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Green Route Synthesis of Amorphous Silica from Oil Palm Decanter Cake: From Literature Review to Experiments

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ABSTRACT

Numerous agricultural wastes are well-defined as low-cost sources and rich in silica content. The residue of oil palm wastes combustion seems a promising silica source and can be recovered through a straightforward method. In this study, the combustion followed by an alkaline extraction method was employed to extract high purity of silica. The oven-dried oil palm decanter cake (DOPDC) was heated at combustion temperatures of 600, 700, 800, and 900°C to produce OPDC ashes (OPDCA), followed by an alkaline extraction using 5M of NaOH solution. Thermogravimetric analysis (TGA) was used to observe the thermal behavior of DOPDC where the suitable combustion temperatures to produce silica ranged between 600 and 1000 °C. X-Ray Fluorescence (XRF) analysis showed that silica contents were 31-36% after combustion, increasing to 76.95% after the chemical treatment. Moreover, the spherical shape of the silica was observed through electron microscope analysis. It was represented by the aggregation of silica after going through chemical treatment. The X-Ray Diffraction analysis also proved that the amorphous silica was produced, characterized by the hump-shaped spectrum. The infrared analysis confirmed that the silica had been successfully extracted from OPDCA by the presence of silica functional groups shown in the spectrum.

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1. INTRODUCTION

Silicon dioxide, also known as silica (SiO_2), is a versatile inorganic element rich in the Earth's crust, mainly as a rock and sand component (Silviana & Bayu, 2018). It can exist in gel, amorphous, or crystalline states, depending on how it was made (Anuar *et al.*, 2020). Amorphous silica is considered a non-toxic and known mesoporous material. Therefore, it is beneficial in various industrial applications such as energy storage, composite materials, photochromic pigment, bio-adsorbent, catalysts, bio-medical materials, biodiesel purification, thin-film or coating materials for electronic and optic materials, ceramics, thermal insulation, chromatography, pharmaceutical products, detergents, adhesives, and anti-corrosion agent (Channoy *et al.*, 2018; Chindaprasirt & Rattanasak, 2020; Mosisa *et al.*, 2019; Naqvi *et al.*, 2011). The other good properties of amorphous silica are it has high pozzolanic, reactivity, specific surface area, chemical inertness, and hardness compared to crystalline, making it preferable to be extracted for multi-purpose applications (Bangwar *et al.*, 2017; Kow *et al.*, 2016; Liang & Zhang, 2020).

The commercialized silica source, known as tetraethyl orthosilicates (TEOS), can be used to synthesize high-purity of silica (Costa *et al.*, 2019). Unfortunately, producing this silica requires a high thermal hydrolysis process, which is energy-consuming, expensive, CO_2 release, and generation of a vast amount of wastewater (Prempeh *et al.*, 2021). Due to these reasons, agricultural wastes were favorable as viable alternative sources to synthesize silica economically while minimizing waste generation (Abdul Samat *et al.*, 2021). Agricultural wastes such as rice husk (RH), wheat husk (WH), corn cob (CC), bamboo leaves (BL), sugarcane bagasse (SB), coconut husk (CH), and oil palm wastes such as palm ash (PA), empty fruit bunches (EFB), and palm kernel shell (PKS) had been explored as low-cost and silica-rich sources (Terzioglu *et al.*, 2019). These wastes mainly consist of 50-90% of silica and possess a comparable quality, high energy content, and finely sized amorphous material (Patel *et al.*, 2017). Silica materials are necessary for plants. They can intensify the plant defense response against disease, protect plants against insect pests, enhance plant photosynthesis and growth, prevent lodging, alleviate water and mineral toxicity stresses, and improve fertilizer use efficiency (Agostinho *et al.*, 2017).

Oil palm decanter cake (OPDC) is a vast by-product produced from crude palm oil (CPO) production in palm oil mills. It is generated via three-phase separation steps in the decantation process. This process is purposedly to recover the remaining CPO from the underflow of the oil clarification settling tank and reduce the sludge material in palm oil mill effluent (POME) before undergoing biological treatment (Adam *et al.*, 2014). Physically, OPDC exists as a brown-blackish paste made up of oil palm debris (Raeze *et al.*, 2017). About 4-5 wt.% of OPDC was generated from the feed fresh fruit bunches (FFB), comprising over 70% of moisture and 12% of residual oil. At the same time, the remaining contains cellulose, lignin, inorganic (ash residue), and organic material (nitrogen, phosphorus, and potassium) (Sahad *et al.*, 2014; Yusoff *et al.*, 2019). The vast amount of OPDC has poorly created an environmental problem since it is usually disposed of and neglected at the factory side, which is expected to decompose without any treatment. Previous studies have explored alternative use of OPDC as animal feed, fertilizer, or composting material (Yahya *et al.*, 2010), biofuel (Razak *et al.*, 2013), biogas fermentation (Eko & Chaiprasert, 2020; Tepsour *et al.*, 2019), bio-adsorbent of heavy metals from wastewater (Yusoff *et al.*, 2019), cellulose extraction, and crude oil recovery (Anuar *et al.*, 2018; Sahad *et al.*, 2014).

Recently, numerous research has employed several green synthesis methods of silica from agricultural wastes, mainly

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involving thermochemical conversion. Usually, the agricultural wastes will be heated at a high combustion temperature (500-900°C) for a certain period (2-8 hours) depending on the waste amount, followed by chemical treatment, such as acid leaching and alkaline extraction (precipitation or sol-gel method) (Anuar *et al.*, 2018).

The synthesis of silica from CC was investigated by precipitation method using three different organic acids: citric acid, acetic acid, oxalic acid, and a combined solution (50% of each) of citric acid and acetic acid, followed by combustion at 550℃ for 2 hours. The comparison study found that citric acid precipitation resulted in the highest yield of silica (Saleem *et al.*, 2014). A comparative study was conducted on RH.

The silica was prepared from the RH using four different chemicals: sulfuric acid, hydrogen chloride, oxalic acid, and ionic liquid (1-butyl-3-methylimidazolium hydrogen sulfate). The precipitated silica was then dried and pyrolyzed in the muffle furnace at 800°C for 24 hours. Chemical treatment with sulfuric acid and ionic liquid produced the highest silica purity of 99.6% and 99.5%, respectively, without affecting its surface properties (Lee *et al.*, 2017).

High purity of silica was produced from CH throughout a study by Anuar *et al.* (2018). The CH was initially ashed at a high combustion temperature (500-700°C) for 2 hours in an electric furnace. The ash produced was further treated using acidic treatment (sulphuric acid) and alkaline treatment (sodium hydroxide). The results displayed that the silica purity of up to 90% after the chemical treatments was employed on the ash.

Alves *et al.* (2017) extracted the silica from sugarcane waste ash (SWA). Alkaline leaching was applied in which this ash was used to produce a sodium silicate solution before adding the acetic acid to form silica gel. Next, gel formation was conducted by the aging process at 80°C for 1 hour. They observed that the silica purity in SWA increased from 81.6 to 99.1% after alkaline treatment was subjected.

Throughout these findings, the green route synthesis of silica from agricultural waste captured much interest with the conjunction of the "waste-to-wealth" concept. However, a limited study was shown on the recovery of silica from OPDC itself. Hence, the objective of this study was to investigate the OPDC as a potential source through the alkaline extraction method.

To determine the silica properties, a few characterizations were conducted, namely Thermogravimetric Analysis (TGA), X-Ray Fluorescence (XRF), Field Emission Scanning Electron Microscopy (FESEM), and X-Ray Diffraction (XRD). Synthesis of silica from OPDC via alkaline extraction seems promising since it helps reduce the environmental problem due to the increase of OPDC in mill sites, a simple, cost-effective method.

2. LITERATURE REVIEW

The green approach to synthesizing silica from agricultural wastes has been crucial since it is cheaper, safer, and environmentally friendly than commercialized silica (Nandiyanto *et al.*, 2017). The high purity of bio-based silica has been proven equivalent to commercialized silica, leaving its potential in multi-applications. Amorphous silica is preferable to crystalline silica because the arrangement of Si and O atoms is random and short-range. After all, it easily deforms and tends to be reactive to other materials. Meanwhile, crystalline silica owns a long-range order in which the structure becomes more rigid and robust (Lunt *et al.*, 2018). **Table 1** shows various silica synthesis methods studied from multiple silica sources. Silica synthesis methods such as combustion, chemical treatments (acid, alkaline, sol-gel), hydrothermal, and ultrasonic spray pyrolysis were highlighted in the previous studies.

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Table 1. Synthesis methods of silica from various sources and their applications.

Silica sources	Extraction method	Nature phase	Application	References
Commercialized silica	Hydrothermal	Crystalline (Quartz)	Precursor material for zeolite	Prihastuti & Kurniawan, (2022)
Commercialized silica	Ultrasonic spray pyrolysis	Amorphous	-	Stopic *et al.* (2021)
Corn leaf	Acid treatment followed by combustion	Amorphous	Precursor material for zeolite	Kurniawan *et al.* (2022)
Rice husk	Fluidized bed combustion	Amorphous	Refractory ceramics	Sobrosa *et al.* (2017)
Rice husk	Ionic liquid	Amorphous	-	Chen *et al.* (2013)
Rice husk	Acid and ionic liquid	Amorphous	Adsorbents for metallic impurities	Lee *et al.* (2017)
Rice husk	Acid treatment followed by combustion	-	Bio-composites	Battegazore *et al.* (2017)
Coconut husk	Combustion followed by acid treatment	Crystalline (tridymite)	Optical	Anuar *et al.* (2020)
Sugarcane bagasse	Combustion followed by alkaline treatment	Amorphous	Dye adsorbent	Rovani *et al.* (2018)
Sugarcane bagasse	Sol-gel	Amorphous	Photochromic pigment filler	Chindaprasirt & Rattanasak (2020)

Those methods may help increase silica's productivity with better quality, which can be applied for multi-purpose applications in the industry. Traditionally, the production of silica precursor in the form of sodium silicate (Na_2SO_3,) is achieved by heating quartz sand and sodium carbonate (Na_2CO_3) at a high temperature of 1300°C. This process is energy-extensive (Terkula *et al.*, 2017). Hence, selecting the economical extraction method of silica is essential to reduce production costs.

3. METHODS

3.1. Materials

Fresh OPDC was collected from the palm oil mill Felcra Nasaruddin, Perak. All chemicals such as sodium hydroxide (NaOH) and concentrated sulphuric acid (H_2SO_4, purity 95-97%) were purchased from Merck. Distilled and deionized water was applied for all extraction and treatment processes.

3.2. Pre-treatment of Silica

Fresh OPDC was oven dried at 105°C overnight to eliminate the moisture content and impurities at a low temperature. The oven-dried OPDC (DOPDC) was ground into finer particles by a heavy-duty blender and sieved using a < 300 µm mesh tray. About 100 g of DOPDC was further heated at high combustion temperatures of 600, 700, 800, and 900°C for 5 hours in the muffle furnace to produce OPDC ash (OPDCA). The OPDCA obtained was further subjected to chemical treatments.

3.3. Alkaline Extraction of Silica

The OPDCA was added to 140 mL of 5 M NaOH solution. Then, the solution was boiled at 100°C for an hour while constantly stirring to dissolve the silica and produce sodium silicate (Na_2SiO_3). The mixture was cooled down for a moment and filtered through Whatman No. 41 ashless filter paper.

The filtrate was then titrated with 2.5 M H_2SO_4 solution under constant stirring until pH 6-7, and a wet white precipitate solution was obtained. The wet white precipitate solution was then thoroughly filtered and rinsed a few times using deionized water to remove the excess soluble impurities. The

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wet white precipitate in gel form was further subjected to oven-dried at 50°C for 2 hours to obtain powdered silica.

3.4. Physicochemical Characterization Analysis

OPDCA was characterized by performing the TGA and the derivative thermogravimetric (DTG) analysis. The TGA was conducted at 25-1000°C and a heating rate of 20°C/min under an ambient atmosphere. The temperature range where an almost constant final weight was obtained indicated the suitable combustion temperatures for the OPDCA production. The elemental composition of silica was analyzed by XRF spectroscopy (Model: S8 Tiger, Bruker) through elemental oxide mode. FESEM (Model: Supra 55VP, Zeiss) was used mainly to observe the surface morphology of the silica. It was operated under 10k magnification.

This model was fully equipped with the Energy Dispersive X-Ray (EDX), allowing for mapping the elements on the surface of the samples. Phase identification of the produced silica was performed using an XRD equipped with High score Plus software (Model: Xpert3 Powder, Panalytical).

The XRD analysis was done using Cuk-α radiation at 45.0 kV and 40.0 mA over the range of angle (2θ) of 10 to 100° with a scan step of 0.026°. The functional groups of silica were identified using a Fourier Transform Infrared (FTIR) spectroscopy (Model: SHIMADZU). The spectra were recorded with 32 scans at a resolution of 4 cm^{-1} in the range of 400-4000 cm^{-1}.

4. RESULTS AND DISCUSSION

4.1. Thermal Behavior Analysis

TGA was performed to investigate the thermal behavior of DOPDC, represented by TG-DTG curves shown in **Figure 1**. The curves provide information about the temperature at which DOPDC loses its weight due to moisture loss or is ignited to leave the required minerals. Hence, the weight loss for DOPDC was determined at each stage.

At stage 1, the initial weight loss of about 11.45% occurred at a temperature between 22.7 and 250°C. This slight weight loss was most likely due to the evaporation of bound water and other light volatile substances during the first heating. The amount of moisture may influence the physical characteristics and quality of liquids when biomass is heated to higher reaction temperatures during pyrolysis; dry feedstocks create very viscous oils (Ragadhita & Nandiyanto, 2022).

At stage 2, a broad peak obtained within the temperature range of 250-600°C represented a rapid and significant weight loss of about 72.49%. In this temperature range, the volatilization of organics occurred through decomposition. Those organics included hemicelluloses, cellulose, and lignin from their natural forms of fiber debris, EFB, trunks, and kernel shells.

The decomposition of hemicellulose and cellulose was attributed to peaks 1 and 2, respectively, while lignin was represented by peak 3 as shown by the DTG pattern in **Figure 1** (Rahib et al., 2019; Nath et al., 2021). Moreover, the weight loss rate increased due to the high oxygen content in the biomass, which shifted the volatilization to a lower temperature (Dewayanto *et al.*, 2015). Generally, hemicellulose volatilization occurs at low temperatures (200-400°C). The decomposition of cellulose and lignin follows it at high temperatures (400-1000°C) (Ninduangdee *et al.*, 2015; Sahad *et al.*, 2014). Despite that, factors such as age and type of plantation may influence the differences in thermal degradation temperature of hemicellulose and cellulose (Yahaya *et al.*, 2017).

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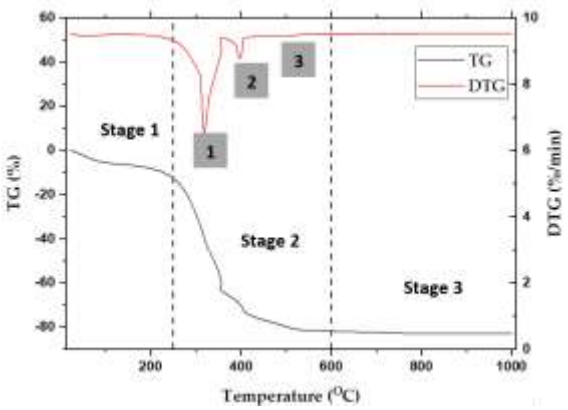

Figure 1. TG-DTG spectrum of the DOPDC after overnight dried.

Stage 3 occurred when the temperatures reached 600°C and were observed constant until 1000°C. In this stage, the remaining fraction contained carbonaceous residues and the OPDCA, which might contain inorganic elements, including silica (Bakar *et al.*, 2016). Further analysis was conducted to emphasize the biomass waste conversion into ash consisting of multi-elements, which then enhance this ash through a chemical treatment to determine changes in physical or chemical properties.

4.2. Ash Production

The combustion of DOPDC was performed in the muffle furnace at four different temperatures 600, 700, 800, and 900°C for 5 hours, producing ash known as OPDCA. The observation results on the ash color change are displayed in **Figure 2**.

The brown-blackish color of DOPDC turned into milky white ash after the combustion temperature was subjected to 600, 700, 800, and 900°C for 5 hours. It can be observed that the amount of ash produced decreased at higher temperatures. The weight loss occurred because the combustion volatilized the existing organic contents in the OPDC, as seen from the TG analysis results. Thus, less carbon was deposited in the ash, making it appears white as the temperature increased. (Sahiron *et al.*, 2017).

Ash is a solid residue mainly consisting of mineral oxides such as K_2O, Na_2O, CaO, MgO, Fe_2O_3, Al_2O_3, SiO_2, and P_2O_5. They are the residue of a combustion process after the volatile organic fraction leaves the agricultural wastes due to excessive heating (Holubcik et al., 2016). Moreover, the formation of ash also tends to be reactive in the presence of alkali metals that can be easily converted into new compounds, resulting in the slagging and fouling issue of the equipment (Pintana & Tippayawong, 2016; Vamvuka et al., 2011). Hence, the scientific community has extensively explored the conversion of ash consisting of minerals into valuable end products due to its content and properties.

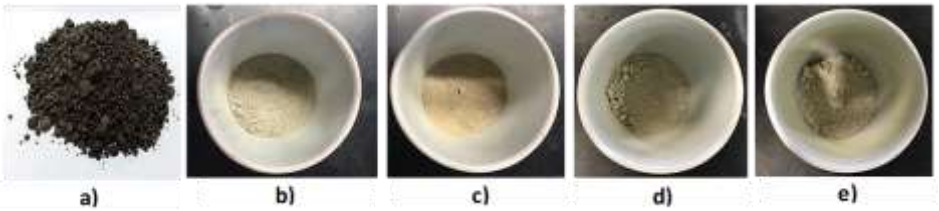

Figure 2. The observation of powder color. Figure (a) is a sample for DOPDC105 (heated at 105°C), Figure (b) is a sample for OPDCA600 (heated at 600°C), Figure (c) is a sample for OPDCA700 (heated at 700°C), Figure (d) is a sample for OPDCA800 (heated at 800°C), and Figure (e) is a sample for OPDCA900 (heated at 900°C).

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4.3. Chemical Analysis

The elemental composition of OPDCA at combustion temperatures 600, 700, 800, and 900°C was investigated through XRF analysis and the results are displayed in **Table 1**. A significant change was shown throughout the XRF analysis for all inorganic elements. The percentage composition of elements such as SiO_2, CaO, P_2O_5, and Al_2O_3 displayed an increment in percentage, while K_2O, Fe_2O_3, SO_3, and other trace elements showed a reduction in the percentage of their composition. This trend liaised with the previous finding by Anuar et al. (2018) after going through the combustion process.

Ultimately, the combustion process occurred at four different temperatures (600-900℃), increasing the SiO_2 content from 22.10 to more than 30%. No significant trend in the SiO_2 content in OPDCA was observed as it varied from 31.08 to 35.66% by the increment of 100°C in each combustion temperature (see **Table 2**). As reported in previous studies, the inconsistency of SiO_2 content depends on the Si-accumulation mechanism taken by plants and the soil itself (Anuar *et al.*, 2020; Prempeh *et al.*, 2021).

The OPDCA at 600°C was further treated using the alkaline extraction method to produce high-purity silica. According to **Table 3**, the element with high purity belongs to SiO_2 (76.95%), followed by K_2O (11.60%) and Al_2O_3 (7.80%). However, the purity of the rest elements showed a considerable reduction after OPDCA had been chemically treated. The silica purity increased rapidly by 40% because the alkaline solvents successfully dissolved the ash's silica. **Equations 1** and **2** depict how silica is produced from OPDCA through alkaline extraction (Anuar et al., 2018; Azlin & Syufiana, 2021).

$$SiO_2 \text{ (in ash)} + 2NaOH \longrightarrow Na_2SiO_3 + H_2O \quad (1)$$

$$Na_2SiO_3 + H_2SO_4 \longrightarrow SiO_2 + Na_2SO_4 + H_2O \quad (2)$$

Table 2. Elemental composition in DOPDC and OPDCA at four different combustion temperatures.

Elements (Oxides)	Percentage Composition (%)				
	DOPDC 105	OPDCA 600	OPDCA 700	OPDCA 800	OPDCA 900
SiO_2	22.10	32.10	31.08	32.58	35.66
CaO	26.00	26.10	28.60	29.70	30.93
K_2O	16.30	12.60	11.30	9.43	5.74
P_2O_5	4.76	6.66	6.78	7.23	8.12
Al_2O_3	4.08	5.53	5.89	6.49	6.89
Fe_2O_3	10.30	4.08	4.54	4.45	4.39
SO_3	5.77	3.16	2.77	1.81	1.46
Others	10.69	9.77	9.04	8.31	6.81

Table 3. Elemental composition of OPDCA at 600℃ before and after treatments.

Elements (Oxide)	Percentage Composition (%)	
	Before Treatment	After Treatment
SiO_2	32.10	76.95
CaO	26.10	0.18
K_2O	12.60	11.60
P_2O_5	6.66	1.71
Al_2O_3	5.53	7.80
Fe_2O_3	4.08	0.21
SO_3	3.16	0.99
Others	9.77	0.76

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The alkaline solvents used possessed an advantage in silica production since the solubility of amorphous silica occurs at a pH of more than 10. The silica can be extracted in pure form by dissolving it in the base state and then deposited in acidic conditions (Permatasari *et al.*, 2016). Besides, the volume of the NaOH solution influenced the contact area between OPDCA and the solvent. The even distribution of solvents to OPDCA will increase the formation of sodium silicate (Na_2SiO_3) and the yield of obtained silica (Setyawan & Wulanawati, 2019).

The high percentage composition of K_2O proved that OPDC is a nutrient-rich source of fertilizer, bio-compost, and animal feedstock. The presence of this element is an essential micro-nutrient for the agricultural sector because it helps to increase productivity, increase plant quality in terms of taste, shape, and color, and also enhances the defense mechanism in plants against adverse impacts of pests and the environment (Nandiyanto *et al.*, 2017**;** Samantray *et al.*, 2020). Meanwhile, the increasing composition of Al_2O_3 or well-known as alumina was significantly revealed after alkaline extraction. This element is beneficially used as concrete material due to its good properties such as thermal stability and high durability (Zailani *et al.*, 2020).

Table 4 illustrates the best purity of silica produced from various agricultural wastes via the alkaline extraction method. Agricultural wastes such as SB, RH, BL, CC, and CH were comprised of high-purity silica (>90%), except for OPDC with only 76.95%. Even so, the different operating conditions such as the molar ratio of ash to NaOH, volumes, types of acid, reaction time, and temperature might affect the formation of silica and its purity.

4.4. Morphological Analysis

FESEM with EDX analysis was used to determine the surface properties of silica from OPDC before and after alkaline extraction. The surface characteristics of silica prepared via combustion and alkaline extraction are portrayed in **Figure 3**.

Based on **Figure 3a**, the particle size in the image is larger than the scale bar, which is equivalent to 1 µm. Low temperature at 105℃ produced particle size of more than 1 µm, represented by the round-shaped agglomerates. It can be seen that no porous surfaces were observed on the agglomerate particles in **Figure 3a**. Findings made by Mu *et al.* (2018) mentioned that these rounded-shaped particles represented the combustible materials present in the DOPDC. The EDX spectra also showed the high intensity of carbon and oxygen element in the DOPDC. **Figure 3b** to **3e** depicted the surface morphology of OPDCAs at combustion temperatures of 600, 700, 800, and 900°C. At the temperature of 600°C (**Figure 3b**), the particle size in the image is smaller than the scale bar (1 µm). It was noted that the combustion process influenced the reduction in particle size.

Table 4. Purity of silica extracted by alkaline treatment from various studies.

Agricultural waste sources	Extraction Method	Silica purity (%)	Reference
Oil palm decanter cake	Precipitation	76.95	Present study
Sugarcane bagasse	Sol-gel	94.27	(Mosisa *et al.*, 2019)
Rice husk	Sol-gel	91.60	(Lima *et al.*, 2011)
Bamboo leaves	Precipitation	98.90	(Rangaraj & Venkatachalam, 2017)
Corncob	Precipitation	96.95	(Ajeel *et al.*, 2021)
Corncob	Sol-gel	97.13	(Okoronkwo *et al.*, 2013)
Coconut husk	Precipitation	90.01	(Anuar *et al.*, 2018)

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The rod-like structure also can be observed in **Figure 3b,** which indicates that the crystalline silica exists in the OPDCA at 600°C (Anuar *et al*. 2020). As the temperature is more elevated, the particles get reduced in size to lesser than 1 µm for OPDCA at 700 and 800°C, while the particle size for OPDCA at 900°C is smaller than 2 µm as compared with the scale bar in the images. Throughout these images, it was observed that the particle size tends to be smaller, and more agglomeration occurred as the combustion temperature got higher. The particle number increased as they were broken down into smaller pieces and an irregular shape was observed.

In addition, the ash structure became more porous and brittle at higher combustion temperatures. The porous structure observed was mainly due to the high combustion temperature that created holes on the particle's surface, thus, creating a larger surface area on the particles (Yahya *et al.*, 2010). As the temperature reaches up to 700°C, more agglomeration into irregular shapes can be seen through images due to mineral content in the crystalline form as the particles become more brittle (Utama *et al.*, 2018; Yang *et al.*, 2022). These results can also be proven through EDX spectra in which the silica intensity increased with the temperature increase. **Figure 3f** represents the image of the particle after alkaline extraction. It can be observed that the particle size is smaller than 500 nm. The spherical clusters displayed in **Figure 3f** indicate the presence of amorphous silica aggregated due to the increase of pH during the treatment using an alkaline solution (Permatasari *et al.*, 2016; Quercia *et al.*, 2013; Utama *et al.*, 2018). The EDX spectra showed an increase in the intensity of silica. Thus, this result may support the obtained purity of silica.

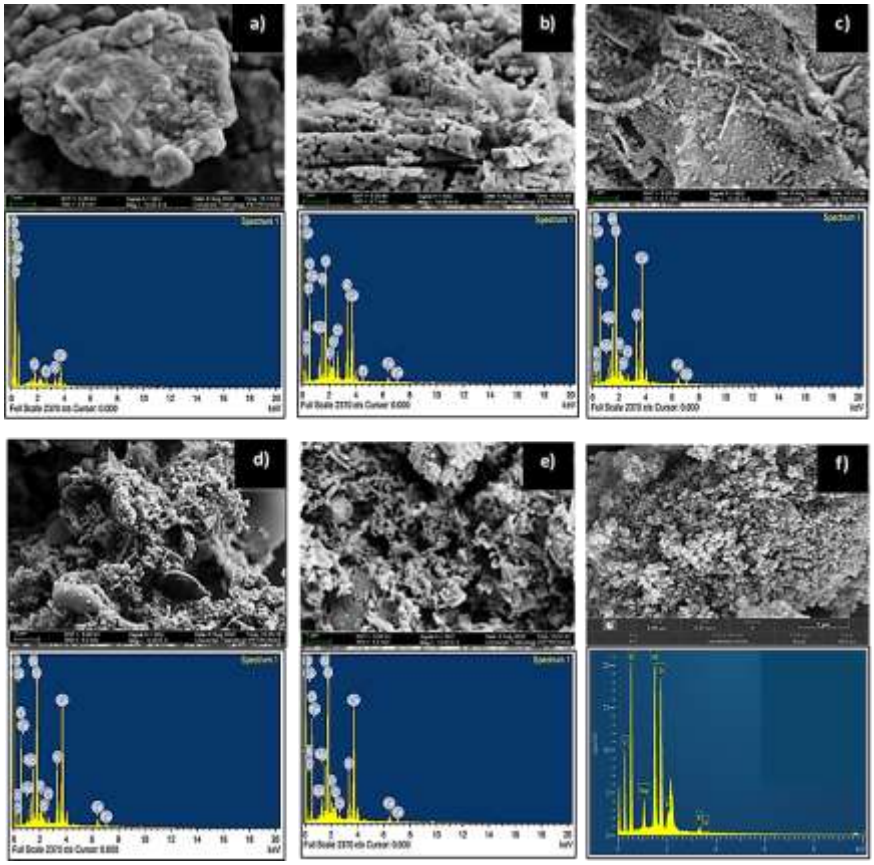

Figure 3. FESEM images with EDX spectra for silica obtained from (a) OPDC105, (b) OPDCA600, (c) OPDCA700, (d) OPDCA800, (e) OPDCA900, and (f) after alkaline extraction.

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4.5. Structural Phase Analysis

The XRD results of the obtained silica nanoparticles from OPDCAs are shown in **Figures 4a** to **4d**. The diffractogram emphasized the crystallinity of the material. DOPDC has been successfully heated at high temperatures ranging from 600 to 900°C for 5 hours producing OPDCAs, consisting of silica material attributed to intense peaks. The silica mainly existed in crystalline form as no hump-shaped peak was observed. A notable low intense peak located at 2θ= 21°, while intense high peaks located at 2θ of between 28 and 29°, were observed in all OPDCAs at temperatures 600-900°C. According to Inorganic Crystal Structures Database (ICSD), it confirmed OPDCA consists of silica that exists in quartz form (crystalline structure) (Azmi *et al*., 2016; Saceda *et al*., 2011). It also has been reported elsewhere to confirm the presence of crystalline silica in ash represented by the sharp peaks (Pa *et al*., 2016; Utama *et al*., 2018). XRD spectrum of the samples after the chemical treatments was illustrated as shown in **Figure 4e**. The OPDCA at 600°C was chosen to be treated with 140 mL of 5M NaOH solution. Subsequently, a broad diffraction peak at 2θ=22° confirmed that the crystalline silica has transformed into an amorphous form after being treated with an alkaline solvent, which is represented by the bell-shaped peak observed in the spectrum (Bakar *et al*., 2016; Mosisa *et al*., 2019; Ngoc *et al*., 2018). No sharp peak was observed on the diffraction pattern, which strongly proved that the crystalline silica has not been exhibited (Anuar et al., 2018).

Another study also proved that the diffraction peak at 2θ=22° belongs to the amorphous region (Javed et al., 2011; Rovani et al., 2018). Amorphous silica is better than crystalline one because it owns random and irregular atoms and patterns, making it more reactive than crystalline silica (Kurniawan et al., 2022). Meanwhile, the crystalline silica is said to be highly toxic and led to silicosis (Rovani, et al., 2018). Based on the diffractogram peaks obtained, it is strongly agreed that the chemical treatment has an impact on the transformation in the structural phase of silica.

4.6. Functional Group Analysis

The presence of silica materials in OPDC was confirmed by FTIR, as seen in **Figure 5**. Transmittance percentage (T%) represents the amount of light that passes through the sample, also called intensity (Zhang *et al*., 2018). The spectrum showed four dominant peaks in the silica powder produced from OPDCA via the alkaline extraction method.

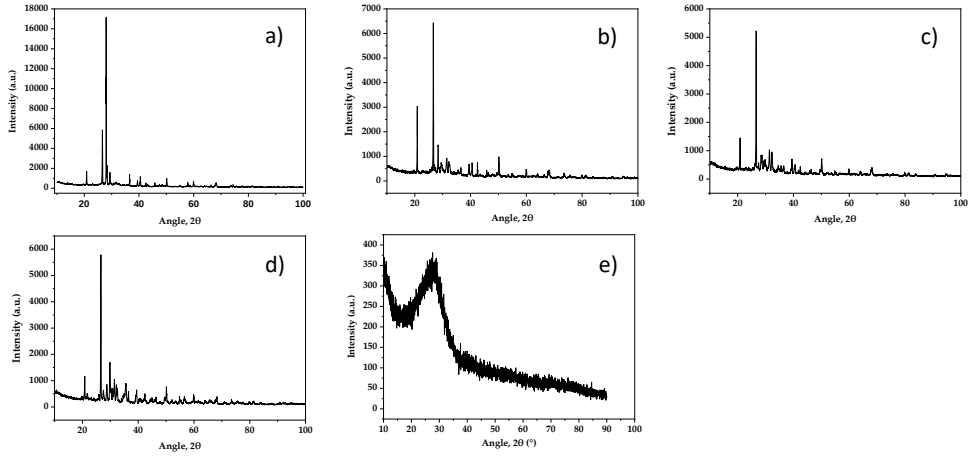

Figure 4. XRD spectra for silica obtained from a) OPDCA600, b) OPDCA700, c) OPDCA800, d) OPDCA900, and e) after alkaline treatment.

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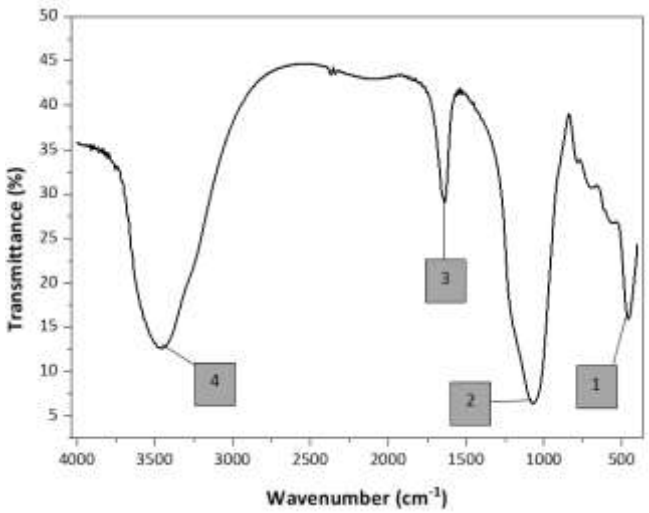

Figure 5. FTIR spectrum of silica extracted from OPDCA after chemical treatment.

he first notable peak with a wavenumber of 462 cm^{-1} is attributed to a network O-Si-O bending vibration (Okoronkwo *et al*., 2013). Meanwhile, the intense peak at a wavenumber of 1074 cm^{-1} represented the siloxane groups or asymmetric Si-O-Si stretching vibration mode (As, Si-O-Si). It revealed the bonding structures of Si and O atoms toward smaller particle sizes (Abdul Samat *et al*., 2021; Rangaraj & Venkatachalam, 2017).

This result agreed with the findings by Anuar *et al.* (2020) and Harish *et al.* (2015). The peak with low intensity in the spectrum indicated C=O stretching with a wavenumber of 1645 cm^{-1} (Anuar *et al*., 2020; Ong *et al*., 2021). A broad and intense band located at 3473 cm^{-1} belongs to the silanol group (Si-OH) due to adsorbed water molecules (Nayak *et al*., 2019). The summary of indication peaks is displayed in **Table 5**.

5. CONCLUSION

The amorphous silica has been successfully extracted from OPDC, which provided a low-cost alternative to producing silica from agricultural waste. The combustion as a pre-treatment method produced about 31% to 36% of silica at four different combustion temperatures (600-900℃). After the alkaline treatment, the percentage of silica obtained effectively increased from 32.10% to 75.96%.

The observation of spherical clusters confirmed that amorphous silica was produced through FESEM images. The diffractogram peaks observed that the silica was crystalline when undergoing combustion at high temperatures but turned into an amorphous form when OPDCA was chemically treated. Furthermore, the FTIR spectrum also strongly supported the existence of silica in the OPDCA. OPDCA can be considered a promising alternative silica source. As demonstrated in this study, high-purity silica can be extracted through a simple and green route to reduce the cost of production.

Table 5. Major functional groups present in silica after chemical treatment.

Peak	Peak wavenumber (cm^{-1})	Functional groups
1	462	O-Si-O bending vibration
2	1074	Asymmetric Si-O-Si stretching vibration
3	1645	C=O
4	3473	Si-OH

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7. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. The authors confirmed that the paper was free of plagiarism.

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