

# BIOGENIC SILICA FROM OIL PALM BIOMASS: A REVIEW ON THE POTENTIAL, EXTRACTION METHODS AND PROPERTIES

HOERUDIN HOERUDIN<sup>1</sup>; TATANG HIDAYAT<sup>1</sup>; ATON YULIANTO<sup>1\*</sup>; SITI AGUSTINA<sup>1</sup>; FAJRIYAN<sup>1</sup>; KARNADI<sup>1</sup>; ABDUL MAJID<sup>1</sup>; AHMAD SUHENDRA<sup>1</sup>; EDDY SAPTO HARTANTO<sup>1</sup> and ACHMAD KAMIL<sup>1</sup>

## ABSTRACT

The oil palm industry has witnessed significant growth and has emerged as one of the world's largest vegetable oil sectors. However, this rapid expansion in production is accompanied by a notable increase in waste generation. While mills are utilising some oil palm biomass, a large portion still goes untapped and underexplored. There is increasing interest in leveraging various types of oil palm biomass as alternative, renewable, and economically viable resources to generate biogenic silica, a valuable material with diverse applications. This approach not only adds value to the biomass but also addresses environmental concerns. This article represents one of the first in-depth reviews of the recent technological advancements in leveraging oil palm biomass for the high-value synthesis of biogenic silica. It explores various aspects, covering the potential extraction methods (including those reported as green techniques, positioning them as a promising alternative to conventional approaches), as well as the properties and relevant applications of biogenic silica derived from oil palm biomass. The findings from this thorough review are expected to provide valuable insights for future research in the efficient production and sustainable utilisation of this bio-based material. Such support has the potential to enhance the sustainability of the oil palm industry.

**Keywords:** characteristics, oil palm, silica, synthesis, valorisation.

**Received:** 28 October 2024; **Accepted:** 17 April 2025; **Published online:** 22 July 2025.

## INTRODUCTION

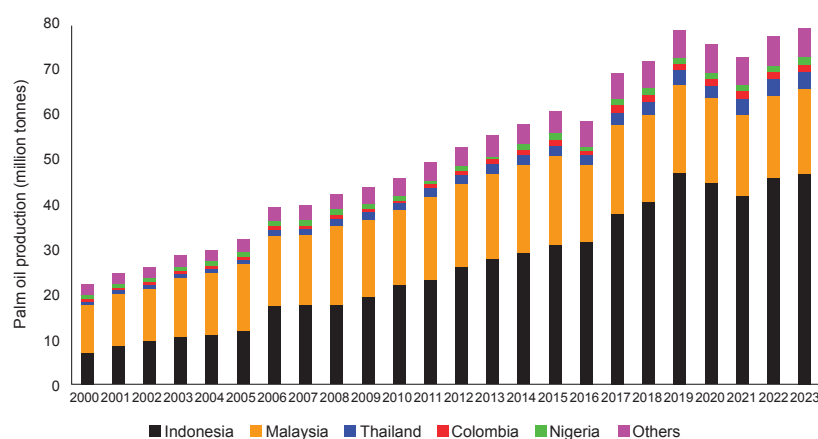
Global palm oil production has undergone significant expansion in the past 20 years. Between 2000 and 2023, palm oil output increased more than three times, rising from 22.23-79.46 million tonnes (Figure 1). During this period, roughly 80%-85% of the global supply has been sourced from only two nations, Indonesia and Malaysia (Food and Agriculture Organisation of the United Nations, Statistics Division [FAOSTAT], 2023; United States Department of Agriculture [USDA], 2023). The forecast for the marketing year (MY) 2023/2024 predicts a 2% increase in global palm oil production, totalling 79.60 million tonnes.

Moreover, worldwide palm oil consumption is anticipated to rise by more than 3% in MY 2023/2024, approaching 78.00 million tonnes (Ates & Bukowski, 2023).

The expansion of the oil palm business, encompassing plantations and mills, results in substantial oil palm biomass production, hence creating the difficulty of excessive waste accumulation. Oil palm biomass consists of agricultural waste generated by the oil palm industry during pruning, replanting and milling operations (Nabila *et al.*, 2023; Nur 'Aisyah Ar-Raudhoh *et al.*, 2024; Onoja *et al.*, 2019). An oil palm plantation may produce a significant quantity of biomass or total dry matter (TDM), with an annual yield of approximately 55 t/ha (Jafri *et al.*, 2021). The production of oil palm agro-industrial biomass waste in Indonesia is expected to continue increasing. By 2030, oil palm biomass production is projected to reach roughly 419 million tonnes (Hambali & Rivai, 2017).

<sup>1</sup> Research Center for Agroindustry, Research Organization for Agriculture and Food, National Research and Innovation Agency, Soekarno Science and Technology Area, Jl. Raya Jakarta-Bogor KM 46, Cibinong 16911, Indonesia.

\* Corresponding author e-mail: [aton001@brin.go.id](mailto:aton001@brin.go.id)



Source: FAOSTAT, (2023); USDA, (2023).

Figure 1. Global production and the top five producers of palm oil from 2000-2023.

Oil palm biomass has been utilised partially across different applications, each employing specific types of biomass and conversion techniques. Its applications range from basic uses like mulch and organic fertilisers (Khairuddin *et al.*, 2018) to more advanced value-added products such as biochar, bio-oil (Abdullah *et al.*, 2017) and adsorbents (Jahi *et al.*, 2020). Traditional uses, such as combustion for energy, are prevalent (Nabila *et al.*, 2023); however, these methods often need more efficiency and sustainability. Advanced and emerging conversion techniques, like pyrolysis, thermochemical processes, nanocomposites, enzymatic saccharification and fermentation, offer pathways to produce higher-value products such as biochar, biofuels, biosugar and bioplastics (Nabila *et al.*, 2023; Norrahim *et al.*, 2022), which can enhance economic returns and environmental benefits. Nonetheless, the adoption of these technologies are still limited due to factors like high initial investment costs, technological complexity, cost-effectiveness, price competition and lack of infrastructure. As a result, significant quantities of oil palm biomass continue to be underutilised or wasted. This indicates that more innovative uses are warranted, especially in high-value applications, to maximise its economic and environmental potential.

Research on the valorisation of oil palm biomass is consistently advancing. Oil palms (*Elaeis guineensis* Jacq.) are recognised as silica accumulators (Greenshields *et al.*, 2023; Munevar & Romero, 2015). This indicates that oil palm biomass may possess a substantial quantity of siliceous material. Consequently, oil palm biomass has been the subject of many previous studies as a potentially viable, renewable and cost-effective source to produce biogenic silica. Faizul *et al.* (2014), extracted high-purity silica (>90.00%) from palm ash (PA) using an eco-friendly citric acid leaching method.

Khan *et al.* (2015) produced silica nanoparticles (20-80 nm) with a surface area of 326 m<sup>2</sup>/g from palm oil fuel ash (POFA), showcasing their suitability for nanomaterial applications. Utama *et al.* (2019) further advanced silica extraction techniques by utilising sol-gel processes combined with mechanical fragmentation and CO<sub>2</sub> impregnation, producing precipitated silica with high purity and specific surface areas ranging from 50-140 m<sup>2</sup>/g, which are ideal for catalyst and adsorption applications. More recently, Imoisili *et al.* (2020a, 2020b) synthesised amorphous mesoporous silica from palm kernel shell ash (PKSA) using sol-gel methods, achieving silica yields up to 96.83% with a specific surface area of 438 m<sup>2</sup>/g, emphasising the material's applicability in drug delivery, energy storage and lightweight composites. Osman *et al.* (2021) explored the application of oil palm frond-derived silica nanomaterials for phenol removal from wastewater, achieving 68.00% removal efficiency and further underlining the potential of biogenic silica in environmental remediation. Additionally, Novita and Idris (2022) demonstrated the effectiveness of silica gel derived from PKSA as a moisture absorber in pharmaceutical packaging, achieving 85.65% moisture absorption efficiency and thus expanding the industrial utility of oil palm biomass. These studies confirm the potential of oil palm biomass as a sustainable and valuable source of silica for diverse industrial applications.

Grand View Research (2023) reported that the global silica market, encompassing precipitated silica, fumed silica, silica gels, silica sols and silica fumes, was valued at RM49.12 billion in 2022, with an anticipated Compound Annual Growth Rate (CAGR) of 9.90% from 2023-2030. Commercial synthetic amorphous silica (SAS) is often derived from mineral-based precursors. The SAS production process comprises two energy-intensive stages: High-temperature

fusion for melting silica sand and soda ash and high-temperature digestion for dissolving sodium silicate. These energy-intensive processes can be significantly expensive (Utama *et al.*, 2018). The traditional technique also produces byproducts, including CO<sub>2</sub> and significant volumes of wastewater, that are detrimental to the environment. As a result, there is an increasing research interest focused on generating amorphous silica from renewable and economical sources using energy-efficient techniques. These initiatives are progressively acknowledged as sustainable methods to reutilise byproducts and reduce ecological harm (Samat *et al.*, 2021). The significant quantity of oil palm biomass presents a viable and sustainable opportunity for silica extraction from this by product.

Although substantial research and reviews have explored the production of biogenic silica from various agricultural residues, such as rice husks (Chun & Lee, 2020; Dizaji *et al.*, 2019; Hossain *et al.*, 2018; Steven *et al.*, 2021) and crop wastes (Kouadri *et al.*, 2023; Razak *et al.*, 2022; Sarkar *et al.*, 2021; Setiawan & Chiang, 2021; Yadav *et al.*, 2022), the unique potential of oil palm biomass as a significant renewable source of silica remains underexplored. Existing studies primarily focus on individual aspects of silica extraction from oil palm biomass. However, a comprehensive review that synthesises these findings and evaluates the specific properties and relevant applications of biogenic silica derived from oil palm biomass is notably lacking. Furthermore, there is limited discussion on sustainable and environmentally-friendly extraction methods tailored specifically for this biomass. Addressing these gaps will highlight oil palm biomass as a valuable contributor to sustainable material production and, hence, the circular economy.

This review aims to critically analyse the potential of oil palm biomass as a sustainable source of biogenic silica by exploring advanced extraction techniques, focusing on environmentally-friendly approaches, assessing the unique properties of the resulting biogenic silica and identifying opportunities for advancing its utilisation in various industrial applications. Several key research questions addressed include identifying the types of oil palm biomass most suitable for sustainable biogenic silica production; examining recent advancements and current challenges in silica extraction methods for oil palm biomass and strategies to address these sustainably; evaluating the unique physical, chemical and functional properties of biogenic silica derived from oil palm biomass; investigating its potential applications in high-value industrial sectors; and highlighting significant research gaps and future directions in this field.

## BIOGENIC SILICA IN OIL PALM BIOMASS

### Biogenic Silica in Oil Palm Trees

Silicon (Si) is vital in numerous ecological and biogeochemical processes. In biogeochemistry, Si is commonly referred to as silica (SiO<sub>2</sub>), as it is invariably associated with oxygen (O) in ecosystems (Tréguer *et al.*, 2021). Si, following oxygen, is the second most prevalent element in the Earth's crust, comprising approximately 28.00% of its composition (Tubaña & Heckman, 2015). Plants absorb soluble Si as orthosilicic acid (H<sub>4</sub>SiO<sub>4</sub>) from the soil solution and translocate it to the roots and aerial structures. Si is ultimately incorporated into plant tissues as hydrated amorphous biogenic silica structures referred to as phytoliths (SiO<sub>2</sub>.nH<sub>2</sub>O) (Haynes, 2017; Puppe *et al.*, 2021). Si has been noted to confer various beneficial effects on plants, including increased resistance to biotic stresses (such as pest infestations and fungal diseases) and abiotic stresses (such as drought, low temperatures and metal toxicity), optimised nutrient availability, enhanced photosynthesis, improved plant growth and elevated productivity (Debona *et al.*, 2017; Dhakate *et al.*, 2022; Pereira *et al.*, 2024).

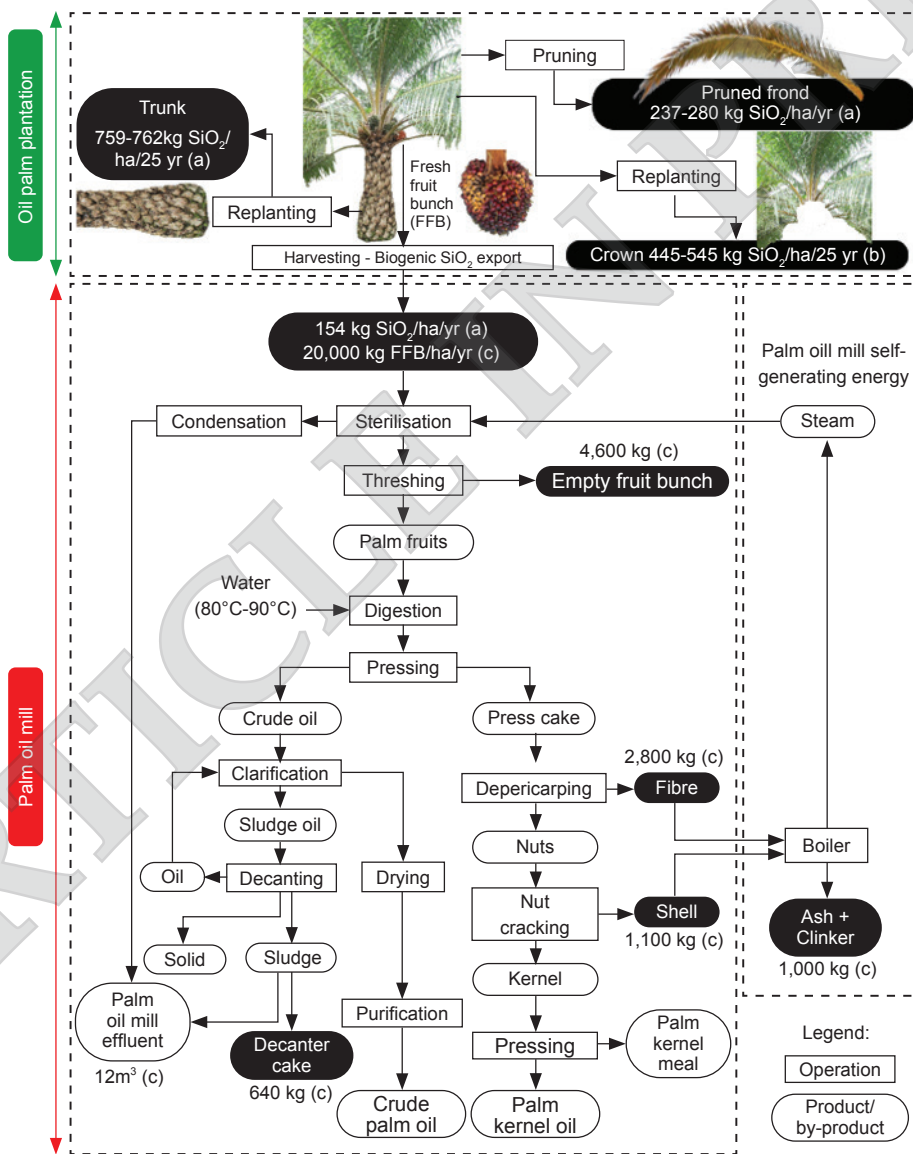
Published data regarding the concentrations of Si or SiO<sub>2</sub> in various regions of an oil palm are typically few. Duangpan *et al.* (2022) examined the concentration and distribution of Si in oil palm seedlings. Si buildup in oil palm seedlings was detected in all tissues, with the highest average concentration in the leaf (0.66%), followed by the root (0.45%) and stem (0.17%). Greenshields *et al.* (2023) evaluated Si concentrations in several mature oil palm components taken from smallholder plantings in Indonesia. Their study also quantified the quantity of (i) accumulated Si in the total above-ground biomass of a mature oil palm tree and in one hectare of an oil palm plantation, (ii) Si storage in pruned palm fronds, and the Si transferred during fruit bunch harvest. Leaflets exhibited an average Si content of at least 1.00%. Conversely, rachises, frond bases, fruit-bunch stalks, fruit pulp and kernels exhibited mean Si contents below 0.50%. Leaflets in senescent fronds exhibited markedly elevated Si concentrations (>3.50%) compared to frond No. 17 (1.30%-1.70%) and frond No. 9 (about 1.10%). The findings aligned with those presented by Von Der Lühe *et al.* (2023), demonstrating that a dead leaf possessed double the quantity of Si relative to a mature leaf. Comparable results were noted in the research conducted by Munevar and Romero (2015), who evaluated Si contents in the leaves of oil palm trees beyond eight years of age, collected from 17 estates in Colombia. The study revealed a gradual increase in Si concentrations in oil palm leaves, from roughly 1.30% in leaf No. 1 to almost 4.00% in leaf No. 25. The results indicate

that Si accumulates as the oil palm leaves age and presumably functions as a non-mobile element within the plant. Comparable Si behaviour was also documented in cereal crops (Ma & Yamaji, 2006).

Figure 2 illustrates the distribution and quantity of accumulated silica in different sections of oil palm biomass, as observed in the plantations and mills. In that graphic and the next discussion, published data on Si storage in oil palm biomass were transformed into SiO<sub>2</sub> storage. In plantations, oil palm fronds (OPF) and oil palm trunk (OPT) constitute the primary biomass produced during pruning and replanting operations. OPF

are considered a significant source of SiO<sub>2</sub> in plantations (Von Der Lühe *et al.*, 2023). The study conducted by Greenshields *et al.* (2023) revealed that SiO<sub>2</sub> accumulation in a senescing OPF (0.13 kg SiO<sub>2</sub>) exceeded that in frond No. 9 (0.04 kg SiO<sub>2</sub>) and frond No. 17 (0.06 kg SiO<sub>2</sub>). This study indicated that SiO<sub>2</sub> deposition in OPF generally escalates with the frond's age. In a smallholder oil palm plantation, around 14-16 fronds are clipped each year. Greenshields *et al.* (2023) estimated that SiO<sub>2</sub> storage in the annually pruned OPF ranged from roughly 237-280 kg/ha.

The core part of an oil palm stem is claimed to possess silica-accumulating tissues. SiO<sub>2</sub>



Note: (a) - Converted from Greenshields *et al.* (2023); (b) - Converted and calculated from Greenshields *et al.* (2023) and PASPI-Monitor (2021); (c) - Calculated from Chavalparit *et al.* (2006).

Source: Abdullah and Sulaiman, (2013); Nabila *et al.* (2023).

Figure 2. Schematic diagram of palm oil production and the potential availability of oil palm silica and silica-containing biomass.

accumulation in the OPT may transpire either within the vascular system or within the cell walls (Greenshields *et al.*, 2023). The lower, middle and higher segments of the OPT demonstrated an increasing trend in SiO<sub>2</sub> concentrations of 1.02%, 1.69% and 4.52%, respectively (Pratiwi *et al.*, 2018). Greenshields *et al.* (2023) reported that a mature oil palm stem could acquire roughly 5.36 kg of SiO<sub>2</sub>. The extraction of OPT from plantations before replanting may lead to a significant export of SiO<sub>2</sub>, estimated at a minimum of 759-762 kg SiO<sub>2</sub>/ha, assuming a planting density of 142 oil palms/ha in a smallholder plantation. Nonetheless, this considerable SiO<sub>2</sub> outflow may occur at periods of 25-30 years, aligning with oil palm replanting cycles (Figure 2).

A mature oil palm tree is typically maintained with 40-48 fronds (PASPI-Monitor, 2021). Considering an average SiO<sub>2</sub> storage of 0.08 kg/frond and a planting density of 142 trees/ha (Greenshields *et al.*, 2023), an oil palm crown may sequester around 445-545 kg SiO<sub>2</sub>/ha. The accumulated SiO<sub>2</sub> may be exported before replanting cycles, which generally take place every 25-30 years. Based on its dimensions and mass, an oil palm fruit bunch might contain about 0.04-0.15 kg of SiO<sub>2</sub>. An oil palm tree is predicted to acquire approximately 8,000-11,000 kg of SiO<sub>2</sub> in its aerial components, including fruit bunches. Based on this computation, roughly 1,178-1,459 kg of SiO<sub>2</sub> may be deposited in the aerial components of one ha in a smallholder oil palm plantation, as noted by Greenshields *et al.* (2023). In this instance, OPT could be the principal source of the estimated SiO<sub>2</sub> storage in the aerial components of an individual oil palm tree. Nevertheless, the SiO<sub>2</sub> contained in the trunks of oil palm trees may only be extracted for subsequent use after a period of 25-30 years, particularly during the replanting phase. Consequently, the SiO<sub>2</sub> reserves in plantations with optimal availability for consistent short-term use are expected to derive from the clipped fronds of oil palm trees. The calculations indicate that a fully developed oil palm tree can absorb an equivalent amount of SiO<sub>2</sub> as rice, which is capable of absorbing 500 kg of Si/ha (Makabe *et al.*, 2009), equal to 1,069 kg of SiO<sub>2</sub>/ha, and is acknowledged as a Si-accumulator (Qurrohman *et al.*, 2023). This suggests the possible categorisation of oil palm as a Si-accumulating plant.

Figure 2 shows exports of fruit bunch harvest and SiO<sub>2</sub> storage from oil palm plantations to palm oil mills. Each year, a mature oil palm tree in a smallholder plantation may produce 12-14 fruit bunches, resulting in an accumulation of approximately 0.51-2.10 kg of SiO<sub>2</sub>. A small-scale oil palm plantation, with a planting density of 142

trees/ha and a fruit bunch production of 9-20 t/ha of dry biomass (Greenshields *et al.*, 2023), was predicted to store around 68-154 kg of SiO<sub>2</sub>/ha annually within its fruit bunches. In other words, approximately 5.00%-10.00% of SiO<sub>2</sub> stored in the aerial components of a one ha oil palm plantation is conveyed to a palm oil mill via the harvesting of fruit bunches.

### Biogenic Silica in Palm Oil Mill By-products

At palm oil mills, fresh fruit bunches (FFB) are processed to yield crude palm oil as the principal product, alongside palm kernel oil, contingent upon the availability of suitable processing equipment (Figure 2). The production of palm oil encompasses several processes: Sterilisation, threshing, digesting, pressing, clarification, purification, drying, depericarping and cracking. During these operations, numerous intermediate products and significant amounts of trash are produced. Approximately 70.00% of the processed FFB in palm oil mills generates substantial waste, including empty fruit bunch (EFB), mesocarp fibre (MF), palm kernel shell (PKS), palm oil mill effluent (POME), palm oil mill sludge (POMS), palm oil decanter cake (PODC), palm kernel meal (PKM), POFA and palm oil clinker (POC). The burning of MF and PKS as boiler fuel in palm oil mills produces biogenic waste in the form of unburned ash. This ash has been identified by various terms in the literature, including PA (Faizul *et al.*, 2014), POFA (Hoerudin *et al.*, 2024; Khan *et al.*, 2015; Liew *et al.*, 2017), palm oil mill fly ash (POMFA) (Aman *et al.*, 2017), oil palm boiler ash (OPBA) (Bukit *et al.*, 2022) and oil palm mill boiler ash (OPMBA) (Adha & Warsiki, 2023). Within the scope of this review, the term "boiler ash" (BA) is employed to characterise the ash, as delineated by Zarina *et al.* (2013). BA comprises porous, flaky and irregular stones, referred to as POC (Karim *et al.*, 2017). For each tonne of FFB processed in conventional palm oil mills, the projected by-product or trash creation is as follows: 23.00% of EFB, 14.00% of MF, 5.50% of PKS, 3.20% of oil palm decanter cake (OPDC), 5.00% of BA, and 0.6 m<sup>3</sup> of POME (Chavalparit *et al.*, 2006). A one ha of mature oil palm plantation with an FFB productivity of 20.00 t would yield approximately 4.60 t of EFB, 2.80 t of MF, 1.10 t of PKS, 0.64 t of OPDC, 1.00 t of BA and 2 m<sup>3</sup> of POME (Figure 2).

Each type of oil palm mill waste possesses distinct physico-chemical characteristics. This analysis examines palm oil mill waste with notable SiO<sub>2</sub> concentrations, as recorded in the existing literature (Table 1). This attention is essential for assessing the prospective opportunity for recovering silica from these palm oil mill by products.

TABLE 1. MINERAL COMPOSITION OF UNTREATED PALM OIL MILL WASTE BY TYPE AND GEOGRAPHICAL ORIGIN

Type of waste	Country	Mineral composition (wt %)											Reference
		SiO <sub>2</sub>	K <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> O	Cl	SO <sub>3</sub>	Others	
PKS	Nigeria	13.65	6.48	13.21	9.18	6.54	1.81	4.37	1.71	n.a	0.84	n.a	Imoisili <i>et al.</i> (2020b)
PKSA	Nigeria	56.76	9.19	12.57	8.58	5.45	0.91	4.21	1.62	n.a	0.71	n.a	Imoisili <i>et al.</i> (2020b)
EFBA	Malaysia	9.50	35.20	39.20	n.a	n.a	2.60	4.20	n.a	2.50	2.10	n.a	Rahmat <i>et al.</i> (2021)
EFBA	Thailand	12.12	55.48	9.65	0.26	1.90	n.a	3.58	0.09	6.84	1.66	n.a	Madhiyanon <i>et al.</i> (2013)
BA	Indonesia	52.41	14.47	7.64	5.10	4.54	4.18	n.a	n.a	n.a	n.a	n.a	Adha and Warsiki (2023)
BA	Malaysia	45.50	23.30	12.80	5.40	3.20	3.26	5.38	n.a	n.a	n.a	n.a	Pa <i>et al.</i> (2016)
BA	Malaysia	55.00	5.40	5.50	5.40	3.50	4.70	3.40	n.a	n.a	n.a	1.10	Khan <i>et al.</i> (2015)
BA	Thailand	50.57	8.45	15.92	1.03	4.73	2.56	6.53	n.a	n.a	n.a	10.21	Kongnoo <i>et al.</i> (2017)
BA	Nigeria	53.52	3.08	4.62	11.40	3.28	12.68	n.a	1.56	n.a	n.a	1.26	Oyejobi <i>et al.</i> (2015)
BA	Bangladesh	63.60	6.90	7.60	1.60	3.90	1.40	n.a	0.10	n.a	n.a	na	Tessema <i>et al.</i> (2023)
OPDC	Malaysia	22.10	16.30	26.00	4.08	n.a	10.30	4.76	n.a	n.a	5.77	10.69	Rahim <i>et al.</i> (2023)
OPDCA	Malaysia	32.10	12.60	26.10	5.53	n.a	4.08	6.66	n.a	n.a	3.16	9.77	Rahim <i>et al.</i> (2023)
POC	Malaysia	63.90	10.20	6.93	3.89	3.37	3.30	2.12	n.a	n.a	n.a	n.a	Khan <i>et al.</i> (2015)

Note: n.a - Data not available, PKS - palm kernel shell, PKSA - palm kernel shell ash, EFBA - empty fruit bunch ash, POC - palm oil clinker.

Published literature indicates that palm oil mill wastes exhibit different concentrations of SiO<sub>2</sub> according to their type. The POC generated concurrently with BA by the identical procedure exhibited the highest SiO<sub>2</sub> concentration, surpassing 45.00%, followed by OPDC at 22.10% and PKS at 13.65% (Table 1). The SiO<sub>2</sub> concentration in PKSA incinerated at 750°C for 3 hr increased significantly by roughly 43.00%, attaining 56.76% (Imoisili *et al.*, 2020b). The incineration procedure at 600°C for 5 hr increased the SiO<sub>2</sub> content in oil palm decanter cake ash (OPDCA) by approximately 10.00%, resulting in a concentration of 32.10% (Rahim *et al.*, 2023). According to the literature assessment, the SiO<sub>2</sub> concentration data for (raw) EFB and MF are inadequately recorded. Table 1 shows that the SiO<sub>2</sub> concentration in empty fruit bunch ash (EFBA) was analogous to that of PKS. Consequently, the SiO<sub>2</sub> concentration in EFB is probably inferior to that in PKS. The existing literature indicates that SiO<sub>2</sub> concentration does not vary widely within the same type of waste, regardless of geographical location. Nonetheless, a considerable variance exists in the composition of K<sub>2</sub>O and CaO in BA sourced from various places. This variety may be ascribed to genetic disparities among plants, cultivation sites, agricultural practices, and/or processing conditions in palm oil mills. BA, including POC, is a highly promising source of SiO<sub>2</sub> derived from palm oil processing waste, owing to its comparatively elevated SiO<sub>2</sub> concentration, ease of subsequent processing, and abundant availability.

### EXTRACTION OF BIOGENIC SILICA

Most industrial silica comes from natural sources, such as quartz, found in nearly all mineral rocks. These rocks are heated to produce sodium silicate as a silica precursor, but this process requires extremely high temperatures (1,300°C), making it energy-intensive and a significant source of greenhouse gas emissions (Zulfiqar *et al.*, 2015). Silica can also be synthesised from toxic and costly alkyl orthosilicate precursors like tetraethyl orthosilicate (TEOS), which pose health risks and are impractical economically and environmentally (September *et al.*, 2023; Tessema *et al.*, 2023). To address these issues, agricultural wastes, such as rice husk, corn cob, sugarcane bagasse and palm oil wastes (*e.g.*, BA, EFBA, PKS, PKSA, OPDC, OPDCA), have been explored as low-cost, silica-rich alternatives. Silica extraction from biomass is eco-friendly, reduces energy consumption, and achieves comparable quality to conventional methods (September *et al.*, 2023).

Biomass can be converted into bioproducts via biochemical or thermochemical methods. Thermochemical conversion, which decomposes

biomass using heat, is particularly suitable for extracting biogenic silica from palm oil solid waste. This waste contains cellulose, hemicellulose, lignin and metal components (*e.g.*, calcium, potassium and iron), which influence silica properties during high-temperature treatments. Pre-treatment processes are often needed to remove these impurities, facilitating extraction and improving yield and product quality (Norsuraya *et al.*, 2016; Nzereogu *et al.*, 2023; Teixeira *et al.*, 2021).

## Extraction Methods

The extraction of biogenic silica from agricultural biomass, such as oil palm biomass, generally follows two stages: Raw material pre-treatment and the extraction process. Raw material pre-treatment is typically carried out before the biogenic silica extraction process. The selection of pre-treatment and extraction methods for biogenic silica production is pivotal in balancing efficiency, cost and environmental considerations. Several considerations in selecting pre-treatment and biogenic silica extraction methods are summarised in Table 2.

Commonly employed pre-treatment methods include acid leaching and combustion, each with distinct advantages and disadvantages. Acid leaching is effective in removing metal impurities, significantly enhancing silica yield and purity (Nzereogu *et al.*, 2023; Pa *et al.*, 2016; Rahmat *et al.*, 2021). However, the use of strong acids, such as hydrochloric, sulfuric and nitric acids, raises concerns regarding environmental safety, human health and waste disposal. Although effective, these drawbacks necessitate the exploration of greener alternatives, such as organic acids, which offer a more sustainable approach.

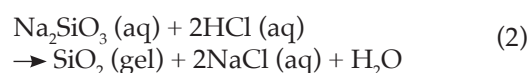
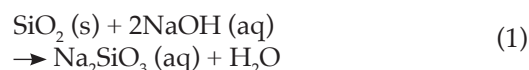
Combustion, on the other hand, is a simpler method that effectively decomposes organic components like cellulose, hemicellulose and lignin, facilitating further silica extraction. Despite its simplicity, combustion alone may not fully remove metal impurities, limiting silica purity. Additionally, its high energy requirements introduce economic and environmental concerns, particularly in large-scale operations. Combining combustion with acid leaching can overcome these limitations, leveraging the strengths of both methods to produce high-purity silica. However, this approach inherits the complexity and resource demands of both processes, making it suitable only for applications where exceptional purity is paramount.

Green extraction methods have emerged as a promising alternative to conventional processes by utilising organic acids and lower energy inputs, thereby mitigating environmental impacts (Aharipour *et al.*, 2022; Hoerudin *et al.*, 2024; Pa

*et al.*, 2016; Rahim *et al.*, 2023; September *et al.*, 2023; Tessema *et al.*, 2023; Utama *et al.*, 2019). These methods are environmentally-friendly and effective in removing impurities, but face challenges in scalability and cost-effectiveness due to the relatively high expense of organic acids. Process optimisation is required to ensure they achieve comparable efficiency to conventional methods.

The sol-gel and calcination methods for biogenic silica extraction are closely aligned with the chemical and physical properties of biogenic silica derived from agricultural biomass waste. Biomass such as PKS and EFB contains silica predominantly in amorphous form, embedded within organic matrices of cellulose, hemicellulose, lignin and metal oxides. Both methods offer distinct mechanisms for silica isolation and purification.

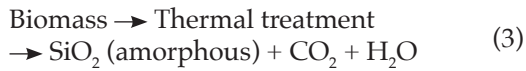
The sol-gel method employs chemical dissolution and precipitation processes to extract high-purity silica. Initially, silica in the biomass is solubilised using an alkaline solution such as NaOH to form soluble sodium silicate [Equation (1)] (Norsuraya *et al.*, 2016; Tessema *et al.*, 2023). To recover pure biogenic silica, an acid, such as HCl or organic acids (*e.g.*, citric acid), is added to reduce the pH to below 10, precipitating silica gel [Equation (2); Tessema *et al.*, 2023]. The resulting silica gel is aged, washed, and dried to obtain amorphous silica. The sol-gel process maintains the amorphous nature of biogenic silica due to its low processing temperature, preventing the formation of crystalline silica (Hoerudin *et al.*, 2024; Imoisili *et al.*, 2020a, 2020b; Rahim *et al.*, 2023; Utama *et al.*, 2019). This method produces fine particle sizes, high surface area and tailored morphologies.



Calcination, in contrast, is a thermal decomposition method that exploits the thermal stability of silica compared to organic components. The organic matrix (cellulose, hemicellulose and lignin) is decomposed at specific temperature ranges: Hemicellulose (220°C-300°C), cellulose (300°C-340°C) and lignin (300°C-900°C) (Bakar *et al.*, 2016; El-Sayed *et al.*, 2024). During calcination at 600°C-800°C, the organic material combusts completely, leaving behind amorphous silica [Equation (3)]. Maintaining temperatures below 900°C is critical to avoid crystallisation into cristobalite or tridymite, which reduces silica's reactivity and industrial suitability (Nelson *et al.*, 2023; Nzereogu *et al.*, 2023).

TABLE 2. ADVANTAGES AND DISADVANTAGES OF PRE-TREATMENT AND EXTRACTION METHODS FOR PRODUCING BIOGENIC SILICA

Criteria	Considerations	Advantages	Disadvantages	Reference
Pre-treatment method	Required to remove impurities and improve the yield/ quality of extracted silica.	Improves purity and extraction efficiency.	May add additional processing steps and costs.	Nelson <i>et al.</i> (2023); Pa <i>et al.</i> (2016); Rahmat <i>et al.</i> (2021)
<ul style="list-style-type: none"> <li>• Acid leaching</li> </ul>	Effectively removes metal impurities; commonly uses HCl, H <sub>2</sub> SO <sub>4</sub> or H <sub>3</sub> PO <sub>4</sub> ; risk of environmental and health hazards.	Significant removal of metal oxides and impurities; proven high leaching efficiency.	Use of strong acids poses health and environmental risks; and disposal challenges.	Bakar <i>et al.</i> (2016); Rahmat <i>et al.</i> (2021); Setiawan and Chiang (2021)
<ul style="list-style-type: none"> <li>• Combustion</li> </ul>	Decomposes organic components (cellulose, hemicellulose, lignin); simplifies raw material processing.	Simplifies treatment and eliminates organic matrix components.	Requires high energy input for combustion; may not fully remove metal impurities.	Imotsili <i>et al.</i> (2020b); Rahim <i>et al.</i> (2023)
<ul style="list-style-type: none"> <li>• Combination of combustion and acid leaching</li> </ul>	Combines impurity removal with decomposition of organic matrix; increases silica purity and yield.	High silica purity due to the combined benefits of both processes.	Combines the complexities of both methods; increases time and cost.	Nelson <i>et al.</i> (2023); Osman and Sapawe (2020); Rahmat <i>et al.</i> (2021)
Extraction method	Used to extract silica efficiently from palm oil waste through chemical or thermal processes.	Facilitates silica extraction from biomass with high efficiency.	The selection of appropriate methods depends on the raw material type; initial pre-treatments may be necessary.	Adha and Warsiki (2023); Hoerudin <i>et al.</i> (2024)
<ul style="list-style-type: none"> <li>• Sol-gel method</li> </ul>	Uses alkaline solution to dissolve silica, followed by precipitation with acid; produces high-purity silica.	Produces high-purity biogenic silica through precise chemical processing.	Involves chemical reagents, requiring precise pH control; extended processing time for precipitation.	Hoerudin <i>et al.</i> (2024); Tessema <i>et al.</i> (2023)
<ul style="list-style-type: none"> <li>• Calcination</li> </ul>	Thermally decomposes organic matter; produces amorphous silica below 800°C; higher temperatures (>900°C) risk crystalline silica formation.	Simple, cost-effective thermal method; produces amorphous silica efficiently.	High temperatures (above 900°C) risk the formation of crystalline silica; an energy-intensive process.	Bakar <i>et al.</i> (2016); Samat <i>et al.</i> (2021)
Green extraction methods	An environmentally-friendly approach with reduced toxicity and lower temperatures; organic acids like citric acid are effective.	Lower environmental impact; effective in removing impurities.	Requires optimisation to match conventional methods' efficiency; organic acids can be costly.	Pa <i>et al.</i> (2016); September <i>et al.</i> (2023)

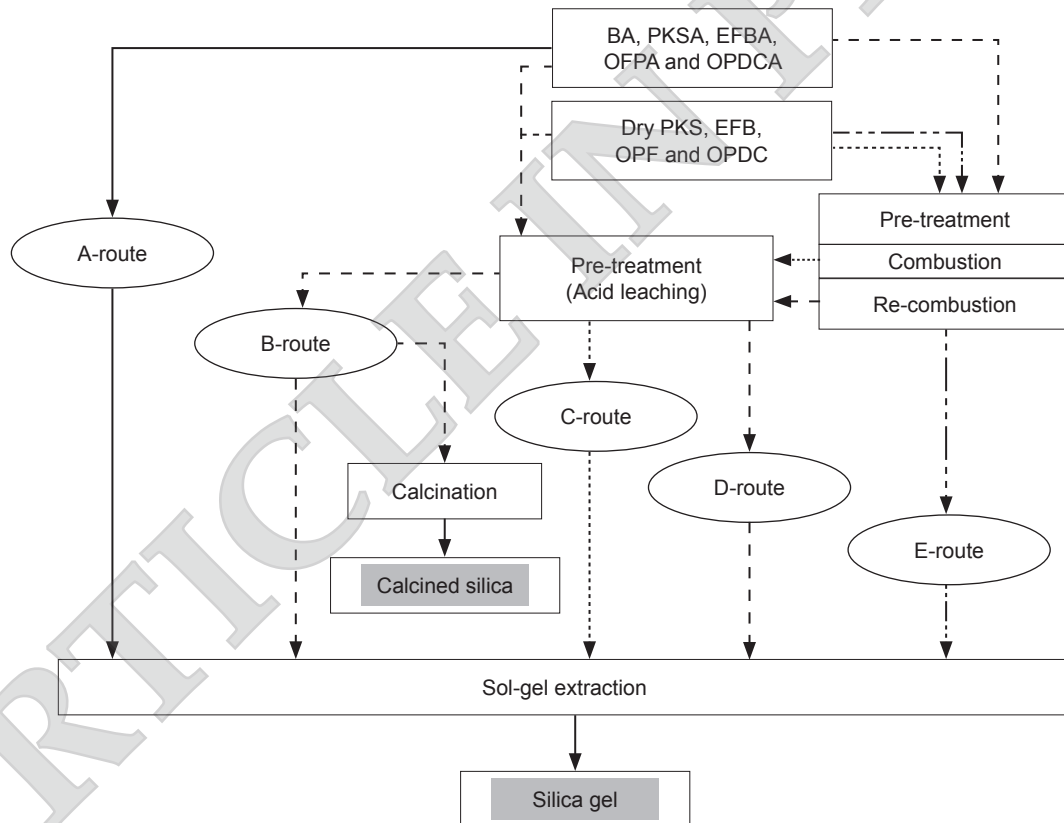


Several pre-treatment/processing routes have been developed for extracting biogenic silica from oil palm solid waste (Figure 3). Each route is tailored to specific raw materials and production goals, with the choice of method depending on the desired purity, cost and environmental impact as described previously (Table 2).

### Extraction Yield of Biogenic Silica

A summary of published works on the extraction yields and purity of biogenic silica from oil palm solid wastes is presented in Table 3, highlighting the comparison between conventional and green extraction methods, sol-gel extraction and calcination methods and the effects of different

processing routes. The comparison between conventional and green extraction methods reveals that green extraction approaches, such as citric acid pre-treatment, offer a more sustainable alternative while improving silica yields in certain cases. For example, Samat *et al.* (2021) demonstrated that using 1 M citric acid as a pre-treatment for PKS and EFB improved the silica yield to 4.35% and 0.95%, respectively. This yield is notably higher compared to conventional extraction with 1 M HCl followed by calcination at 800°C, which resulted in lower yields of 1.49% for PKS and 0.80% for EFB (Samat *et al.*, 2018). The significant weight loss during calcination in the conventional methods limits the overall yield, whereas citric acid leaching mitigates this issue. However, despite the modest yield improvement, green methods are preferred for their reduced environmental impact and sustainability.



Note: A-route: Extraction without pre-treatment, typically applied to combusted raw materials like BA, followed by the sol-gel extraction process (Utama *et al.*, 2018, 2019).

B-route: Acid leaching pre-treatment, suitable for both combusted (BA) and dry raw materials (PKS, EFB, OPF and OPDC), followed by the sol-gel extraction process for ash raw materials (Adha & Warsiki, 2023) or calcination for dry raw materials (Samat *et al.*, 2021).

C-route: Combustion followed by acid leaching, used for dry raw materials like EFB OPE, followed by the sol-gel extraction process (Osman & Sapawe, 2020; Rahmat *et al.*, 2021).

D-route: Combusted ash undergoes re-combustion before extraction with the sol-gel extraction process (Hoerudin *et al.*, 2024; Nelson *et al.*, 2023).

E-route: Combustion of dry raw materials without acid leaching, followed by the sol-gel extraction process (Imoisili *et al.*, 2020a, 2020b; Rahim *et al.*, 2023).

Figure 3. Pre-treatment routes and extraction methods for producing biogenic silica from oil palm solid waste.

TABLE 3. EXTRACTION YIELD AND SiO<sub>2</sub> CONCENTRATION OF BIOGENIC SILICA FROM OIL PALM BIOMASS

Type of biomass	Methods (Pre-treatments and extraction)	Route/type of silica	Results (yield and silica purity)	Reference
<b>Conventional Extraction</b>				
BA	Acid leaching pre-treatment (1.2 M HCl, 24 hr), alkaline extraction (4-8 M NaOH, 30-90 min), and precipitation (1 M HCl).	B/Silica gel	Silica yield was 41.17% <sup>**</sup> and silica purity were 79.20% under optimal extraction conditions.	Adha and Warsiki (2023)
EFBA	Re-carbonised (600°C-800°C) and acid leaching (1% HCl) pre-treatment, alkaline extraction (NaOH), precipitation (1 M HCl+3 M NH <sub>4</sub> OH), and calcination (550°C, 3 hr).	D/Calcined silica	Silica yield ranged from 14.70%-17.30% <sup>**</sup> and silica purity was 59.85% after re-carbonisation at 800°C.	Nelson <i>et al.</i> (2023)
PKS	Acid leaching pre-treatment (1 M HCl) and calcination (400°C-800°C, 6 hr).	B/Calcined silica	Weight loss was 98.51% (~silica yield was 1.49%) during calcination at 800°C.	Samat <i>et al.</i> (2018)
EFB	Acid leaching pre-treatment (1 M HCl) and calcination (400°C-800°C, 6 hr).	B/Calcined silica	Weight loss was 99.20% (~silica yield was 0.8%) during calcination at 800°C.	Samat <i>et al.</i> (2018)
	Combustion (600°C-800°C, 2 hr) and acid leaching (5 N H <sub>2</sub> SO <sub>4</sub> , 30 min) pre-treatment.	C/Ash	Burning at 600°C-800°C increased the silica purity from 9.50%-45.60% after leaching.	Rahmat <i>et al.</i> (2021)
<b>Green Extraction</b>				
BA	Acid leaching pre-treatment (1.00%-6.00% citric acid) and calcination (800°C, 30 min).	B/Ash	Silica purity was 92.00% at a citric acid leaching concentration of ≥3.00%.	Pa <i>et al.</i> (2016)
	Alkaline extraction (1.5 N NaOH, 60 min, ratio sample to NaOH 0.23 g/cm <sup>3</sup> , temperature 75°C-100°C, stirring speed 500-1,200 rpm), precipitation (10.00% H <sub>2</sub> SO <sub>4</sub> ), and ageing (18 hr).	A/Silica gel	60.42% of silica in the sample can be extracted, and silica purity was 95.33% under the optimum extraction conditions.	Utama <i>et al.</i> (2018)
	Alkaline extraction (1.4 N NaOH, 50 min, 105°C, sample-to-NaOH ratio 0.23 g/cm <sup>3</sup> , stirring speed 1,065 rpm) and precipitation using CO <sub>2</sub> impregnation and mechanical fragmentation.	A/Silica gel	Silica purity was 96.90% under the optimum precipitation conditions.	Utama <i>et al.</i> (2018)
	Re-ashing (600°C, 2 hr) and acid leaching (6.00% citric acid, 600°C, 1.5 hr) pre-treatment, alkaline extraction (6.00%-10.00% NaOH, 100°C, 1.5 hr), and precipitation (3.00% HCl, pH 7), ageing (18 hr).	D/Silica gel	Silica purity was 94.68% under optimal extraction conditions.	Hoerudin <i>et al.</i> (2024)
PKS	Combustion pre-treatment (750°C, 3 hr), alkaline extraction (2 N NaOH, 2 hr), precipitation (2 N HCl, pH 7.5-8.5), and ageing (24 hr).	E/Silica xerogel	Silica yield was 56.65% <sup>**</sup> and silica purity were 96.83%.	Imoisili <i>et al.</i> (2020b)
	Combustion pre-treatment (750°C, 3 hr), alkaline extraction (3 N NaOH, 2 hr), precipitation (3 N HCl), and ageing (24 hr). Refluxed silica xerogel (3 M HCl, 70°C, 4 hr), dissolved with 3 M NaOH, and silica precipitation (H <sub>2</sub> SO <sub>4</sub> , pH 7.5).	E/Silica nanoparticles	Silica nanoparticle yield was 54.35% <sup>**</sup> and nano silica purity was 96.59%.	Imoisili <i>et al.</i> (2020a)
	Acid leaching pre-treatment (1 M citric acid, 2 hr) and calcination (400°C-800°C, 6 hr).	B/Calcined silica	Weight loss was 95.65% (~silica yield was 4.35%) during calcination at 800°C.	Samat <i>et al.</i> (2021)
EFB	Acid leaching pre-treatment (1 M citric acid, 2 hr) and calcination (400°C-800°C, 6 hr).	B/Calcined silica	Weight loss was 99.05% (~silica yield was 0.95%) during calcination at 800°C.	Samat <i>et al.</i> (2021)
OPF	Combustion (600°C, 3 hr) and acid leaching (3.00% citric acid, 70°C, 1 hr) pre-treatment, alkaline extraction (2 M NaOH, 1 hr), precipitation (1 M H <sub>2</sub> SO <sub>4</sub> , pH 7), and ageing (18 hr).	C/Silica gel	1 kg of OPF produced 34.7 g of ash (3.50%); after leaching, it produced 18.7 g of leached ash (53.90%), with a silica yield of 12.8 g (1.28% <sup>*</sup> from the OPF; 36.89% <sup>**</sup> from the ash).	Osman and Sapawe (2020)
OPDC	Combustion pre-treatment (600°C-900°C, 5 hr), alkaline extraction (5 M NaOH, 100°C, 1 hr) and precipitation (2.5 M H <sub>2</sub> SO <sub>4</sub> , pH 6-7).	E/Silica gel	Silica purity ranged from 32.10%-75.96%.	Rahim <i>et al.</i> (2023)
	Acid leaching pre-treatment (1 M citric acid, 2 hr) and calcination (400°C-800°C, 6 hr).	B/Calcined silica	Weight loss 83.95% (~silica yield 16.05% <sup>*</sup> ) under calcination at 800°C.	Samat <i>et al.</i> (2021)

Note: <sup>\*</sup> - Silica yield from dry raw material; <sup>\*\*</sup> - Silica yield from ash raw material; n.a. - Not available.

Among the extraction techniques, the sol-gel methods have shown considerable advantages over calcination routes regarding silica purity. For instance, Utama *et al.* (2018) can convert silica in samples by 60.38%-60.42% with a SiO<sub>2</sub> purity of 95.33% using the sol-gel method on BA. Further refinement, such as CO<sub>2</sub> impregnation during gelation, increased the SiO<sub>2</sub> purity to 96.90% (Utama *et al.*, 2019). In contrast, the calcination method, although simpler, tends to produce lower purity silica due to incomplete removal of impurities (Pa *et al.*, 2016), where BA treated with ≥3.00% citric acid and calcined at 800°C resulted in a silica product with 92.00% SiO<sub>2</sub> purity. These findings suggest that while calcination is effective for bulk processing, sol-gel methods are more suitable for applications requiring high-purity silica, such as in catalysts, electronics and pharmaceutical industries.

The comparison across different types of oil palm solid waste raw materials also highlights significant variations in yield and purity. BA emerges as the most promising biomass due to its high silica yield and purity without requiring pre-treatment. Direct extraction using the sol-gel method can convert silica in samples by 60.38%-60.42% (Utama *et al.*, 2018). In contrast, OPF and EFB exhibited lower yields. For instance, OPF subjected to combustion at 600°C and subsequent citric acid leaching achieved a silica yield of only 1.28% when calculated from raw materials or 36.89% when calculated from ash (Osman & Sapawe, 2020). On the other hand, OPDC demonstrated significant potential, achieving a silica yield of 16.05% with a purity of 75.96% (Rahim *et al.*, 2023; Samat *et al.*, 2021). This result suggests that OPDC, due to its lower weight loss during calcination, is suitable for bulk silica production with balanced yield and purity.

The choice of extraction route also strongly influences both the silica yield and purity. For example, Imoisili *et al.* (2020b) optimised the process for PKS by using combustion at 750°C for 3 hr followed by alkaline extraction and precipitation, which resulted in a significantly high yield of 56.65% and SiO<sub>2</sub> purity of 96.83%. A subsequent modification to the process, involving refluxing with 3 M HCl and re-extraction with 3 M NaOH, enabled the production of silica nanoparticles with a yield of 54.35% (Imoisili *et al.*, 2020a). These findings underscore the effectiveness of alkaline extraction and sol-gel methods in producing high-purity silica or advanced materials like silica nanoparticles, which are critical for high-value applications in nanotechnology.

From the comparative analysis, BA stands out as the most favourable source of biogenic silica, offering both high yield and significant SiO<sub>2</sub> purity without requiring intensive pre-treatment. However, for applications demanding high-

purity silica (*e.g.*, electronics, pharmaceuticals and speciality catalysts), processes such as alkaline extraction or sol-gel methods are preferred. In contrast, for bulk silica production where cost-effectiveness is essential, calcination remains a viable option, particularly for raw materials like OPDC and PKS, which demonstrate balanced yield and purity. In terms of applications, the choice of silica purity and particle size determines its suitability for specific uses. High-purity silica (>95.00%) obtained via sol-gel methods is ideal for high-value applications, such as nanocomposites and catalysts. Silica produced through calcination with moderate purity is suitable for bulk applications like fillers in rubber composites and as a raw material in construction materials. Moreover, the production of silica nanoparticles, as demonstrated by Imoisili *et al.* (2020a), opens opportunities in advanced technologies requiring materials with enhanced surface area and reactivity.

The comparative review highlights the importance of selecting appropriate extraction routes based on the desired silica yield, purity and intended application. Green extraction methods offer environmental benefits and sustainable processing. Sol-gel techniques remain superior for applications requiring high-purity silica, such as electronics, pharmaceuticals and speciality catalysts. Among the raw materials, BA demonstrates the greatest potential for silica production, offering high yields and significant purity without requiring intensive pre-treatment.

## PROPERTIES OF BIOGENIC SILICA FROM OIL PALM BIOMASS

### Chemical Composition

Table 4 shows the chemical composition of biogenic silica extracted from oil palm biomass. The SiO<sub>2</sub> concentration is influenced by various factors, including the type of biomass (BA, EFB, PKS, OPF, OPDC), pre-treatment route and extraction methods. According to Adha and Warsiki (2023), biogenic silica from BA processed through the B-route had a SiO<sub>2</sub> concentration of 79.20%. This SiO<sub>2</sub> concentration was relatively low because various impurities could not be removed, such as Al<sub>2</sub>O<sub>3</sub> (8.20%), Na<sub>2</sub>O (6.20%) and K<sub>2</sub>O (1.50%). Rahmat *et al.* (2021) conducted a pre-treatment using the C-route method to increase SiO<sub>2</sub> concentrations in ash and silica from EFB. In their study, the structure of the silica ash observed was crystalline following combustion and acid leaching pre-treatment involving sulfuric acid. Although acid leaching led to an increase in SiO<sub>2</sub> concentration in EFBA, it was unable to eliminate

metal oxide impurities, such as CaO (17.80%), K<sub>2</sub>O (16.40%), SO<sub>3</sub> (3.50%) and Fe<sub>2</sub>O<sub>3</sub> (3.30%). Nelson *et al.* (2023) performed a multi-step process to produce biogenic silica from EFBA. This involved re-combustion of EFBA, an acid leaching pre-treatment using HCl (D-route), followed by sol-gel extraction using NaOH and gelation through the co-precipitation method. The resulting SiO<sub>2</sub> concentration increased to 58.95% and the silica structure exhibited an amorphous nature. Despite these improvements, the concentration of other metal oxides as impurities remained notably high.

Pa *et al.* (2016) utilised organic acid, specifically citric acid, as an alternative chemical to replace the strong acids (HCl and H<sub>2</sub>SO<sub>4</sub>) in the leaching process of BA. The use of citric acid as a leaching pre-treatment agent (B-route) has been demonstrated to be effective, resulting in a significant increase in SiO<sub>2</sub> concentration to 92.0%. However, the subsequent calcination at 800°C for a short period (30 min) was unsuccessful in converting the crystalline structure to an amorphous form.

Biogenic silica has been extracted from OPDC involving a pre-treatment through combustion at 600°C for 5 hr (E-route), followed by sol-gel extraction. This process resulted in biogenic silica with a SiO<sub>2</sub> concentration of 76.95% (Rahim *et al.*, 2023). The remaining impurity components include K<sub>2</sub>O (11.60%), Al<sub>2</sub>O<sub>3</sub> (7.80%), P<sub>2</sub>O<sub>5</sub> (1.21%), SO<sub>3</sub> (0.99%), Fe<sub>2</sub>O<sub>3</sub> (0.21%) and CaO (0.18%). Similarly, the extraction of biogenic silica from PKS involved a comparable pre-treatment to OPDC, followed by sol-gel extraction. In this case, the resulting SiO<sub>2</sub> concentration was notably higher at 96.83%, with remaining impurities present in relatively low concentrations (Imoisili *et al.*, 2020b).

Biogenic silica with relatively high SiO<sub>2</sub> concentrations, ranging from 95.33%-96.90%, was obtained by simple extraction of BA without pre-treatment (A-route) (Utama *et al.*, 2018, 2019). This was achieved by optimising the sol-gel extraction conditions (extraction temperature and stirring speed) (Utama *et al.*, 2019) or modifying the sol-gel method through CO<sub>2</sub> impregnation during the gelation process (Utama *et al.*, 2019). The remaining metal oxide impurities in both studies were Na<sub>2</sub>O (1.59%-2.50%), K<sub>2</sub>O (1.29%), Al<sub>2</sub>O<sub>3</sub> (0.39%-0.46%) and SO<sub>3</sub> (0.48%). The SiO<sub>2</sub> concentrations of BA-derived biogenic silica were higher than those of the biogenic silica from sugarcane bagasse ash, 91.58% (Affandi *et al.*, 2009). Additionally, they were comparable to that of the commercial silica, 95.37% (Setyawan *et al.*, 2021), but lower than those of rice husk ash-derived biogenic silica, 99.25%-99.61% (Fernandes *et al.*, 2017).

TABLE 4. CHEMICAL COMPOSITION OF TREATED ASH AND BIOGENIC SILICA FROM OIL PALM BIOMASS

Type of biomass	Route/type of silica	SiO <sub>2</sub> (%)	Na <sub>2</sub> O (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Cl (%)	K <sub>2</sub> O (%)	P <sub>2</sub> O <sub>5</sub> (%)	CaO (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	SO <sub>3</sub> (%)	MgO (%)	MnO (%)	TiO <sub>2</sub> (%)	ZnO (%)	Others (%)	Reference
Conventional extraction																
BA	B/Silica gel	79.20	6.20	8.20	3.40	1.50	0.60	0.20	0.20	0.40	n.a	n.a	0.001	0.001	n.a	Adha and Warsiki (2023)
EFBA	D/Calcined silica	59.85	0.56	1.97	n.a	11.66	6.28	7.34	1.55	n.a	8.62	0.44	0.150	n.a	n.a	Nelson <i>et al.</i> (2023)
EFB	C/Ash	45.60	n.a	n.a	0.00	16.40	0.00	17.80	3.30	3.50	n.a	n.a	n.a	n.a	n.a	Rahmat <i>et al.</i> (2021)
Green extraction																
BA	A/Silica gel	95.33	2.50	0.39	n.a	1.29	n.a	n.a	n.a	0.48	n.a	n.a	n.a	n.a	n.a	Utama <i>et al.</i> (2018)
	A/Silica gel	96.90	1.59	0.46	n.a	1.29	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	Utama <i>et al.</i> (2018)
	C/Ash	92.00	n.a	0.00	n.a	3.58	0.00	1.22	2.13	n.a	n.a	n.a	n.a	n.a	n.a	Pa <i>et al.</i> (2016)
PKS	D/Silica gel	94.64	0.17	2.63	0.22	0.22	0.53	0.68	0.26	0.16	0.46	n.a	n.a	n.a	0.03	Hoerudin <i>et al.</i> (2024)
	E/Silica xerogel	96.83	0.97	0.00	n.a	1.43	0.00	0.43	0.17	0.00	0.17	n.a	n.a	n.a	n.a	Imoisili <i>et al.</i> (2020b)
OPDC	E/Silica gel	76.95	n.a	7.80	n.a	11.60	1.71	0.18	0.21	0.99	n.a	n.a	n.a	n.a	0.76	Rahim <i>et al.</i> (2023)
Commercial silica	-	95.37	2.47	0.63	0.07	0.01	n.a	0.02	0.06	n.a	0.06	0.00	n.a	n.a	0.04	Setyawan <i>et al.</i> (2021)

Note: n.a - not available.

## Crystallinity and Amorphicity

Crystallinity refers to the proportion of crystalline substances within a blend of both crystalline and non-crystalline materials. Conversely, amorphicity exhibits an inverse relationship with the crystallinity of materials. The extent of crystallinity plays a crucial role in pozzolanic activity, as only amorphous materials actively participate in the pozzolanic reaction (Karim *et al.*, 2017). X-ray diffraction (XRD) serves as a characterisation technique employed to ascertain the presence of crystalline compounds. The method is particularly useful for crystal structure analysis due to the distinct patterns associated with each compound. By referencing the known diffraction pattern of an element in this analysis, it becomes possible to identify the specific compound.

Table 5 shows XRD  $2\theta$  values for treated ash derived from EFB and BA, as well as biogenic silica extracted from BA, EFB, PKS and OPDC. The  $2\theta$  values are presented for both before and after undergoing a leaching or extraction process, employing both conventional and green extraction methods. The raw materials derived from palm oil solid waste exhibit a crystalline nature before undergoing the extraction process. According to Rahmat *et al.* (2021), EFBA retained its crystalline nature when subjected only to leaching without subsequent extraction (Figure 4a). Similarly, Faizul *et al.* (2013) reported that BA maintained a crystalline structure even after undergoing pre-treatment and subsequent calcination at a temperature of  $800^{\circ}\text{C}$  for a short time (30 min). Nelson *et al.* (2023) asserted that the transformation of crystalline silica into its amorphous counterpart could be achieved through a thermochemical process. Additionally, Samat *et al.* (2018, 2021) reported that amorphous silica from EFB, PKS and OPDC could be produced by extraction involving calcination at a temperature of  $800^{\circ}\text{C}$  for 6 hr.

In general, amorphous silica is characterised by a broad hump at diffraction angles  $2\theta$  between  $15.0^{\circ}$  and  $35.0^{\circ}$ . The XRD pattern of biogenic silica obtained from palm oil solid waste through the sol-gel method exhibits a pronounced absence of sharp peaks, indicating the amorphous structure of the resulting product. For example, the XRD pattern of biogenic silica extracted from EFBA by the sol-gel method showed a  $2\theta$  value of  $31.8^{\circ}$ , confirming the amorphous nature of the silica (Nelson *et al.*, 2023). The amorphous structure of biogenic silica extracted from PKS was identified with an XRD  $2\theta$  value of  $22.5^{\circ}$ , as shown in Figure 4b (Imoisili *et al.*, 2020b). Biogenic silica extracted from OPDC by the sol-gel method exhibited a broad diffraction peak at a  $2\theta$  value of  $22.0^{\circ}$ , indicating the transformation of crystals into an amorphous form due to alkali

treatment (Rahim *et al.*, 2023). The results align with XRD patterns observed for amorphous biogenic silica obtained from other sources such as rice husk ash (Hoerudin *et al.*, 2022), corn cob ash (Velmurugan *et al.*, 2015), sugarcane bagasse ash (Chindaprasirt & Rattanasak, 2020) and commercial amorphous silica (Setyawan *et al.*, 2021).

Depending on its applications, amorphous silica is usually preferred over crystalline silica due to its random and irregular atomic structure and patterns, which enhance its reactivity. It is widely acknowledged that chemical treatment induces structural phase transformation in biogenic silica. In addition, amorphous silica is generally considered safe and non-toxic, in contrast to crystalline silica, which can be toxic and may lead to the development of silicosis, as highlighted by Rovani *et al.* (2018). A study by Erawati *et al.* (2024) investigated the preparation, characterisation and cytotoxicity of calcium silicate derived from amorphous  $\text{SiO}_2$  extracted from black, red and white rice husks. The results demonstrated that all three calcium silicate samples were non-toxic, with mean cell viability ranging from 78.72%-123.51%, as per ISO 10993-5 standards. This confirms the biocompatibility of the materials. This expands the opportunities for the broader utilisation of biogenic silica derived from oil palm biomass in various fields.

## Functional Groups

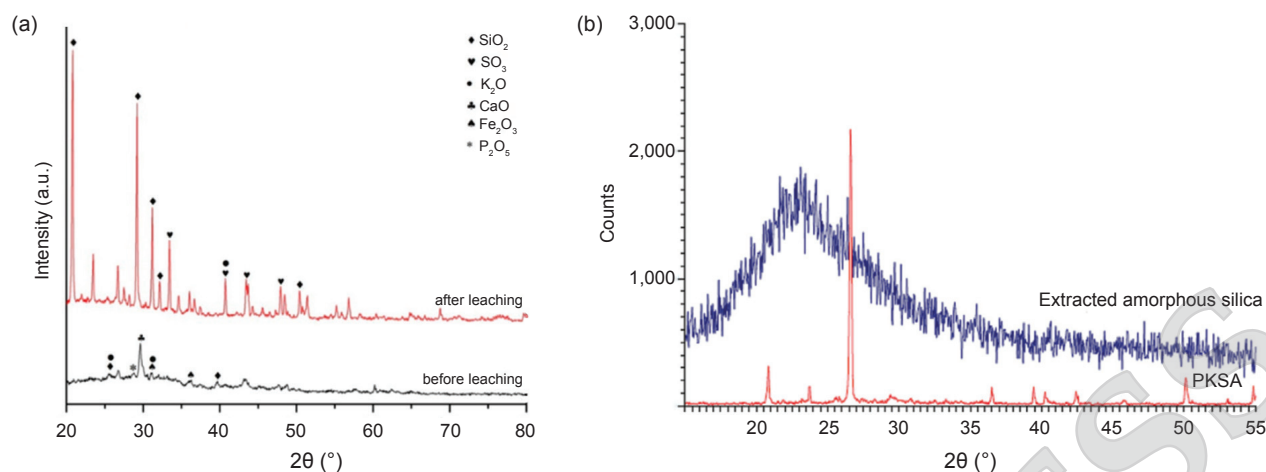
Fourier transform infrared spectroscopy (FTIR) is a well-known vibrational spectroscopy technique based on the observation of molecular vibrations that absorb infrared radiation. This method offers insights into the molecular structure of materials and functional groups within compounds (Tessema *et al.*, 2023). Nelson *et al.* (2023) reported that the FTIR spectra of biogenic silica extracted from EFBA exhibited vibration bands corresponding to Si-OH, O-Si-O, and Si-O-Si functional groups. According to Okoronkwo *et al.* (2013), the band at wavenumbers  $463\text{-}475\text{ cm}^{-1}$  was associated with bending vibrations of the O-Si-O network, while  $791\text{-}807\text{ cm}^{-1}$  corresponded to symmetric stretching vibrations of Si-O-Si. The band at wavenumbers  $1,071\text{-}1,090\text{ cm}^{-1}$  represented the siloxane group or the asymmetric Si-O-Si stretching vibration. This reveals the bond structure of Si and O atoms towards smaller particle sizes. Meanwhile, the broad bands at  $1,633\text{-}1,645\text{ cm}^{-1}$  and  $3,350\text{-}3,750\text{ cm}^{-1}$  were caused by O-H bending and stretching vibrations of the Si-OH silanol groups and due to the adsorption of  $\text{H}_2\text{O}$  molecules on the silica surface (Imoisili *et al.*, 2020a).

The infrared (IR) spectra of biogenic silica obtained from palm oil solid waste (BA, EFB, PKS, OPF, OPDC) using the conventional and

TABLE 5. XRD PATTERN OF ASH AND BIOGENIC SILICA FROM OIL PALM BIOMASS

Type of biomass	Methods (pre-treatments and extraction)	Route	Before leaching/extraction			After leaching/extraction			Reference
			Metal oxide	Structure	2θ value(°)	Metal oxide	Structure	2θ Value(°)	
Conventional extraction									
EFB	Combustion (600°C-800°C, 2 hr) and acid leaching (5 N H <sub>2</sub> SO <sub>4</sub> , 30 min) pre-treatment	C	SiO <sub>2</sub>	Hexagonal	26.74	SiO <sub>2</sub>	Rhombohedral	20.93	Rahmat <i>et al.</i> (2021)
			CaO	n.a.	39.38			29.18	
			K <sub>2</sub> O	n.a.	29.76			31.10	
			P <sub>2</sub> O <sub>5</sub>	n.a.	25.78			32.87	
			Fe <sub>2</sub> O <sub>3</sub>	n.a.	29.55	K <sub>2</sub> O	Hexagonal	40.61	
				40.32	SO <sub>3</sub>	Orthorhombic	32.34		
							43.83		
							47.99		
EFBA	Re-carbonised (600°C-800°C) and acid leaching (1% HCl) pre-treatment, alkaline extraction (NaOH), precipitation (1 M HCl + 3 M NH <sub>4</sub> OH), and calcination (550°C, 3 hr)	D	SiO <sub>2</sub> KAlSiO <sub>4</sub> CaCO <sub>3</sub>	Quartz	30.00	SiO <sub>2</sub>	Amorphous	31.80	Nelson <i>et al.</i> (2023)
Green Extraction									
BA	Acid leaching pre-treatment (1%-6% citric acid) and calcination (800°C, 30 min)	B	SiO <sub>2</sub> KAlSiO <sub>4</sub> C	Quartz	n.a.	SiO <sub>2</sub> C	n.a.	n.a.	Pa <i>et al.</i> (2016)
			n.a.	n.a.	n.a.	n.a.	n.a.		
PKS	Alkaline extraction (1.4 N NaOH, 50 min, 105°C, sample-to-NaOH ratio 0.23 g/cm <sup>3</sup> , stirring speed 1,065 rpm) and precipitation using CO <sub>2</sub> impregnation and mechanical fragmentation	A	n.a.	n.a.	n.a.	SiO <sub>2</sub>	Amorphous	23.00	Utama <i>et al.</i> (2019)
			SiO <sub>2</sub>	Quartz	26.70	SiO <sub>2</sub>	Amorphous	22.50	Hoerudin <i>et al.</i> (2024)
			SiO <sub>2</sub>	Quartz	24.00	SiO <sub>2</sub>	Amorphous	22.50	Imoisili <i>et al.</i> (2020b)
			SiO <sub>2</sub>	Quartz	43.00	SiO <sub>2</sub>	Amorphous	22.50	Imoisili <i>et al.</i> (2020a)
OPDC	Combustion pre-treatment (600°C-900°C, 5 hr), alkaline extraction (5 M NaOH, 100°C, 1 hr) and precipitation (2.5 M H <sub>2</sub> SO <sub>4</sub> , pH 6-7)	E	CaCO <sub>3</sub>	Calcite	22.00	SiO <sub>2</sub>	Amorphous	22.00	Rahim <i>et al.</i> (2023)
					44.00			28.00	
					47.00			29.00	

Note: n.a. - Not available.



Source: Imoisili *et al.* (2020b); Rahmat *et al.* (2021).

Figure 4. XRD pattern, (a) EFB ash before and after leaching and (b) amorphous silica.

green extraction methods are presented in Table 6. The functional groups in biogenic silica derived from solid palm oil waste exhibit some variation. This is likely due to differences in raw materials (BA, EFB, PKS, OPF, OPDC), pre-treatment route and extraction methods employed. The evident variations in the IR spectra are particularly pronounced in the extraction of biogenic silica using the sol-gel method (silica-gel), a process that typically involves NaOH as a solvent (Imoisili *et al.*, 2020a, 2020b; Nelson *et al.*, 2023; Osman & Sapawe, 2020; Rahim *et al.*, 2023; Utama *et al.*, 2018, 2019) and the calcination method (calcined silica), especially when conducted at high temperatures for an extended period, *e.g.*, 800°C for 6 hr. These specific calcination conditions have been considered optimal for biogenic silica production from EFB, PKS and OPDC (Samat *et al.*, 2018, 2021).

In the studies by Samat *et al.* (2018; 2021), the calcined silica showed no detectable infrared spectrum in the range of 3,350-3,750  $\text{cm}^{-1}$ . In contrast, this range was observed in silica gel, appearing as broad bands in the IR spectrum. The difference is evident in the IR spectra of biogenic silica from PKS processed using the sol-gel and calcination method (Figure 5).

According to Usman *et al.* (2015), the bands at 1,450-3,450  $\text{cm}^{-1}$  were undetected, indicating the absence of all traces of water molecules and polar functional groups during the calcination process at high temperatures. Similarly, the IR spectrum at wavenumbers 447-473  $\text{cm}^{-1}$  is generally undetected in calcined silica from EFB, PKS and OPDC. Geetha *et al.* (2016) observed that no band was detected at 447-473  $\text{cm}^{-1}$ , indicating the loss of all traces of original organic compounds found in plants during the calcination at high temperatures. However, in the calcination process of BA carried out by Faizul (2013) using the

B-route pre-treatment, an IR spectrum at a wavenumber of 3,445  $\text{cm}^{-1}$  was still observed. This may be due to the relatively short calcination time of 30 min at 800°C. The short duration of the calcination process may not have permitted the complete combustion of organic compounds, resulting in the persistence of certain functional groups, as indicated by the observed IR spectrum.

### Surface Properties

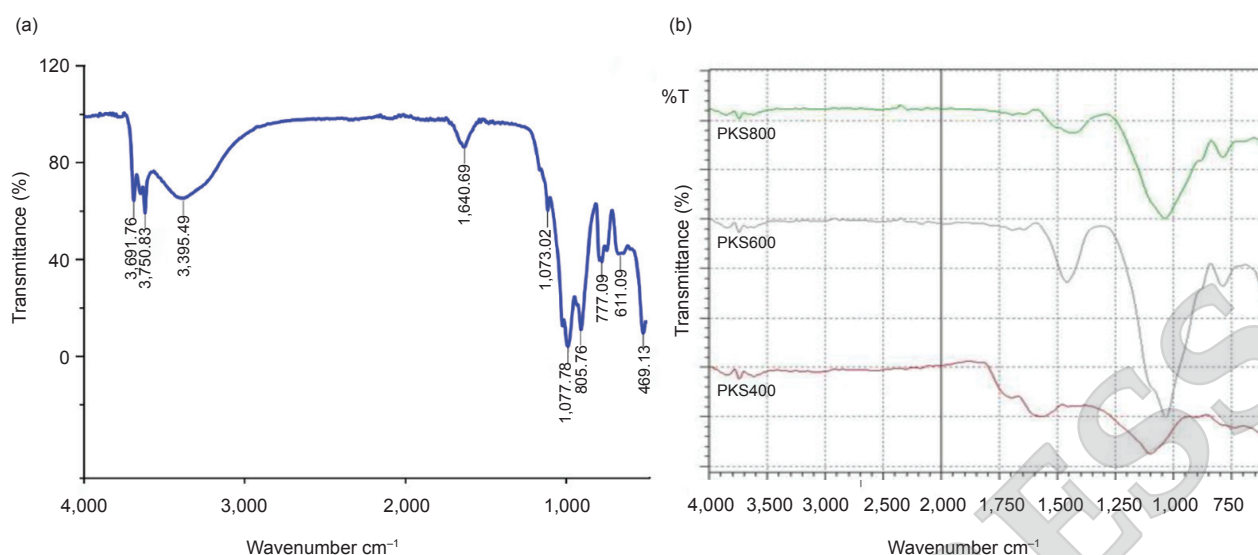
Available data on the surface properties of biogenic silica extracted from oil palm biomass have been limited. Table 7 shows the surface properties of biogenic silica extracted from various oil palm biomass sources using different extraction and pre-treatment methods. These properties vary depending on factors such as the biomass type (BA, EFB, EFBA, PKS, OPDC), pre-treatment route and extraction method. A multi-stage process for producing biogenic silica from EFBA, involving re-ashing, acid leaching pre-treatment with hydrochloric acid (conventional extraction / D-route), followed by sol-gel extraction with sodium hydroxide and gelation through a coprecipitation method, resulted in a low Brunauer-Emmett-Teller (BET) surface area of 0.38  $\text{m}^2/\text{g}$  and a very high average pore size of 23.9  $\mu\text{m}$  (Nelson *et al.*, 2023). This relatively low surface area might be due to the relatively brief combustion period, leading to lower surface porosity. In contrast, biogenic silica extracted from EFB using citric acid leaching pre-treatment (green extraction / B-route), followed by calcination at 800°C produced a higher BET surface area of 15.10  $\text{m}^2/\text{g}$  (Samat *et al.*, 2021). This discrepancy may be due to the incomplete removal of impurities (such as alkali metals) in the biogenic silica from EFBA, attributed to eutectic reactions occurring during the re-ashing process.

TABLE 6. THE IR SPECTRA OF ASH AND BIOGENIC SILICA FROM OIL PALM BIOMASS

Type of biomass	Methods (Pre-treatments and extraction)	Route/Type of silica	Wavenumber (cm <sup>-1</sup> )	Type of bond	Reference
Conventional Extraction					
EFBA	Re-carbonised (600°C-800°C) and acid leaching (1% HCl) pre-treatment, alkaline extraction (NaOH), precipitation (1 M HCl + 3 M NH <sub>4</sub> OH) and calcination (550°C, 3 hr)	D / Calcined silica	619 1,151	Symmetric stretching of the Si-O-Si bond Asymmetric stretching of the Si-O-Si bond	Nelson <i>et al.</i> (2023)
EFB	Acid leaching pre-treatment (1 M HCl) and calcination (400°C-800°C, 6 hr)	B / Calcined silica	447 792 1,076	Si-O bending vibration of the O-Si-O bond Symmetric stretching of the Si-O-Si bond Asymmetric stretching of the Si-O-Si bond	Samat <i>et al.</i> (2018)
PKS	Acid leaching pre-treatment (1 M HCl) and calcination (400°C-800°C, 6 hr)	B / Calcined silica	474 788 1,035	Si-O bending vibration of the O-Si-O bond Symmetric stretching of the Si-O-Si bond Asymmetric stretching of the Si-O-Si bond	Samat <i>et al.</i> (2018)
Green extraction					
BA	Acid leaching pre-treatment (1%-6% citric acid) and calcination (800°C, 30 min)	B / Ash	460 796 1,099	Si-O bending vibration of the O-Si-O bond Symmetric stretching of the Si-O-Si bond Asymmetric stretching of Si-O-Si, vibration of the Si-O bond	Faizul <i>et al.</i> (2013)
	Alkaline extraction (1.4 N NaOH, 50 min, 105°C, sample-to-NaOH ratio 0.23 g/cm <sup>3</sup> , stirring speed 1,065 rpm) and precipitation using CO <sub>2</sub> impregnation and mechanical fragmentation	A / Silica gel	471-473 800 1,107 1,639-1,641 3,452-3,458	Stretching vibration of the O-H bond in silanol (Si-OH) and adsorbed water molecules Stretching vibration of the O-H bond in silanol (Si-OH) and adsorbed water molecules Si-O bending vibrations of the O-Si-O bond Symmetric stretching of the Si-O-Si bond Asymmetric stretching of the Si-O-Si bond Bending vibrations of water molecules Stretching vibration of the O-H bond in silanol (Si-OH) and adsorbed water molecules	Utama <i>et al.</i> (2018; 2019)
	Re-ashing (600°C, 2 hr) and acid leaching (6% citric acid, 600°C, 1.5 hr) pre-treatment, alkaline extraction (6%-10% NaOH, 100°C, 1.5 hr) and precipitation (3% HCl, pH 7), ageing (18 hr)	D / Silica gel	467 791 1,081 1,635 3,450	Si-O bending vibration of the O-Si-O bond Symmetric stretching of the Si-O-Si bond Asymmetric stretching of the Si-O-Si bond Bending vibration of the O-H bond in silanol groups Stretching vibration of the O-H bond in silanol (Si-OH)	Hoerudin <i>et al.</i> (2024)

TABLE 6. THE IR SPECTRA OF ASH AND BIOGENIC SILICA FROM OIL PALM BIOMASS (continued)

Type of biomass	Methods (Pre-treatments and extraction)	Route/Type of silica	Wavenumber (cm <sup>-1</sup> )	Type of bond	Reference
PKS	Combustion pre-treatment (750°C, 3 hr), alkaline extraction (3 N NaOH, 2 hr), precipitation (3 N HCl) and ageing (24 hr). Refluxed silica xerogel (3 M HCl, 70°C, 4 hr), dissolved with 3 M NaOH and silica precipitation (H <sub>2</sub> SO <sub>4</sub> , pH 7.5)	E/Silica xerogel/nanoparticle	469	Si-O bending vibration of the O-Si-O bond	Imoisili <i>et al.</i> (2020b; 2020a)
			611	Symmetric stretching of the Si-O-Si bond	
EFB	Acid leaching pre-treatment (1 M citric acid, 2 hr) and calcination (400°C-800°C, 6 hr)	B/Calcined silica	777	Asymmetric stretching of Si-O-Si, vibration of the Si-O bond	Samat <i>et al.</i> (2021)
			805	Bending vibration of the O-H bond in silanol (Si-OH)	
			1,073	Stretching vibration of the O-H bond in silanol (Si-OH) and adsorbed water molecules	
			1,077		
			1,640		
			3,395		
			3,691		
			3,750		
			794	Symmetric stretching of the Si-O-Si bond	
			880	Si-C bond	
OPDC	Acid leaching pre-treatment (1 M citric acid, 2 hr) and calcination (400°C-800°C, 6 hr)	B/Calcined silica	1,046	Asymmetric stretching of Si-O-Si, vibration of the Si-O bond	Samat <i>et al.</i> (2021)
			1,417	In-plane C=H bond	
			790	Symmetric stretching of the Si-O-Si bond	
			1,045	Asymmetric stretching of Si-O-Si, vibration of the Si-O bond	
OPDC	Combustion pre-treatment (600°C-900°C, 5 hr), alkaline extraction (5 M NaOH, 100°C, 1 hr) and precipitation (2.5 M H <sub>2</sub> SO <sub>4</sub> , pH 6-7)	E/Silica gel	1,070	Asymmetric stretching of Si-O-Si, vibration of the Si-O bond	Rahim <i>et al.</i> (2023)
			462	Si-O bending vibration of the O-Si-O bond	
			1,074	Asymmetric stretching of the Si-O-Si bond	
			1,645	Stretching of the C=O bond	
			3,473	Stretching vibration of the O-H bond in silanol (Si-OH) and adsorbed water molecules	
OPF	Acid leaching pre-treatment (1 M citric acid, 2 hr) and calcination (400°C-800°C, 6 hr)	B/Calcined silica	779	Symmetric stretching of the Si-O-Si bond	Samat <i>et al.</i> (2021)
			880	Si-C bond	
			1,026	Asymmetric stretching of Si-O-Si, vibration of the Si-O bond	
			1,409	In-plane C=H bond	
			610	Symmetric stretching of the Si-O-Si bond	
OPF	Combustion (600°C, 3 hr) and acid leaching (3% citric acid, 70°C, 1 hr) pre-treatment, alkaline extraction (2 M NaOH, 1 hr), precipitation (1 M H <sub>2</sub> SO <sub>4</sub> , pH 7) and ageing (18 hr)	C/Silica gel	1,040-1,100	Asymmetric stretching of the Si-O-Si bond	Osman and Sapawe (2020)
			1,600-1,640	Si-OH bond	
			3,350-3,390	Stretching vibration of the O-H bond in silanol (Si-OH) and adsorbed water molecules	



Source: Imoisili *et al.* (2020a); Samat *et al.* (2018).

Figure 5. FTIR spectra of biogenic silica, from PKS processed by (a) the sol-gel and (b) the calcination method.

TABLE 7. SURFACE PROPERTIES OF BIOGENIC SILICA FROM OIL PALM BIOMASS

Type of biomass	Methods (pre-treatments and extraction)	Route/type of silica	BET surface area (m <sup>2</sup> /g)	Pore size (nm)	Particle size (nm)	Reference
Conventional Extraction						
EFBA	Re-carbonised (600°C-800°C) and acid leaching (1% HCl) pre-treatment, alkaline extraction (NaOH), precipitation (1 M HCl + 3 M NH <sub>4</sub> OH) and calcination (550°C, 3 hr)	D/ Calcined silica	0.38	23.90	n.a	Nelson <i>et al.</i> (2023)
Green Extraction						
BA	Alkaline extraction (1.4 N NaOH, 50 min, 105°C, sample-to-NaOH ratio 0.23 g/cm <sup>3</sup> , stirring speed 1,065 rpm) and precipitation using CO <sub>2</sub> impregnation and mechanical fragmentation	A/ Silica gel	138.00	n.a	58.96	Utama <i>et al.</i> (2019)
	Re-ashing (600°C, 2 hr) and acid leaching (6% citric acid, 600°C, 1.5 hr) pre-treatment, alkaline extraction (6%-10% NaOH, 100°C, 1.5 hr) and precipitation (3% HCl, pH 7), ageing (18 hr)	D/ Silica gel	390.80	n.a	n.a	Hoerudin <i>et al.</i> (2024)
PKS	Combustion pre-treatment (750°C, 3 hr), alkaline extraction (3 N NaOH, 2 hr), precipitation (3 N HCl), and ageing (24 hr). Refluxed silica xerogel (3 M HCl, 70°C, 4 hr), dissolved with 3 M NaOH and silica precipitation (H <sub>2</sub> SO <sub>4</sub> , pH 7.5)	E/ Nanoparticles	438.00	2.20-6.30	n.a	Imoisili <i>et al.</i> (2020a)
	Acid leaching pre-treatment (1 M citric acid, 2 hr) and calcination (400°C-800°C, 6 hr)	B/ Calcined silica	20.08	n.a	n.a	Samat <i>et al.</i> (2021)
EFB	Acid leaching pre-treatment (1 M citric acid, 2 hr) and calcination (400°C-800°C, 6 hr)	B/ Calcined silica	15.10	n.a	n.a	Samat <i>et al.</i> (2021)
OPDC	Acid leaching pre-treatment (1 M citric acid, 2 hr) and calcination (400°C-800°C, 6 hr)	B/ Calcined silica	9.49	n.a	n.a	Samat <i>et al.</i> (2021)

Metal impurities present during the combustion process may lead to the formation of crystalline silica, causing a notable reduction in surface area. Similarly, extracting biogenic silica from OPDC and PKS with the same treatment applied to EFB yielded higher BET surface areas than EFBA, at 9.49 m<sup>2</sup>/g and 20.08 m<sup>2</sup>/g, respectively (Samat *et al.*, 2021).

Utama *et al.* (2019) reported that a relatively high BET surface area of 138 m<sup>2</sup>/g for biogenic silica was achieved from BA using the A-route (green extraction) process. The extraction process developed used 1.4 N NaOH, while the gelation process employed CO<sub>2</sub> impregnation and mechanical fragmentation. The surface area of biogenic silica from BA was further enhanced with the D-route process, as demonstrated by Hoerudin *et al.* (2024). The high surface area from the D-route, particularly, suggests improved silica purity and porosity due to re-combustion and strong leaching with NaOH, making it suitable for applications requiring high surface reactivity.

A significant increase in the surface area of biogenic silica was achieved from PKS through the E-route, which involves combustion pre-treatment at 750°C for 3 hr, followed by the sol-gel method to obtain biogenic silica. By continuing the process with refluxing the previously produced silica with 3 M HCl for 4 hr and re-extracting it with 3 M NaOH, silica nanoparticles were produced with a BET surface area of 438 m<sup>2</sup>/g and a pore size distribution ranging from 2.2-6.3 Nm (Imoisili *et al.*, 2020a).

Biogenic silica from each biomass type has distinct surface properties based on extraction methods, pre-treatment routes and combustion conditions. The significant differences in BET surface area and particle sizes across different routes imply that selecting an appropriate pre-treatment and extraction method is crucial. The extraction route and biomass type substantially impact the surface properties of biogenic silica. High BET surface areas and fine particle sizes obtained through specific pre-treatment and extraction routes open up opportunities for high-performance applications.

Real-world applications of biogenic silica from oil palm biomass remain scarce, if not unavailable. Most recent applications are largely confined to laboratory-scale research. Moreover, studies investigating the use of biogenic silica generated from different oil palm biomasses for the same type of application within a single study have not yet been reported, highlighting the limited scope of existing research.

Nonetheless, biogenic silica shows considerable potential for sustainable use in medical, pharmaceutical, healthcare and food

industries, particularly due to the desirable properties of amorphous silica, including its non-toxic nature, high porosity and superior adsorption capacity. For example, biogenic silica derived from oil palm biomass holds significant promise for sustainable applications in biomedical fields, as demonstrated in the study by Sreekantan *et al.* (2020). This study explored the synthesis of a sustainable super-hydrophobic coating composed of silica from POFA and polydimethylsiloxane (PDMS), intended for biomedical applications. The silica was extracted from POFA through a series of thermal and chemical treatments, resulting in a silica solution (SS) that was incorporated into a PDMS-based super-hydrophobic coating. The coating, applied to a glass substrate via spray coating, exhibited a remarkable water contact angle of 151°, confirming its superior hydrophobicity. Biocompatibility and cytotoxicity assessments using fibroblast cell lines (L929 and V79) revealed that the toxicity of the coating was concentration-dependent, with concentrations exceeding 12.5 mg/mL leading to cell toxicity. The study's findings validate the potential of POFA-derived silica for biomedical applications, particularly as a material for super-hydrophobic coatings that require biocompatibility and cytotoxicity control. This innovative application highlights the value of oil palm biomass as a sustainable source of biogenic silica, paving the way for further advancements in environmentally-friendly and functional materials for biomedical use.

Novita and Idris (2022) demonstrated the successful synthesis of silica gel from PKSA as a moisture absorber for pharmaceutical bottle packaging. Their study revealed that PKSA, containing 55.20% SiO<sub>2</sub>, could be processed into silica gel with a yield of 34.00%, achieving an 85.65% moisture absorption efficiency over a two-week period. These findings highlight the potential of PKSA-derived silica gel for pharmaceutical applications while also emphasising the importance of reducing impurities to enhance its performance and viability for broader use.

Biogenic silica derived from oil palm biomass has demonstrated significant potential in environmental remediation, particularly as an adsorbent for wastewater treatment, where silica with a high BET surface area is essential. Osman *et al.* (2021) explored the synthesis of silica nanomaterials from OPF using the sol-gel method and achieved a notable phenol removal efficiency of 68.00% from aqueous solutions under optimised conditions. The biogenic silica nanomaterials displayed an adsorption capacity of 34 mg/g, with structural properties comparable to those of commercially available silica.

These findings highlight the diverse applications of biogenic silica from oil palm biomass and emphasise the need to optimise extraction processes to improve its purity, surface characteristics and amorphicity. Overcoming challenges related to cost-effectiveness, impurity removal and scalability will be critical to advancing the transition from laboratory-scale research to industrial-scale applications.

## CONCLUSIONS

This review highlights the significant potential of palm oil solid waste as an alternative, renewable, and cost-effective source to produce biogenic silica. This review underscores the importance of tailoring extraction routes to specific types of palm oil solid waste to maximise yield and production efficiency while minimising sustainability issues. Among the different types of oil palm solid waste, BA demonstrates superior yield performance and economic viability. This is attributed to the fact that BA stands out for not requiring combustion pre-treatment, and its abundant availability further contributes to its profitability. However, its effective utilisation requires addressing several challenges, particularly in extraction methodologies and scalability for industrial applications. Emerging green methods, such as using organic acids (*e.g.*, citric acid) as leaching agents and optimised sol-gel techniques, show promise in reducing environmental impacts while improving biogenic silica yield and purity. These methods offer a viable pathway for sustainable extraction but need further refinement to minimise costs and scale up for industrial use. The properties of biogenic silica extracted from solid oil palm biomass exhibit similarities with those of biogenic silica obtained from other agricultural waste sources and closely resemble the characteristics of commercial silica. Producing amorphous silica with high BET surface areas and controlled particle sizes is critical for advanced applications. This requires fine-tuning of pre-treatment and extraction parameters, including benign and cheap leaching agents and an optimised gelation process.

Several aspects merit attention in future research endeavours aimed at achieving low-cost input materials, producing pure silica products and maintaining environmental friendliness. The following considerations are crucial: (i) Exploration of untapped palm oil solid waste by investigating other types of palm oil solid waste/byproducts, such as OPDC, clinkers and other potential sources, that may yield high silica concentration but have not been extensively studied, (ii) scaling

up green extraction techniques, such as organic acid leaching and CO<sub>2</sub>-assisted sol-gel processes, while exploring alternative eco-friendly reagents and energy-efficient pre-treatment and extraction technologies, such as microwave-assisted heating, to reduce operational costs, bridge the gap between laboratory and industrial applications, and enhance process sustainability, (iii) comprehensive life cycle analyses of green extraction methods to identify the most sustainable and economically viable approaches, (iv) functionalisation of biogenic silica for specific applications, which require advanced characterisation and functional testing to tailor silica properties to target industries, (v) integration of biogenic silica production units directly within palm oil mills that will reduce transportation costs associated with BA and harness surplus steam from the mill's boiler, which can significantly lower energy requirements, ultimately optimising biogenic silica production costs and (vi) development of integrated processing systems that combine silica extraction with the recovery of other valuable byproducts, such as lignin, cellulose and alkali metals, to improve overall process efficiency and economic viability.

A multidisciplinary approach is essential to unlock the full potential of oil palm biomass as a biogenic silica source, encompassing advancements in green technologies, industrial collaboration and sustainability assessments. By addressing these challenges, oil palm biomass can transition from an underutilised byproduct to a critical component of the global circular economy, providing a sustainable and eco-friendly alternative for silica production in various applications. Eventually, this can contribute to the development of sustainable oil palm industries.

## ACKNOWLEDGEMENT

The authors acknowledge the Indonesian Oil Palm Plantations Fund Management Agency (BPDPKS) for their support through the oil palm research grant No. PRJ-04/DPKS/DIT.IV/2023. Gratitude is extended to Mulyana Hadipernata, Head of the Research Center for Agroindustry, for his invaluable guidance and input in developing this manuscript. Special thanks are also given to Sulhan Iskandar for generously providing the oil palm photographs with courtesy.

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