purity, and quality of the silica are affected by many factors, including the processing parameters, further studies will be needed to optimize the process conditions to improve these characteristics.

Waste Treatment

The synthesis of silica from rice husk, rice straw, and corncob using the sol-gel method with successive pre-treatment produces a large volume of acid waste. Acid waste without further processing can cause groundwater pollution so that it is damaging to the environment (Pasae et al., 2020). To avoid acid waste pollution that can be damaging to the environment, we neutralized the HCl waste with KOH to produce KCl, a by-product that can be used as a fertilizer. The major elemental composition of the neutralized waste was analysed using ICP and compared with the Indonesian National Standards (SNI) and the Regulation of the Minister of Agriculture (Permentan) for liquid fertilizer. The result is given in Table 3.

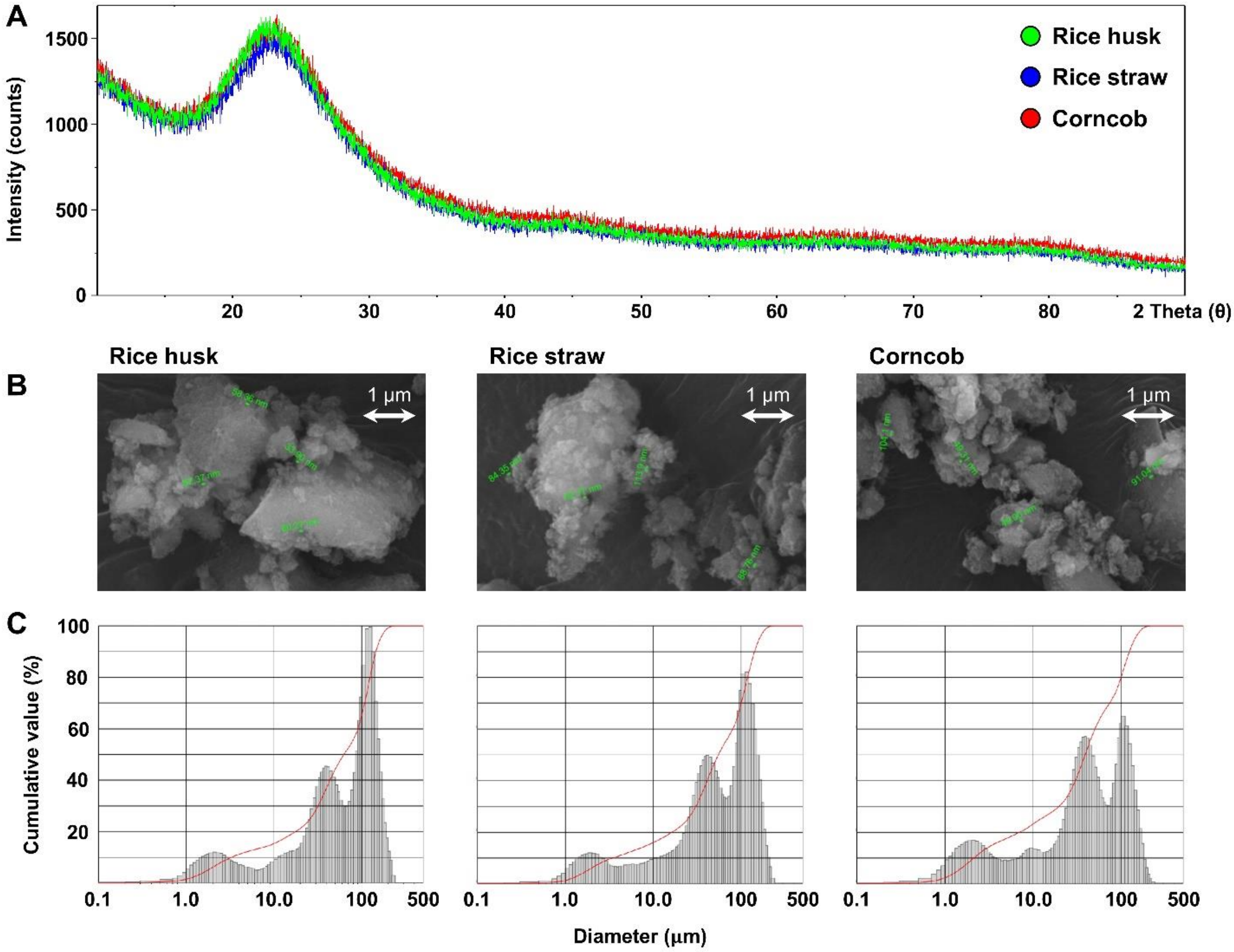

Figure 1. Results from XRD (**A**), FESEM (**B**), and PSA (**C**) analyses show the phase, morphology, and size distribution of the silica particles obtained from rice husk, rice straw, and corncob.

Table 3. Comparison of the neutralized waste minerals with national regulatory standards

Element	Unit	Rice husk	Rice straw	Corncob	Standard
K	mg/L	64.3	95.5	91.5	min. 60*)
Si	mg/L	0.194	0.114	0.216	min. 0.06**)
Mg	mg/L	1.603	5.006	6.02	0.1- 6**)
Ca	mg/L	2.912	3.516	3.13	0.1- 5**)
Fe	mg/L	0.016	0.014	0.018	0.009–0.09**)

*)SNI 02-2805:2005; **)Peraturan No. 43/Permentan/SR.140/8/2011

Based on the ICP result, the neutralized wastes have met the regulatory standards in SNI and Permentan for KCl liquid fertilizer. The parameters used refer to the content of macro and micro nutrients that are essential for plant growth (Ariani et al., 2015).

Potential Applications

From an applied perspective, the production of silica particles using the method described in this study has potential economic feasibility. First, the raw materials used are derived from agro-industrial wastes that are available in large quantities and has negative value due to the cost associated with their disposal. Assuming an average yield of 20%, around 400 million tons of biogenic silica can be produced from 2 billion tons of global rice husk, rice straw, and corncob wastes. Second, the silica synthesis can be performed using a low energy input with an estimated total power consumption of around 2.7 KW/h. This is much lower than commercial silica production, which generally uses expensive raw materials and extremely high processing temperatures that consume huge amounts of power, reaching up to 11–13 MW/h (Mor et al., 2017). Third, the liquid wastes generated from the silica synthesis can be turned into a fertilizer, which makes the process environmentally friendly. Fourth, biogenic silica has potential applications in various fields such as medicine, food, materials, and cosmetics (Vallet-Regi et al., 2018; Indrasti et al., 2020). With industries continuously growing, biogenic silica will be on high demand. This can be seen from the global market for silica that is expected to reach USD 5 billion in 2025 (Al-Ghurabi et al., 2020)

Conclusion

An energy-efficient and environmentally friendly production process has been described to synthesize silica from rice straw, rice husk, and corncob wastes. Although the method still needs optimization, development of processes that reduce energy consumption, generate less wastes, promote agroindustrial waste utilization, and reduce practices that contribute to air and groundwater contamination will, in the long run, create impact on sustainability. Exploration of benign conditions, combination of treatments, and other biomass materials is recommended to facilitate such process developments.

Declarations

Conflict of interests The authors declare no competing interests.

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