Bioresource Technology Reports 22 (2023) 101452

Contents lists available at ScienceDirect

Bioresource Technology Reports

journal homepage: www.sciencedirect.com/journal/bioresource-technology-reports

The production of bio-silica from agro-industrial wastes leached and anaerobically digested rice straws

Emeka Boniface Ekwenna [*], Yaodong Wang, Anthony Roskilly

Department of Engineering, University of Durham, Durham DH1 3LE, UK

ARTICLE INFO

Keywords:
Cassava-steep wastewater
Corn-steep liquor
Bio-silica precursor
Rice straw ash
Hydrolysed rice straw digestates
Leaching agents

ABSTRACT

Silicon extraction from rice straw (RS) has gained attention due to its increasing demand for various applications. This study investigated the potential for producing bio-silica from RS digestates, and RS leached with agro-industrial waste, such as corn-steep liquor (CSTL) and cassava-steep wastewater (CSWW). The results indicated that pretreated (PT) and digested methanogenic RS ash (RSA) samples contain amorphous silica, as confirmed by SEM, EDX and XRD analysis. The EDX results showed high levels of silica with minimal inorganic elements, while the XRD showed that the RSA from methanogenic reactors contained amorphous silica, indicated by a broad peak at 2Θ ranging from 16^0 to 28^0. The leaching potential of CSTL and CSWW was confirmed through SEM and EDX, with the XRD results indicating that CSWW was a more effective leaching agent than CSTL. The CSWW-leached RSA samples showed slight amorphousness with a broad peak at 2Θ between 16^0 and 25^0.

1. Introduction

Silica is a naturally occurring mineral composed of silicon and oxygen. It is generally produced for industrial purposes by synthetic methods despite being the most readily available component after oxygen in the Earth's lithosphere (Permatasari et al., 2016; Steven et al., 2021). The various silica sources can be obtained from quartz sand, rock, clay and volcanic soil, phytoplankton, rice and wheat husks and straws. Silica exists in gel, crystalline and amorphous forms depending on the process of production (Barik et al., 2008; Mirmohamadsadeghi and Karimi, 2018; Rahim et al., 2023). The amorphous silica form is the most widely used as it is highly reactive and non-toxic, whereas the crystalline silica is hard, chemically inert, and has a high melting point (Chandrasekhar et al., 2003; Mirmohamadsadeghi and Karimi, 2018). Silica has a versatile commercial value as it could be used as raw materials for numerous industrial processes ranging from ceramics making, fillers, electronic components, adsorbents, biomedicine, catalysts, drug delivery systems, thermal insulators, rubber, glass, and chromatography (Londeree, 2002; Hao et al., 2006; Adam et al., 2008; Azizi and Yousefpour, 2010; Liou and Yang, 2011; Ghorbani et al., 2013; Permatasari et al., 2016; Nandiyanto et al., 2020; Rahim et al., 2023). In elemental form, silica can be used as a component for building material and in vitreous form, it can be employed in glass wires and optical element manufacturing (Londeree, 2002; Patel et al., 2017). Silica in amorphous form is also used as a thickening and absorbent agent in cosmetic products, in toothpaste as an abrasive agent, as a matting and thickening agent in ink production and as an anti-corrosion agent in preventing metal corrosion (Chen et al., 2013; Patel et al., 2017; Nandiyanto et al., 2020). More so, silica materials could be employed in the future in the development of more advanced materials such as carbon/silica composites, soluble silicates, silicon carbides, silicon nitride, elemental silicon, magnesium silicide, alloys (Chandrasekhar et al., 2003; Kumagai and Sasaki, 2009; Mirmohamadsadeghi and Karimi, 2018; Rahim et al., 2023), biocatalysts (Artkla et al., 2009; Azizi and Yousefpour, 2010; Wattanasiriwech and Wattanasiriwech, 2023), in the production of hydrogen and CO_2 capture materials and metallic ions adsorbents (Chen et al., 2010; Liou and Yang, 2011). Adebisi et al. (2021) reported that silicon forms the basis of most commercialised photovoltaic (PV) materials.

Conventionally, silica precursors that are used commercially are

---

Abbreviations: AD, anaerobic digestion; BGDB, borosilicate glass Duran bottle (s); COD, chemical oxygen demand; CSTL, corn-steep liquor; CSWW, cassava-steep wastewater; EDX, energy-dispersive X-ray fluorescence spectrometer; MDT, microbial digestion technique; PT, pretreated; PV, photovoltaic; RS, rice straw; RSA, rice straw ash; SEM, scanning electron microscope; SCFA, short-chain fatty acid (s); VS, volatile solids; XRD, X-ray diffraction.

[*] Corresponding author.
E-mail address: emylsin@gmail.com (E.B. Ekwenna).

https://doi.org/10.1016/j.biteb.2023.101452
Received 19 February 2023; Received in revised form 18 April 2023; Accepted 19 April 2023

alkoxysilane compounds such as tetraethylorthosilicate (TEOS), sodium silicate and tetramethylorthosilicate (TEMS) (Permatasari et al., 2016), which are produced mainly from quartz and sol-gel process (Patel et al., 2017; Nandiyanto et al., 2020; Rahim et al., 2023). Recently, sodium silicate has been used in the industrial production of nano-silica (Affandi et al., 2009). Nano-silica refers to microscopic silica particles, typically <100 nm in size. These particles have unique properties, such as improved mechanical strength and thermal stability, that make them useful in various applications, such as electronics, coatings, and biomedical devices. Conversely, due to high-temperature requirements, high-cost implications, health challenges and death associated with the production of silica from these compounds, there have been renewed efforts to source silica in low-cost, safer, and environmentally friendly process (Fadhlulloh et al., 2014; Permatasari et al., 2016; Patel et al., 2017; Nandiyanto et al., 2020; Rahim et al., 2023; September et al., 2023).

Among the cheap source of bio-silica are agricultural wastes, which include but are not limited to rice husks (Adam et al., 2008; Umeda and Kondoh, 2008, 2010; Athinarayanan et al., 2015; Askaruly et al., 2020; Steven et al., 2021; Rahim et al., 2023); rice straw (Wattanasiriwech et al., 2010; Khorsand et al., 2012; Lu and Hsieh, 2012; Permatasari et al., 2016; Mirmohamadsadeghi and Karimi, 2018; Bakar and Carey, 2020), wheat straw (Chen et al., 2010), corn cob (Shim et al., 2015; Velmurugan et al., 2015) and bagasse (Vaibhav et al., 2015; Sapawe et al., 2018). Bio-silica is a term commonly used to refer to the silica compound frequently present in biomass ash (Steven et al., 2021). Furthermore, the silicon extracted from this agricultural waste could produce silica with high porosity and surface area (Liou and Yang, 2011; Bakar and Carey, 2020; Steven et al., 2021). In addition, agricultural wastes are considered a good source for bio-silica production because of their low cost, high silica content, comparable silica quality, high energy content, fine-sized amorphous material and environmental friendly (Patel et al., 2017).

Rice Straw (RS), which is the vegetative stem of the rice plant that is removed during rice harvesting, can be used for silica fabrication because its inorganic component, known as rice straw ash (RSA), makes up 10–15 % weight of RS (Agbagla-Dohnani et al., 2001; Sangnark and Noomhorm, 2004; Bakar and Carey, 2020). These inorganic constituents are rich in silica, silicon compounds, alkali, and alkaline earth metals (Agbagla-Dohnani et al., 2001; Guzmán et al., 2015). RS is the most abundant waste globally, accounting for almost 787 million tonnes in annual supply (Food and Agricultural Organisation (FAO), 2021), resulting from rice being the third most important crop after barley and wheat in terms of total crop production (Sen et al., 2016). According to Yuan et al. (2002) research, rice straw production during rice harvesting and processing was twice as high as the yield of rice paddy. RS is among the biomass wastes that constitute 76 % of most developing nations' total primary energy supply, especially from cooking (International Energy Agency (IEA), 2020). Therefore, the over-reliance on RS biomass as the primary energy source has contributed to the generation of greenhouse gases, notably anthropogenic CH_4, CO_2, CO, and NO_x and volatile organic acids, an ozone precursor (International Energy Agency (IEA), 2020; September et al., 2023). In addition, the RSA produced from such a combustion method has high impurities, reduced reactivity, and a crystalline structure, which can cause silicosis (Della et al., 2002). Hence, this enormous amount of biomass waste should be considered for socioeconomic gains, especially in sustainable energy and bio-silica production. This idea is evident in RS anaerobic digestion (AD) process, where biogas is recovered from the RS feedstock, and the digestate is employed for bio-silica production. The silica made from such a procedure is highly amorphous because the impurities usually present in raw RS that cause decreased reactivity may have been leached and utilised for metabolic activities by the digesting microbes (Elbeshbishy et al., 2017; Juntupally et al., 2017, 2023; Baniamerian et al., 2021) for biogas production.

Silica is formed in some tropical plant organisms as a direct competition between more photosynthetic C4 plants and lesser C3 plants, e.g., rice, that may have led the latter to have evolved in the uptake of silica (Van-Soest, 2006; Bakar and Carey, 2020) absorbed in the form of water-soluble silicic acid (orthosilicate (Si $(OH)_4$). Although orthosilicate does not have the buffering capacity in plant metabolism as it exists in the un-ionised form, the silicic acid is saturated, leading to eventual polymerisation into soluble polysilicic acids. The polysilicic acids are then deposited on the plant cell walls as amorphous silica (Van-Soest, 2006; Bakar and Carey, 2020). This polymerisation is because the pKa value of silica is 9.8–11.8 in the plant sap.

There is much literature on the extraction processes of silica from agricultural waste. According to Fadhlulloh et al. (2014) and Patel et al. (2017), these processes are generally grouped into three main approaches: thermal, chemical, and biological or microbial extraction methods. Typically, the structure, composition and morphology of silica derived from agricultural biomass are strongly influenced by the extraction method employed (Soltani et al., 2015). In the thermal extraction process, agricultural biomass is valorised to ash in a muffle-furnace, fixed bed furnace, inclined step-grate furnace, cyclonic furnace, fluidised bed reactor, rotary kiln, or tubular reactor at 500 to 900 °C for a certain period (2 to 8 h) (Patel et al., 2017; Steven et al., 2021; Rahim et al., 2023). The significant drawbacks of thermal technology are longer reaction time, hot spot formation and insufficient complete carbon oxidation due to a lack of free-flowing air (Patel et al., 2017). For example, Lu and Hsieh (2012) produced amorphous silica nano-disks using pyrolysis at 575 °C and dissolution, followed by precipitation using NaOH and H_2SO_4, respectively. Similarly, nano-silica materials were effectively made from wheat straw by thermal treatment at a heating rate of 10 °C/min at 400, 500, 600 and 700 °C after initial combustion at a temperature of 500 °C for 8 h (Chen et al., 2010).

Perhaps, the simplest extraction process is open burning. However, as Della et al. (2002) reported, silica's desirable characteristics, such as high reactivity of the surface area and amorphousness, may be lost. In addition, crystalline silica, such as cristobalite or tridymite reported causing a debilitating lung disease known as silicosis after continuous exposure may be formed at a prolonged-firing temperature above 500 °C (Della et al., 2002). These crystalline forms have been reported previously to reduce silica's reactivity in synthesising downstream industrial products such as zeolites used widely as adsorbents and biocatalysts (Della et al., 2002; Bakar et al. (2016).

Before these extraction methods, acid leaching is paramount to remove/reduce the impurities and increase the surface area of silica, thereby improving the quality (Kongmanklang and Rangsriwatananon, 2015). After acid treatment, these impurities (metals and inorganic compounds) are converted to their respective individual ions (Vaibhav et al., 2015). In the research experiment of Bakar et al. (2016) on high-purity amorphous silica production from rice husk, they suggested that high-purity silica can be produced by controlled combustion after acid treatments. In their study, rice husk leaching with sulphuric acid and hydrochloric acid was carried out before combustion at 500 to 900 °C for 2 h to obtain pure silica. They stated that acid treatments could eliminate metallic impurities such as iron, manganese, calcium, sodium, potassium, and magnesium, influencing silica colour and purity before combustion. Bakar and Carey (2020) also produced nano-silica from RS using alkaline hydrolysis pretreatment. In addition, Rafiee et al. (2012) reported using 1 M of HCl in silica production from rice husk and obtained silica with improved surface area. A wheat straw sample was leached by applying 5 M sulphuric acid in the ratio 1:10 (g ml^{-1}) with constant stirring at 1000 rpm under RT for 24 h preceding heating treatment at different temperatures and times in a furnace (Ahmad-Alyosef et al., 2015).

The conventional use of strong acids in leaching processes has proven costly, environmentally damaging, and corrosive. To mitigate these limitations, researchers have increasingly explored the potential of weaker acids, such as citric, lactic, and acetic acids, which are abundant, environmentally friendly, and non-toxic (Umeda and Kondoh, 2008, 2010). Umeda and Kondoh (2010) reported the successful extraction of 99 % pure silica from rice husk using citric acid as a leaching agent and a hydrolysis process at elevated temperatures. Additionally, the chelate reaction between the metal impurities in rice husk and the carboxyl group of citric acid was found to remove metal impurities effectively. The present study explores the feasibility of utilising agro-industrial by-products, such as cassava-steep wastewater (CSWW) and corn-steep liquor (CSTL), as environmentally sustainable leaching agents for removing metallic impurities from RS. This hypothesis is based on the premise that CSWW and CSTL contain concentrated levels of short-chain fatty acids (SCFA) that exhibit weak acidic properties, thereby enabling their utilisation as effective leaching agents.

As documented by Kalapathy et al. (2000) and (2002), Zaky et al. (2008), Patel et al. (2017) and Rahim et al. (2023), a chemical extraction method can be used to produce high-purity bio-silica from RSA using an alkaline agent followed by acid neutralisation or using other chemical agents such as toluene, ethanol, or ionic liquids. Alkaline extraction involves dissolving the rice straw or rice husk ash in an alkali (NaOH) at 100 °C for 1 h under constant stirring, followed by precipitation of sodium silicate using acid (1 N HCl) at pH 7.0 (Eqs. (1) and (2)). The base approach is because amorphous silica solubility is high at pH $>$ 10 and very low at pH $<$ 10 (Kalapathy et al., 2000, 2002). Alternatively, an ionic liquid was used by Chen et al. (2013) and Lee et al. (2017) to produce silica of high quality from agricultural waste. The chemical extraction limitation is the solution's corrosiveness, high-cost implication, the complexity of the processes in silica recovery, environmental issues, and difficulty in eliminating the by-products trapped in the nano-silica pores Na_2SO_4 or NaCl (September et al., 2023).

$$\underset{\text{White ash}}{SiO_2} + \underset{\text{Sodium Hydroxide}}{2NaOH} \rightarrow \underset{\text{Sodium Silicate}}{Na_2SiO_3} + H_2O \tag{1}$$

$$\underset{\text{Sodium Silicate}}{Na_2SiO_3} + \underset{\text{Hydrochloric acid}}{HCl} \rightarrow \underset{\text{Silica gel form}}{SiO_2} + \underset{\text{Sodium Chloride}}{NaCl} + H_2O \tag{2}$$

Biological or microbiological methods offer a cleaner and greener approach to bio-silica production by utilising microorganisms, such as fungi, bacteria, cyanobacteria, *Chysophytes* such as *Diatoms*, *Porifera* (*Sponges,* also called Californian red worms) (Estevez et al., 2009; Steven et al., 2021). These organisms could use silica-based materials as a source of nutrition, which leads to silica accumulation within their cells through a process known as bio-silicification. The resulting product can be extracted through cell disruption, followed by precipitation, purification, and drying to achieve over 90 % purity bio-silica. The process takes about 7 h for acid leaching and baking (Steven et al., 2021). Estevez et al. (2009) produced silica nanoparticles with a size range of 55 to 250 nm and a silica recovery of 88 % from the bio-digestion process of rice husk by worms after 5 months of processing. In another study, Rohatgi et al. (1987) explored the potential of using white-rot fungi species (Cyathus) to produce high-quality silica from rice husks. The process involved microbial fermentation for 60 days, followed by drying at 80 °C, sieving to a prescribed size and combustion at 450 °C. The authors found that the process resulted in a high concentration of inorganic material (SiO_2) and reduced organic matter. However, it can be concluded that the main drawback of biological processes is the lengthy processing time required, process upscaling challenges and low product yield (Estevez et al., 2009; Steven et al., 2021).

Alternatively, employing the microbial digestion technique (MDT), which is not a conventional method for bio-silica extraction, involves the application of microorganism or their parts (enzymes) to digest the organic component of agricultural biomass, leaving the silica intact for extraction. This process results in a decrease in the organic content and an increase in the inorganic constituents, reducing the time required for the thermal extraction process. Although MDT can be referred to as a biological method, as aforementioned, it is not a direct traditional method for silica production but a process that supports producing quality and amorphous silica. This idea is because hydrolytic organisms can degrade biomass's organic components. Secondly, the residual metallic ions (impurities) are consumed during the microbial hydrolytic and digestion process to support numerous metabolic activities ((Elbeshbishy et al., 2017; Juntupally et al., 2017, 2023; Baniamerian et al., 2021). Thirdly, the organic acids produced during digestion can act as a leaching agent for metallic impurities, eliminating the need for pre-leaching. Finally, the microbial hydrolysis method leaves the residual inorganic component of the lignocellulose material intact, which can then be subjected to combustion to produce silica, thereby preserving the quality of the silica, and reducing the temperature and time required for silica production.

Despite the limited studies on silica production from MDT, Wattanasiriwech et al. (2010), and Mirmohamadsadeghi and Karimi (2018), conducted research in this area. Wattanasiriwech et al. (2010) experimented producing amorphous silica nanoparticles from RS using microbial hydrolysis pretreatment. The 73.6 and 82.5 % silica content in pretreated (PT) ash confirmed microbial hydrolysis silica extraction is a promising technique. Still, the process was expensive, and the 72-h hydrolysis duration may not have been sufficient for the complete leaching of impurities. On the other hand, Mirmohamadsadeghi and Karimi (2018) found that high-quality nano-silica could be produced from RS via dry AD, but there was a flawed digestion process due to a lack of biomass pretreatment before the AD process. The present study examined the feasibility of producing amorphous bio-silica from pretreated RS digestates from acidogenic and methanogenic bioreactors. Pretreating RS will break matrices, increase surface area, create micropores on lignocellulose and improve enzyme accessibility before subjection to the AD process. Hence, the hypothesis is unique and novel as more energy recovery, reduced digestion and combustion time is achieved. Finally, as aforementioned, the possibility of removing or leaching impurities from RS using agro-industrial waste materials such as cassava-steep wastewater and corn-steep liquor before bio-silica production through thermal extraction was investigated. Agro-industrial waste materials are considered a greener and cleaner alternative to leaching with strong acids, which can be costly and cause environmental problems and thus is a novel approach for leaching in bio-silica production.

2. Materials and methods

2.1. Agro-industrial wastes collection and preparation

2.1.1. Corn seed collection and preparation of corn-steep liquor

The corn seeds were procured from an African shop at Westgate Road, Newcastle Upon Tyne, UK. The CSTL was made to have close qualities to those available in corn-based industries. The dried corn was coarsely crushed and soaked in sulphuric-added deionised water (0.1 %) in a plastic container at room temperature for 2 days. The wastewater was changed every 24 h. The effluent from the mixture, called corn-steep liquor, was stored in a container at a temperature of −25 °C until it was used in the study. The CSTL were analysed for SCFA and chemical oxygen demand (COD) contents prior to use.

2.1.2. Cassava collection and preparation of cassava-steep wastewater

Fresh cassava root tubers were purchased from a Hutchinson fruit shop in Fenham Newcastle Upon Tyne, UK. The CSWW used in the study is the spent water generated during the processing of the raw cassava into edible forms through anaerobic fermentation. In the fermentation procedure, small-sized peeled cassava was placed in a sealed container filled with water and allowed to ferment for 4 days at RT. The SCFA and COD contents of the CSWW were determined before application as a pretreatment agent.

2.2. Digestate preparation from acidogenic and methanogenic reactors

The RS digestate, typically employed as a manure substitute (Tambone et al., 2009) for agricultural purposes, is used for silica production.

The digestates were collected from various AD bioreactors for hydrogen and methane production. While the acidogenic fermenter was fed with untreated RS, the methanogenic reactors were fed raw and PT RS. Before enzymatic hydrolysis, the pretreatment was achieved chemically with NaOH, HCl, and potash extract (PE). The pH of the RS samples from acidogenic reactors was 5.4 ± 0.2, while that from methanogenic digesters was 7.05 ± 0.4. The RS digestates were separated from the fermenter liquor and thoroughly washed with tap water on a 250 μm sieve to remove the seed sludge. The digestate RS residues were then dried at 80 °C for 24 h and stored at RT until use.

2.3. Preparation of leached rice straw using agro-industrial wastes

Already ground-raw RS was placed in 500 mL grade 3.3 borosilicate glass Duran bottles (BGDB) (VWR 215-1594) containing either CSWW or CSTL solution in a ratio of 1:4. The mixtures were kept for 30 days at RT on a magnetic stirrer at 100 rpm. The reaction setup was done in triplicates. At the end of the leaching process, the RS samples were filtered, washed with tap water, and dried at 80 °C for 24 h. Later, the dried-leached RS residues were stored at RT until use. Finally, untreated RS leached with water following the same procedure was used as the control.

2.4. Silica preparation from various digestates and leached rice straw residues

The bio-silica was prepared using the modified method prescribed by Chen et al. (2010) and Wattanasiriwech et al. (2010). About 10 g of the various dried digestates and leached RS residues were placed in a well-labelled porcelain crucible and calcined in an electric furnace at 550 °C for 6 h with a constant heating rate of 10 °C/min. Raw RS was also prepared using the same method as the control. After cooling down in an air-tight desiccator, the RSA samples were weighed and immediately stored for further analysis.

2.5. Analyses of rice straw ash

The standard methods 2540 B and 5220 B, as described in the American Public Health Association (APHA) (2005), were used to measure the biomass solids (TS, VS, and ash) and the chemical oxygen demand, respectively. In addition, the HPLC Thermo-scientific DIONEX AQUION with a Dionex IonPacTM ICE-ASI column was utilized to measure the concentration of SCFA metabolites, including acetate, butyrate, formate, and lactate. The microstructure of RSA was observed using a scanning electron microscope (SEM) HITACHI NEXUS. The different RSAs were also analysed using an energy-dispersive X-ray fluorescence spectrometer (EDX) (Quantex 70) operated at 15 kV from the SEM to determine the chemical contents of the RSA. At the same time, the phase analysis was examined with an X-ray powder diffractometer (XRD) using the PANalytical X'pert pro-Multipurpose Diffractometer. The analyses were done in triplicates, while the mean values were presented based on a 5 % statistical significance level, and results were shown within + 2 SD.

3. Results and discussion

3.1. Characterisation of agro-industrial wastes

The chemical characteristics of CSWW and CSTL are shown in Table 1. In both samples, the pH was between 3.0 and 4.0, which confers acidity resulting from the organic acids. The predominant SCFA were acetic and butyric acid. These were employed in the leaching of raw RS for 30 days.

3.2. Thermal analysis of rice straw samples

The dried-leached RS residues and the dried-digested RS samples from hydrogen and methane reactors (Fig. 1) were analysed to determine their solid content and proximate characteristics (Table 2). The same was done for the control sample. From Table 2, it was observed that the rate of volatile solids (VS) degradation, also known as the energy conversion efficiency (%), was between 72 and 87 %, with the raw RS (control) having the highest percentage of 87 and the methanogenic digestates producing the least at 72 + 7 %. Although this outcome is slightly higher than the reported values by Maguyon-Detras et al. (2020), the variation could be from the mode of energy conversion technology. The result showed that there were high levels of ash content (20.75 to 27.86 %) from the methanogenic reactors (reactors A to D), which perhaps is explained by the removal of the digestible organic part of the RS during AD operations for methane (Table 2). However, the low ash content of 17.59 % and high VS content (82.4 %) from the acidogenic reactor (reactor E) compared with those from methane-producing digesters might be from poor digestion of the untreated RS evident from the low yield of hydrogen gas.

The RS ash content (9.02 to 9.96 %) and VS content (90.04 to 90.90 %) of water and agro-industrially-leached samples were slightly close, which agrees with the values reported by Agbagla-Dohnani et al. (2001) and Sangnark and Noomhorm (2004). In contrast, there was a significant variation from the ash content (13.02 %) of the control (raw RS). Therefore, the reduced ash content in leached samples compared with the control sample could be from the leaching of inorganic and metallic impurities of the RS during the leaching period (Vaibhav et al., 2015; Kongmanklang and Rangsriwatananon, 2015). Although these findings are marginally different from Chen et al. (2010) study on the preparation of nano-silica: the concept from wheat, the disparity could be from the type of biomass and approach employed. They achieved a 93 % weight loss, while 8 % represents the silica and metallic impurities. Nonetheless, the result is closely related to Wattanasiriwech et al. (2010) outcome on the production of amorphous silica nanoparticles from RS with microbial hydrolysis pretreatment They reported 10 %, 12 %, and 23 % ash content from untreated RS, LDD1, and TR-hydrolysed RS.

3.3. Rice straw ash characterisation

As previously noted, using AD digestate as agricultural manure is associated with environmental hazards, including disruption of normal soil flora and suboptimal energy recovery as a significant portion of the organic matter remains unconverted in the digestate (Monlau et al., 2015; Agarwal et al., 2022). However, it has been observed that maximum energy recovery can be achieved when AD digestate is safely combusted for bio-silica production. Therefore, from an economic perspective, utilising digestate from the RS digestion process for bio-

Table 1
Characterisation of cassava-steep wastewater and corn-steep liquor.

Agro-industrial sample	Acetic acid (mg/L)	Butyric acid (mg/L)	Formic acid (mg/L)	Lactic acid (mg/L)	Total COD (mg/L)	Soluble COD (mg/L)	pH
CSWW	2330.90	2876.68	NA	NA	12,947.07	5490.00	3.81
CSTL	1625.12	1231.97	NA	NA	7600.10	3470.00	3.45

NA: not available.

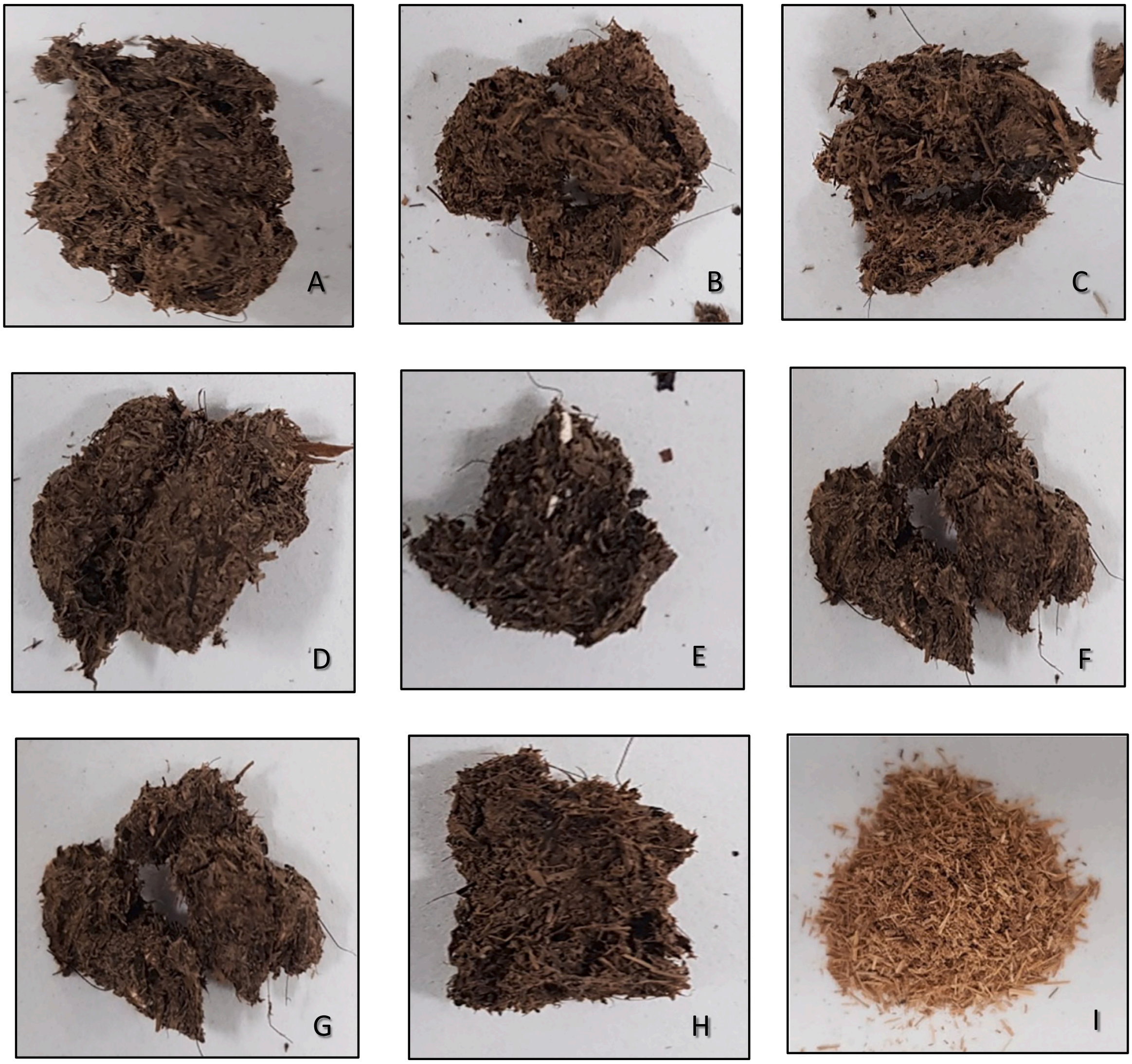

Fig. 1. Various dried methane digestates (A: Untreated-digested RS; B: CSTL-L RS; C: CSWW-L RS; D: HCl-PT RS; E: NaOH-PT RS; F: PE-PT RS; G: Water-L RS), H: Digestate from hydrogen reactor and I: Raw RS (control).

Table 2
The solid/thermogravimetric analysis of PT RS digestates, leached RS and raw RS samples.

Substrates	TS (g)	VS (g)	Ash (g)	VS (%)	Ash (%)
Raw RS (Control)	0.937	0.815	0.122	86.980	13.020
CSSW-L RS	0.994	0.895	0.099	90.040	9.960
CSTL-L RS	0.992	0.899	0.093	90.625	9.375
Water-L RS	0.987	0.898	0.089	90.983	9.017
Reactor A	0.989	0.725	0.264	73.306	26.694
Reactor B	0.987	0.712	0.275	72.138	27.862
Reactor C	0.985	0.715	0.270	72.589	27.411
Reactor D	0.983	0.779	0.204	79.247	20.753
Reactor E	0.989	0.815	0.174	82.406	17.594

Reactor A: Digestate from NaOH-PT RS methane reactor.
Reactor B: Digestate from PE-PT RS methane reactor.
Reactor C: Digestate from HCl-PT RS methane reactor.
Reactor D: Digestate from untreated RS methane reactor.
Reactor E: Digestate from hydrogen reactor.
The letter "L" in the above table denotes "leached".

silica production could offer greater benefits than application as organic fertilizers.

3.3.1. *Morphological and physical appearance of silica precursor*

Fig. 2 shows the various silica material preparation from the different samples. From the figure, the RSA obtained from the leached samples (Fig. 2b, d, and g), methanogenic samples (Fig. 2d, e and f), and acidogenic sample (Fig. 2h) could be said to be much better morphologically and aesthetically in quality, consistency, and colour which was perhaps indicative of relatively pure silica as compared to the control RSA (Fig. 2i). In terms of colour, the leached and digested samples were grey-white, while the raw RSA (control) was black. Even though there is no clear explanation for the colour differences, the colour variations compared to the control sample could be from the residual carbon materials requiring higher temperature or a longer combustion time (Wattanasiriwech et al., 2010; Askaruly et al., 2020; Rahim et al., 2023) and the presence, and absence of metallic impurities in raw RS and leached/digested samples respectively. These impurities are believed to have been leached during the leaching period/the digestion period, giving the samples a white colour (Umeda and Kondoh, 2008, 2010; Vaibhav et al., 2015; Kongmanklang and Rangsriwatananon, 2015; Bakar et al., 2016). This postulation is supported by the findings of Bakar

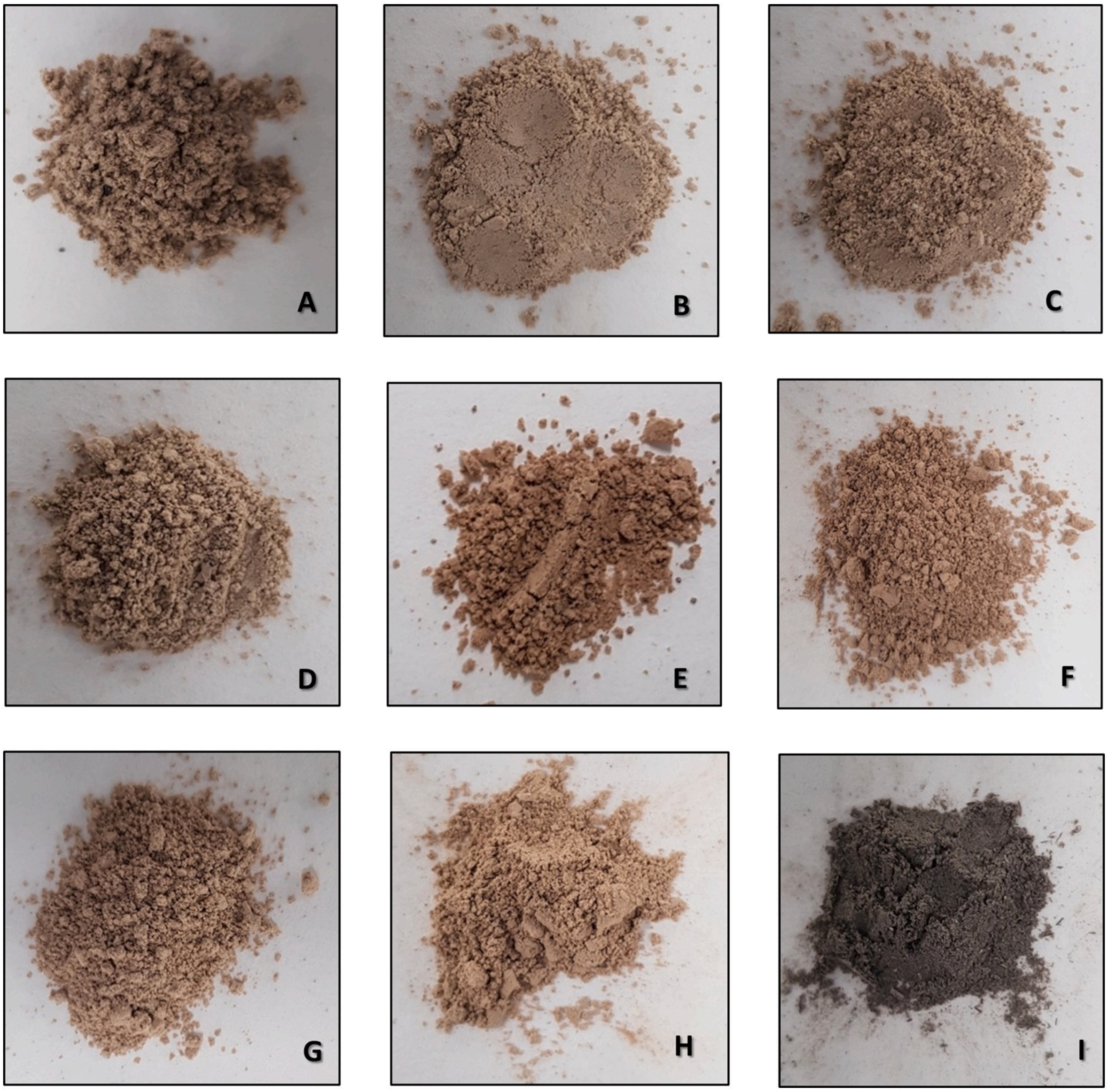

Fig. 2. RSA (silica material) preparation from A: Untreated-digested RS; B: CSTL-L RS; C: CSWW-L RS; D: HCl-PT RS; E: NaOH-PT RS; F: PE-PT RS; G: Water-L RS; H: Digestate from hydrogen reactor and I: Raw RS (control).

et al. (2016) on the production of high-purity amorphous silica from rice husks. They suggested that high-purity silica can be produced by controlled combustion after acid treatments. Furthermore, they observed that acid treatments could eliminate metallic purities such as iron, manganese, calcium, sodium, potassium, and magnesium, influencing silica colour and purity before combustion. Similar findings were obtained by Rafiee et al. (2012), where 1 M of HCl was used to produce silica from rice husk and achieved silica with a good surface area.

In contrast, the raw RS (control) contained inorganic compounds and metallic ions that will constitute reduced quality if used directly for silica production and give a dark colour to silica precursors (Agbagla-Dohnani et al., 2001; Guzmán et al., 2015). The same result was obtained by Wattanasiriwech et al. (2010) and Mirmohamadsadeghi and Karimi (2018). In addition, the ash sample from the control (raw RS) looks edgy and brittle on physical inspection and lacks consistency, which could be from the formation of a crystalline form of silica, such as potassium silicate and calcite, compared to the leached and digested samples, which appear to be soft and tender on physical evaluation and have increased surface areas that can be likened to cement (Fig. 2).

3.3.2. *Scanning electron images of silica materials*

The SEM micrographs of the RS ash samples are shown in Fig. 3. Although the SEM images cannot clearly be defined from the micrograph, the bio-silica precursor could be described to be in an amorphous form from the PT methanogenic digestates (Fig. 3d, e and f). The SEM result was supported by elemental composition analysis (Figs. 4 and 5) obtained from the energy-dispersive X-ray fluorescence spectrometer (Quantex 70) operated at 15 kV from the SEM. The leached (Fig. 3b and c) and untreated-digested RS samples (Fig. 3a) also showed a bit of amorphousness under scanning microscopy. In contrast, the SEM images from control (raw RS) (Fig. 3i), water-leached RS (Fig. 3g), and acidogenic RS (Fig. 3h) samples presented the silica in crystalline forms, which might be from metallic impurities from the samples. Incomplete combustion of RS samples could also be another reasonable cause—the results tally with Mirmohamadsadeghi and Karimi (2018) and Askaruly et al. (2020) findings.

3.4. *Chemical analysis of rice straw ash*

The elemental composition of bio-silica precursors is shown in Fig. 4.

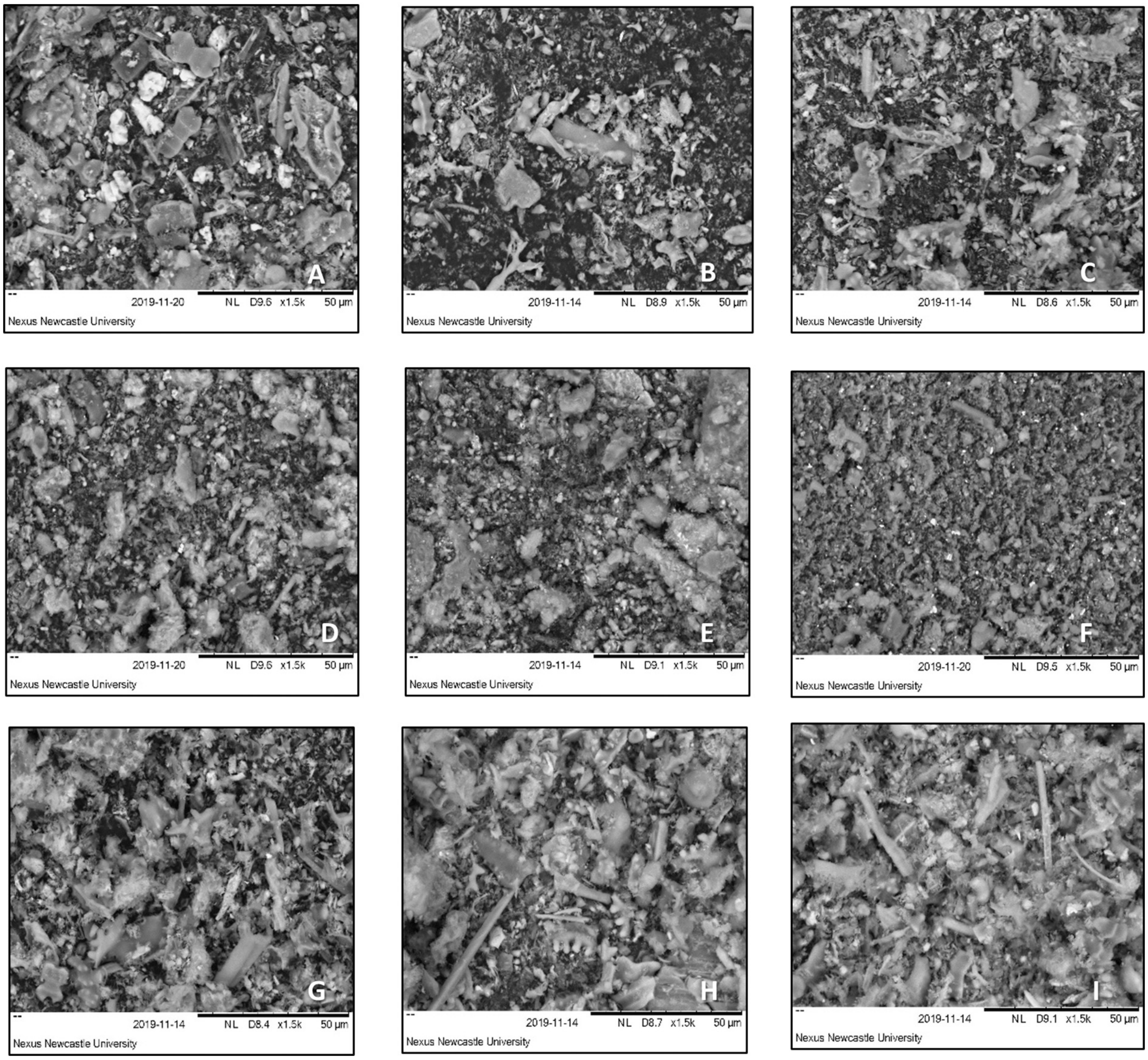

Fig. 3. SEM micrograph of the different RSA samples (A: Untreated-digested RS; B: CSTL-L RS; C: CSWW-L RS; D: HCl-PT RS; E: NaOH-PT RS; F: PE-PT RS; G: Water-L RS; H: Digestate from hydrogen reactor and I: Raw RS (control)).

It is seen from the graphs that silica was the principal element with the highest peaks, followed by oxygen from the EDX analysis, which affirms silica (SiO_2) as the chief element in the sample.

This result is consistent with Chen et al. (2010) and Vaibhav et al. (2015) report on applying agricultural waste as a source from the production of silica nanoparticles. The findings also agree with Askaruly et al. (2020) and Imoisili et al. (2020) research outcomes on nano-silica. A similar result was also obtained from the elemental spread of RSA digestates, where silica was also the dominant element (Fig. 5), which confirms that RS is an excellent raw material for bio-silica production (Wattanasiriwech et al., 2010; Khorsand et al., 2012; Lu and Hsieh, 2012; Permatasari et al., 2016; Mirmohamadsadeghi and Karimi, 2018). Nevertheless, there were peaks of other elements, notably potassium, sodium, calcium, chloride, magnesium, manganese, iron, aluminium, and lead. Others that were insignificant quantities include tellurium, chromium, antimony, and zirconium. These inorganic compounds in oxidised forms were reported by Wattanasiriwech et al. (2010), Vaibhav et al. (2015) and Mirmohamadsadeghi and Karimi (2018). Imoisili et al. (2020) also obtained inorganic impurities, such as sodium and potassium, from the substrate used for the SEM/EDX analysis. The carbon element in all the graphs was from the mounting adhesives made from carbon. These elements have been reported to contribute to the impurities associated with biological silica production (Kongmanklang and Rangsriwatananon, 2015).

Of particular importance is the compound potassium ions, which causes the melting of nano-silica at relatively low temperatures during combustion due to the eutectic phenomenon with SiO_2 (Mirmohamadsadeghi and Karimi, 2018). Therefore, acid leaching is essential before silica extraction (Bakar et al., 2016). This leaching activity could explain the reason the methanogenic RSAs were more amorphousness (Fig. 3d, e, and f) than the control (raw) RSA (Fig. 3i), as the inorganic impurities were negligible in methanogenic RS samples (Fig. 4d, e, and f) compared to the raw RSA (Fig. 2i and Fig. 4i). The control RSA has varying significant inorganic elements. These impurities are believed to be converted to their respective individual ions after acid treatment (Vaibhav et al., 2015) or consumed for metabolic activities during digestion.

Even though the leached samples (Fig. 3b and c) and untreated-digested RSA (methane-reactor control) (Fig. 3a) also displayed a bit of amorphousness under SEM, they still had some amount of impurities (Fig. 4a, b and c). This ambiguity could be explained by the low concentration of the weak acid employed in the leaching process for the

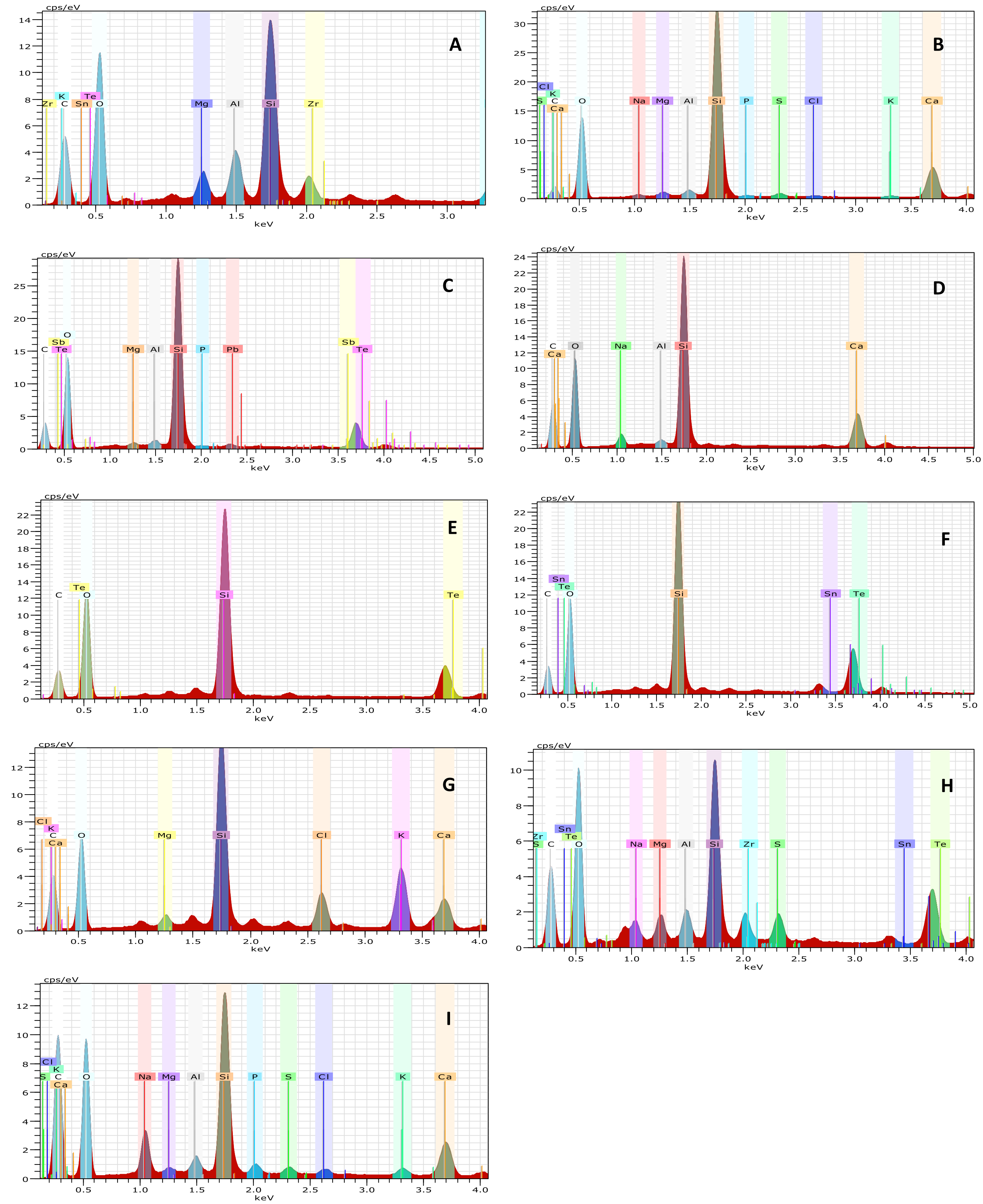

Fig. 4. The elemental composition of bio-silica precursors (A: Untreated-digested RS; B: CSTL-L RS; C: CSWW-L RS; D: HCl-PT RS; E: NaOH-PT RS; F: PE-PT RS; G: Water-L RS; H: Digestate from hydrogen reactor and I: Raw RS (control)).

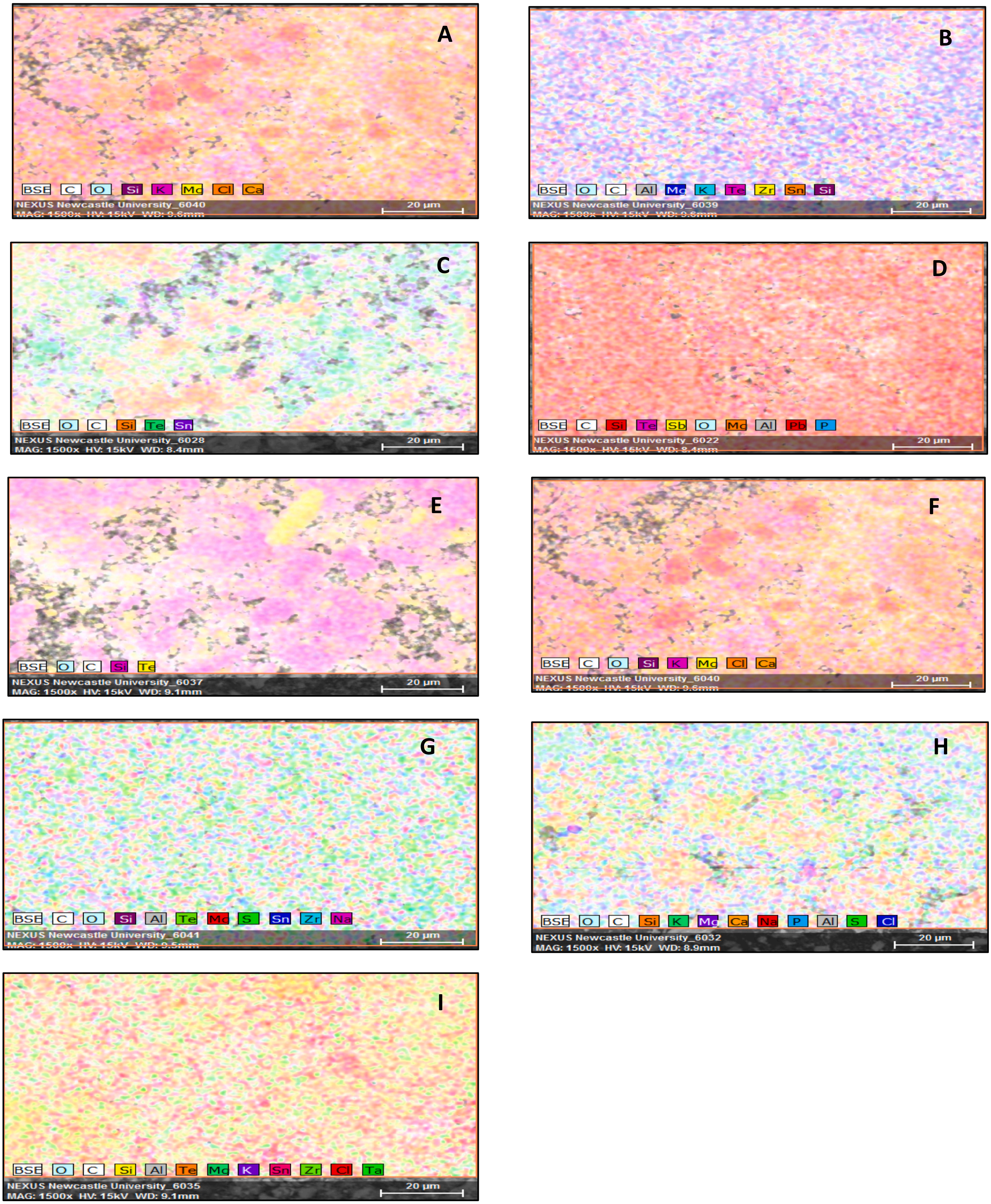

Fig. 5. The elemental spread of RSA samples (A: Untreated-digested RS; B: CSTL-L RS; C: CSWW-L RS; D: HCl-PT RS; E: NaOH-PT RS; F: PE-PT RS; G: Water-L RS; H: Digestate from hydrogen reactor and I: Raw RS (control) with silica ion having the most concentration.

samples (Table 1). There is no clear explanation for inorganic impurities in the untreated-digested RSA compared with other methanogenic RS samples. However, it could have been from the basal media employed, the seed sludge and exogenous salt applied for pH stability and nutrient supplementation. The same inorganic elements were achieved by Wattanasiriwech et al. (2010), Vaibhav et al. (2015) and Mirmohamadsadeghi and Karimi (2018) in their respective works on silica production from agricultural wastes. The numerous peaks of inorganic elements recorded in the water-leached (Fig. 4g), acidogenic RSA (Fig. 4h), and raw RS (control) samples (Fig. 4i) explain the crystal forms of silica material and, thus, reduced specific surface area reported under SEM images (Fig. 3g, h and i). Furthermore, the impurities further reaffirm the need for removing metallic elements with acids before the thermal extraction process for silica.

As mentioned previously, the increased number of inorganic elements in hydrogen-producing RSA could be from the basal media used for microbial growth during the RS digestion process and the exogenous addition of salt compounds (NaOH and HCl) required to maintain the pH during the hydrogen production process (Yang et al., 2020). In addition, the low quantity of organic acids generated from RS's incomplete

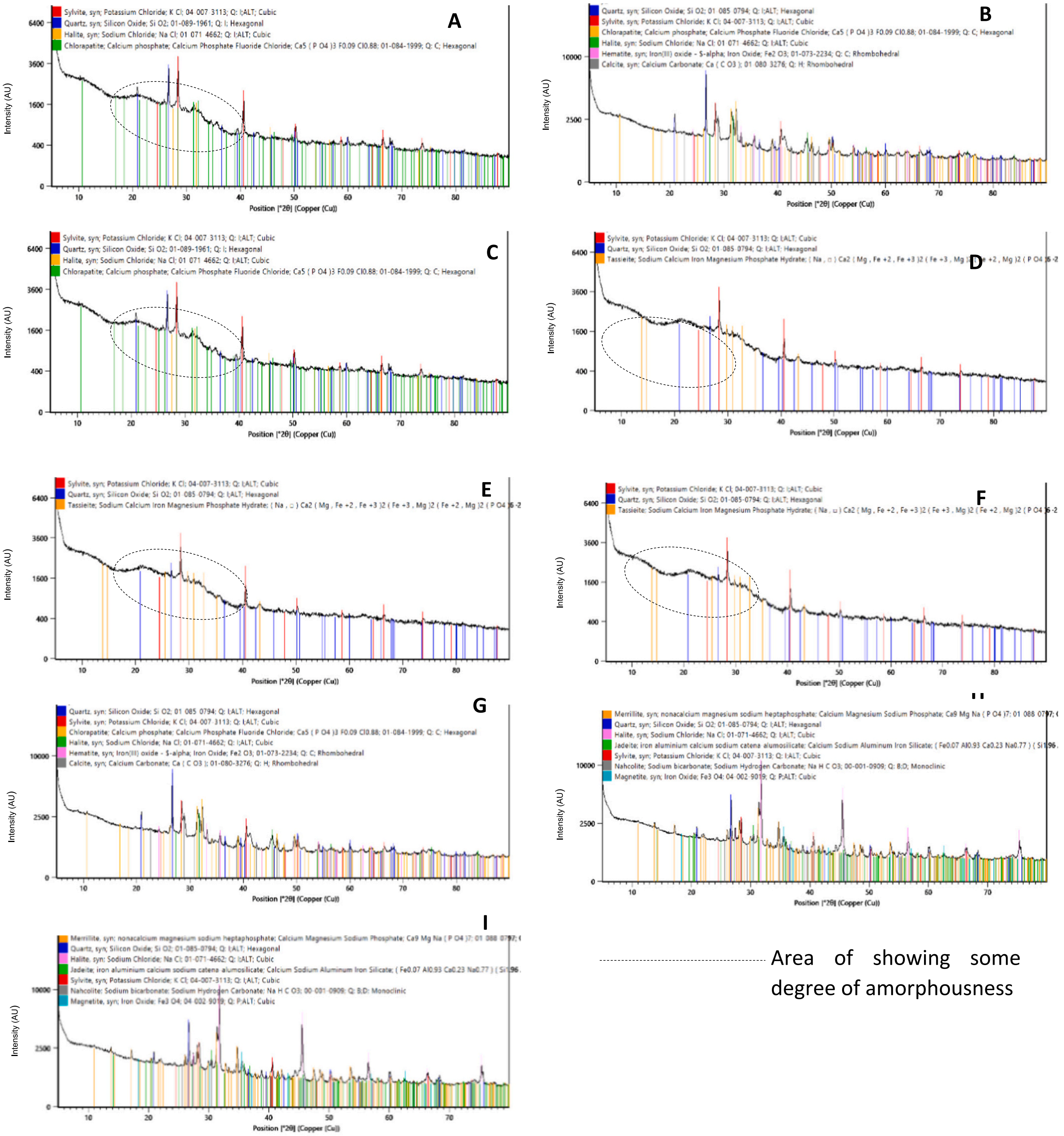

Fig. 6. The XRD spectra of RSA samples (A: Untreated-digested RS; B: CSTL-L RS; C: CSWW-L RS; D: HCl-PT RS; E: NaOH-PT RS; F: PE-PT RS; G: Water-L RS; H: Digestate from hydrogen reactor and I: Raw RS (control)).

digestion (fermentation) during hydrogen production, as RS is highly recalcitrant, is used for methanogenesis, as seen from the high CH_4 but low H_2 content (data not included). Therefore, the acidogenic fermenter had insufficient SCFA required for the leaching process. Moreover, the structural robustness of untreated RS to microbial degradation during biohydrogen production will affect the metabolic pathways to shift to methane production rather than acidogenesis. This metabolic alteration could be prevented using RS degradation products (sugar monomers) or enriching seeded culture employed with sucrose before application for biohydrogen production. In this study, the RS digestate from the latter was employed. Hence, more alkali (NaOH) was added during the sugar enrichment to balance the evolution of SCFA, leading to more Na^+ concentration in the reactor. Also, the acidogenic digestates used were from one digestion cycle (hydraulic retention time (HRT 1)). Thus, some inherent metallic ions (Guzmán et al., 2015) have not been wholly eliminated before silica production.

Wattanasiriwech et al. (2010) affirmed these reasons in their experiment on producing amorphous silica nanoparticles from RS with microbial hydrolysis pretreatment. They reported elevated potassium ions on the elemental composition from external potassium addition employed to enhance cellulase activity.

No apparent leaching activity was observed for water-leached RS (Figs. 4g and 5g) and raw RS (control) (Figs. 4i and 5i) samples, as there were numerous peaks of impurities, notably potassium, sodium, calcium, chloride, magnesium, manganese, iron, aluminium, tellurium, sulphur, and lead. Others that were insignificant quantities include tin, chromium, antimony, and zirconium. The lack of leaching activity is because water is a neutral compound with no leaching ability.

3.5. *X-ray powder diffractometer pattern analysis*

The XRD patterns showed that the RSA from methanogenic reactors contained amorphous silica (Fig. 6) as seen from the broad peak observed at 2Θ ranging from 16^0 to 28^0, which confirmed the presence of amorphous silica (Fig. 6d, e and f). Similar peaks were reported by Mirmohamadsadeghi and Karimi (2018). The peaks were also consistent with the findings by Chen et al. (2010), Shim et al. (2015), Askaruly et al. (2020), Imoisili et al. (2020) and Wattanasiriwech and Wattanasiriwech (2023) in their nano-silica production from agricultural wastes. A similar result was achieved by Abd-Rabboh et al. (2022) on silica material from rice biomass. However, their peaks were much more defined and broader due to other silica purification approaches employed.

Although there were minor contaminants at the 29^0 and 40^0 representing sylvite (potassium chloride), which could have been obtained from exogenous addition during the AD process, the absence of significant peaks indicates the lack of crystals on the silica material (Fig. 6d, e and f). The formation of these phases by the contaminants was also reported by Vaibhav et al. (2015). These findings further validate the SEM and EDX reports on the production of amorphous bio-silica from methanogenic digested RSA samples (Figs. 3, 4 and 5).

In contrast, the broad peak was not seen in the XRD spectra for water-leached, acidogenic and raw RSA samples, demonstrating the lack of amorphousness in the bio-silica precursor (Fig. 6g, h and i). Instead, the samples have sharp and several peaks, mainly quartz (silicon oxide), sylvite (potassium chloride), chlorapatite (calcium phosphate) and Halite (Iron (III) oxide), which shows the crystalline nature of the silica material in the various RSA samples. This result also confirms the SEM images above.

Even though the untreated-digested RSA and the CSWW-leached RSA samples contained sharp peaks similar to water-leached, acidogenic and control-RSA samples, they have a slightly broad peak at the 2Θ ranging from 16^0 to 25^0 (Fig. 6a and c), which shows some degree of amorphousness.

The findings also tally with the SEM and EDX reports, where the CSWW-leached sample (Fig. 3c) and untreated-digested RSA (Fig. 3a) showed a bit of amorphousness. Thus, the sharp peaks could have been from incomplete leaching activity from the weak acids employed in CSWW and exogenous salts used during the AD process for untreated-digested RSA samples. Nonetheless, there was no explanation for the lack of broad peaks at the 2Θ from about 30^0 in the CSTL-leached RSA sample (Fig. 6b), which indicates the absence of amorphousness in the silica compound. This result contradicts the SEM and EDX interpretations reported earlier, but the reason could also be from incomplete leaching activity from the weak acids employed in CSTL agro-industrial waste.

4. Conclusions

The study findings showed that pretreated and digested methanogenic RSA samples contain amorphous silica materials, confirmed by the SEM, EDX and XRD results. In contrast, the result of untreated-digested acidogenic RSA samples appeared in crystalline forms seen from the XRD patterns and SEM, even though they still contain a high concentration of silica compounds with a considerable amount of other elements from the EDX graphs. The leaching potential of CSTL and CSWW was confirmed through SEM and EDX analysis, with the XRD results indicating that CSWW was a more effective leaching agent than CSTL. The study suggests bio-silica precursors can be produced from RS digestates from methanogenic reactors and RS leached with CSWW. However, more studies and laboratory analyses are required to produce pure silica nanoparticles, which are not within the scope of this study, from bio-silica precursors using chemicals, as discussed previously.

CRediT authorship contribution statement

Emeka Boniface Ekwenna: Conceptualization, Methodology, Software, Validation, Formal Analysis, Investigation, Data Curation, Writing – Original Draft, Visualization.

Yaodong Wang: Writing-Reviewing and Editing.

Anthony Roskilly: Conceptualization, Resources, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

Acknowledgement

A special thanks to the School of Civil Engineering and Geosciences, the SWAN Centre (Mechanical Engineering) at Newcastle University, and the Durham Energy Institute, Durham University, for the opportunity to create this work.

References

Abd-Rabboh, H.S., Fawy, K.F., Hamdy, M.S., Elbehairi, S.I., Shati, A.A., Alfaifi, M.Y., Ibrahim, H.A., Alamri, S., Awwad, N.S., 2022. Valorisation of rice husk and straw agriculture wastes of Eastern Saudi Arabia: production of bio-based silica, lignocellulose, and activated carbon. Mater. 15 (11), 3746.

Adam, F., Ahmed, A.E., Min, S.L., 2008. Silver modified porous silica from rice husk and its catalytic potential. J. Porous. Mater. 15 (4), 433–444.

Adebisi, J.A., Agunsoye, J.O., Ahmed, I.I., Bello, S.A., Haris, M., Ramakokovhu, M.M., Hassan, S.B., 2021. Production of silicon nanoparticles from selected agricultural wastes. Mater. Today Proc. 38, 669–674.

Affandi, S., Setyawan, H., Winardi, S., Purwanto, A., Balgis, R., 2009. A facile method for the production of high-purity silica xerogels from bagasse ash. Adv. Powder Technol. 20 (5), 468–472.

Agbagla-Dohnani, A., Nozière, P., Clément, G., Doreau, M., 2001. In sacco degradability, chemical and morphological composition of 15 varieties of european rice straw. Anim. Feed Sci. Technol. 94 (1–2), 15–27.

Agarwal, N.K., Kumar, M., Kumar, S.S., Singh, L., Vijay, V.K., Kumar, V., 2022. Anaerobic digestion of sugarcane bagasse for biogas production and digestate valorisation. Chemosphere 295, 133893.

Ahmad-Alyosef, H., Schneider, D., Wassersleben, S., Roggendorf, H., Weiß, M., Eilert, A., Denecke, R., Hartmann, I., Enke, D., 2015. Meso/macroporous silica from miscanthus, cereal remnant pellets, and wheat straw. ACS Sustain. Chem. Eng. 3 (9), 2012–2021.

American Public Health Association (APHA), 2005. Standard Methods for the Examination of Water and Wastewater, 21st Eds. American Public Health Association, American Water Works Association, Water Environment Washington, DC, USA.

Artkla, S., Kim, W., Choi, W., Wittayakun, J., 2009. Highly enhanced photocatalytic degradation of tetramethylammonium on the hybrid catalyst of titania and MCM-41 obtained from rice husk silica. Appl. Catal., B 91 (1–2), 157–164.

Askaruly, K., Azat, S., Sartova, Z., Yeleuov, M., Kerimkulova, A., Bekseitova, K., 2020. Obtaining and characterisation of amorphous silica from rice husk. J. Chem. Technol. Metall. 55 (1), 88–97.

Athinarayanan, J., Periasamy, V.S., Alhazmi, M., Alatiah, K.A., Alshatwi, A.A., 2015. Synthesis of biogenic silica nanoparticles from rice husks for biomedical applications. Ceram. Int. 41 (1), 275–281.

Azizi, S.N., Yousefpour, M., 2010. Synthesis of zeolites NaA and analcime using rice husk ash as silica source without using an organic template. J. Mater. Sci. 45 (20), 5692–5697.

Bakar, A.H.A., Carey, C.J.N., 2020. Extraction of silica from rice straw using alkaline hydrolysis pretreatment. In: IOP Conference Series: Mat. Sci. Eng, 778(1), p. 012158.

Bakar, R.A., Yahya, R., Gan, S.N., 2016. Production of high-purity amorphous silica from rice husk. Procedia Chem. 19, 189–195.

Baniamerian, H., Ghofrani-Isfahani, P., Tsapekos, P., Alvarado-Morales, M., Shahrokhi, M., Angelidaki, I., 2021. Multicomponent nanoparticles as a means to improve anaerobic digestion performance. Chemosphere 283, 131277.

Barik, T.K., Sahu, B., Swain, V., 2008. Nano-silica – from medicine to pest control. Parasitol. Res. 103 (2), 253–258.

Chandrasekhar, S., Satyanarayana, K.G., Pramade, P.N., Raghavan, P., Gupta, T.N., 2003. Review processing, properties and applications of reactive silica from rice husk – an overview. J. Mater. Sci. 38 (15), 3159–3168.

Chen, H., Wang, W., Martin, J.C., Oliphant, A.J., Doerr, P.A., Xu, J.F., DeBorn, K.M., Chen, C., Sun, L., 2013. Extraction of lignocellulose and synthesis of porous silica nanoparticles from rice husks: a comprehensive utilisation of rice husk biomass. ACS Sustain. Chem. Eng. 1 (2), 254–259.

Chen, H., Wang, F., Zhang, C., Shi, Y., Jin, G., Yuan, S., 2010. Preparation of nano-silica materials: the concept from wheat straw. J. Non-Cryst. Solids 356 (50–51), 2781–2785.

Della, V.P., Kühn, I., Hotza, D., 2002. Rice husk ash as an alternate source for active silica production. Mater. Lett. 57 (4), 818.

Elbeshbishy, E., Dhar, B.R., Nakhla, G., Lee, H.S., 2017. A critical review on the inhibition of dark biohydrogen fermentation. Renew. Sust. Energ. Rev. 79, 656–668.

Estevez, M., Vargas, S., Castano, V.M., Rodriguez, R., 2009. Silica nanoparticles are produced by worms through a bio-digestion process of rice husk. J. Non-Cryst. Solids 355 (14–15), 844–850.

Fadhlulloh, M.A., Rahman, T., Nandiyanto, A.B.D., Mudzakir, A., 2014. Review on synthesis of SiO2 nanoparticles. J. Integr. Process. 5 (1), 30–45.

Food and Agricultural Organisation (FAO), 2021. https://www.fao.org/faostat/en/#data/QCL. (Accessed 28 January 2023).

Ghorbani, F., Younesi, H., Mehraban, Z., Çelik, M.S., Ghoreyshi, A.A., Anbia, M., 2013. Preparation and characterization of highly pure silica from sedge as agricultural waste and its utilization in the synthesis of mesoporous silica MCM-41. J. Taiwan Inst. Chem. Eng. 44 (5), 821–828.

Guzmán, A.A., Delvasto, A.S., Sánchez, V.E., 2015. Valorisation of rice straw waste: an alternative ceramic raw material. Cerâmica 61, 126–136.

Hao, L., Gong, X., Xuan, S., Zhang, H., Gong, X., Jiang, W., Chen, Z., 2006. Controllable fabrication and characterisation of biocompatible core-shell particles and hollow capsules as drug carriers. Appl. Surf. Sci. 252 (24), 8724–8733.

Imoisili, P.E., Ukoba, K.O., Jen, T.C., 2020. Synthesis and characterisation of amorphous mesoporous silica from palm kernel shell ash. Bull. Soc. Esp. Ceram. Vidrio 59 (4), 159–164.

International Energy Agency (IEA), 2020. https://www.iea.org/countries/nigeria#overview. (Accessed 1 March 2023).

Juntupally, S., Begum, S., Allu, S.K., Nakkasunchi, S., Madugula, M., Anupoju, G.R., 2017. Relative evaluation of micronutrients (MN) and its respective nanoparticles (NPs) as additives for the enhanced methane generation. Bioresour. Technol. 238, 290–295.

Juntupally, S., Begum, S., Anupoju, G.R., 2023. Impact of additives (macronutrient and nanoparticles of micronutrients) on the anaerobic digestion of food waste: Focus on feeding strategy for improved performance. Biomass Bioenergy 172, 106751.

Kalapathy, U., Proctor, A., Shultz, J., 2000. A simple method for production of silica from rice hull ash. Bioresour. Technol. 73 (3), 257–262.

Kalapathy, U., Proctor, A., Shultz, J., 2002. An improved method for the production of silica from rice hull ash. Bioresour. Technol. 85 (3), 285–289.

Khorsand, H., Kiayee, N., Masoomparast, A.H., 2012. Rice straw ash – a novel of silica nanoparticles. J. Mech. Res. Appl. 4 (3), 1–9.

Kongmanklang, C., Rangsriwatananon, K., 2015. Hydrothermal synthesis of high crystalline silicate from risk husk ash. J. Spectrosc. 2015, 1–5.

Kumagai, S., Sasaki, J., 2009. Carbon/silica composite fabricated from rice husk by means of binderless hot-pressing. Bioresour. Technol. 100 (13), 3308–3315.

Lee, J.H., Kwon, J.H., Lee, J.W., Lee, H.S., Chang, J.H., Sang, B.I., 2017. Preparation of high-purity silica originated from rice husks by chemically removing metallic impurities. J. Ind. Eng. Chem. 50, 79–85.

Liou, T.H., Yang, C.C., 2011. Synthesis and surface characteristics of nano silica produced from alkali-extracted rice husk ash. Mater. Sci. Eng. B 176 (7), 521–529.

Londeree, D.J., 2002. Silica-titania Composites for Water Treatment. University Florida. Doctoral dissertation.

Lu, P., Hsieh, Y.L., 2012. Highly pure amorphous silica nano-disks from rice straw. Powder Technol. 225, 149–155.

Maguyon-Detras, M.C., Migo, M.V.P., Van Hung, N., Gummert, M., 2020. Thermochemical conversion of rice straw. In: Gummert, M., Hung, N., Chivenge, P., Douthwaite, B. (Eds.), Sustainable Rice Straw Management. Springer, Cham, Switzerland, pp. 43–64.

Mirmohamadsadeghi, S., Karimi, K., 2018. Energy recovery together with amorphous nano-silica production from rice straw via dry anaerobic digestion. Bioresources 13 (1), 1872–1884.

Monlau, F., Sambusiti, C., Ficara, E., Aboulkas, A., Barakat, A., Carrère, H., 2015. New opportunities for agricultural digestate valorisation: current situation and perspectives. Energy Environ. Sci. 8 (9), 2600–2621.

Nandiyanto, A.B.D., Ragadhita, R., Istadi, I., 2020. Techno-economic analysis for the production of silica particles from agricultural wastes. Moroccan J. Chem. 8 (4), 8-4.

Patel, K.G., Shettigar, R.R., Misra, N.M., 2017. Recent advances in silica production technologies from agricultural waste stream. J. Adv. Agric. Technol. 4 (3).

Permatasari, N., Sucahya, T.N., Nandiyanto, A.B.D., 2016. Agricultural waste as a source of silica materials. Indones. J. Sci. Technol. 1 (1), 82–106.

Rafiee, E., Shahebrahimi, S., Feyzi, M., Shaterzadeh, M., 2012. Optimisation of synthesis and characterisation of nano-silica produced from rice husk (a common waste material). Int. Nano Lett. 2 (1), 1–8.

Rahim, N.A., Harun, N.Y., Saeed, A.A.H., Bilad, M.R., 2023. Green route synthesis of amorphous silica from oil palm decanter cake: from literature review to experiments. Indones. J. Sci. Technol. 8 (2), 141–156.

Rohatgi, K., Prasad, S.V., Rohatgi, P.K., 1987. Release of silica-rich particles from rice husk by microbial fermentation. J. Mater. Sci. Lett. 6 (7), 829–831.

Sangnark, A., Noomhorm, A., 2004. Chemical, physical and baking properties of dietary fibre prepared from rice straw. Food Res. Int. 37 (1), 66–74.

Sapawe, N., Osman, N.S., Zakaria, M.Z., Fikry, S.A.S.S.M., Aris, M.A.M., 2018. Synthesis of green silica from agricultural waste by sol-gel method. Mater. Today Proc. 5 (10), 21861–21866.

Sen, B., Chou, Y.P., Wu, S.Y., Liu, C.M., 2016. Pretreatment conditions of rice straw for simultaneous hydrogen and ethanol fermentation by mixed culture. Int. J. Hydrog. Energy 41 (7), 4421–4428.

September, L.A., Kheswa, N., Seroka, N.S., Khotseng, L., 2023. Green synthesis of silica and silicon from agricultural residue sugarcane bagasse ash–a mini review. RSC Adv. 13 (2), 1370–1380.

Shim, J., Velmurugan, P., Oh, B.T., 2015. Extraction and physical characterisation of amorphous silica made from corn cob ash at variable pH conditions via sol-gel processing. J. Ind. Eng. Chem. 30, 249–253.

Soltani, N., Bahrami, A., Pech-Canul, M.I., Gonzalez, L.A., 2015. Review on the physicochemical treatments of rice husk for the production of advanced materials. Chem. Eng. J. 264, 899–935.

Steven, S., Restiawaty, E., Bindar, Y., 2021. Routes for energy and bio-silica production from rice husk: a comprehensive review and emerging prospect. Renew. Sust. Energ. Rev. 149, 111329.

Tambone, F., Genevini, P., D'Imporzano, G., Adani, F., 2009. Assessing amendment properties of digestate by studying the organic matter composition and the degree of biological stability during the anaerobic digestion of the organic fraction of MSW. Bioresour. Technol. 100 (12), 3140–3142.

Umeda, J., Kondoh, K., 2008. High-purity amorphous silica originated in rice husks via the carboxylic acid leaching process. J. Mater. Sci. 43 (22), 7084–7090.

Umeda, J., Kondoh, K., 2010. High-purification of amorphous silica originated from rice husks by a combination of polysaccharides hydrolysis and metallic impurities removal. Ind. Crops Prod. 32 (3), 538–544.

Vaibhav, V., Vijayalakshmi, U., Roopan, S.M., 2015. Agricultural waste as a source for the production of silica nanoparticles. Spectrochim. Acta A 139, 515–520.

Van-Soest, P.J., 2006. Rice straw, the role of silica and treatments to improve quality. Anim. Feed Sci. Technol. 130 (3–4), 137–171.

Velmurugan, P., Shim, J., Lee, K.J., Cho, M., Lim, S.S., Seo, S.K., Cho, K.M., Bang, S.K., Oh, B.T., 2015. Extraction, characterisation, and catalytic potential of amorphous silica from corn cobs by sol-gel method. J. Ind. Eng. Chem. 29, 298–303.

Wattanasiriwech, S., Wattanasiriwech, D., 2023. Nano-silica derived from power generation rice husk ash waste by precipitation. Ceramics-Silikáty 67 (1), 20–28.

Wattanasiriwech, S., Wattanasiriwech, D., Svasti, J., 2010. Production of amorphous silica nanoparticles from rice straw with microbial hydrolysis pretreatment. J. Non-Cryst. Solids 356, 1228–1232.

Yang, J., Liu, X., Liu, X., Xu, Q., Wang, W., Wang, D., Yang, G., Fu, Q., Kang, Z., Yang, Q., Liu, Y., Wang, L., Ni, B.J., 2020. Enhanced dark fermentative hydrogen production from waste-activated sludge by combining potassium ferrate with alkaline pretreatment. Sci. Total Environ. 707, 136105.

Yuan, Z., Wu, C., Huang, H., Lin, G., 2002. Research and development on biomass energy in China. Int. J. Energy Technol. Policy 1 (1–2), 108–144.

Zaky, R.R., Hessien, M.M., El-Midany, A.A., Khedr, M.H., Abdel-Aal, E.A., El-Barawy, K.A., 2008. Preparation of silica nanoparticles from semi-burned rice straw ash. Powder Technol. 185 (1), 31–35.