Biochar & Compost Technology, 1(1), 21-35
10.21608/bct.2024.304315.1001

Journal home page: https://bct.journals.ekb.eg/

Recycling of rice husk waste to produce nano–silica for fertilization purposes via an easy protocol

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ARTICLE INFORMATION

Received: 18 July, 2024, Received in revised form 03 August, 2024
Accepted: 06 August, 2024, Available online 13 August, 2024

ABSTRACT

Recycling agricultural waste is crucial for reducing pollution and gas emission of hazardous gases in the surrounding areas. Two alkaline solutions, NaOH and KOH, were used to extract SiO2 nano particles from rice husk waste. Various examination techniques (Energy-dispersive X-ray spectroscopy (EDS), Fourier transform infrared spectra (FTIR), X-ray diffraction (XRD), transmission electronic microscopy (TEM), and specific surface area (SSA)) were utilized to characterize the nanoparticles which were found to be to be amorphous spherical lumpy nanoparticles (16 nm in size) with a high surface area of 361.92 m2 g-1.However,the amount of silica extracted by KOH was higher than that extracted by Na OH beside avoiding the hazard of Na which is found in the extracted as impurities. Based on previous data, nano-SiO2 produced by KOH was experimentally evaluated using maize grown on a sandy soil of poor levels of bioavailable-Si. In the plant shoots and roots, nano-SiO2 extracted by KOH enhanced the contents of leaf chlorophyll, N, P, K, and Si, and, hence, improved the vegetative growth characteristics. These results suggest that the SiO2 extracted by KOH is still in need for further studies in which higher concentrations of KOH can be used for probably extracting silica than the concentration used in the current study.

Keywords: Nano silica; Nano fertilizer; Rice husk; Sandy soil; Recycling of agricultural wastes.

1 Introduction

The agricultural production rises with time, consequently significant amounts of agricultural waste, amounting to millions of agricultural wastes are generated. The production quantities of rice straw, wheat straw, maize straw, and bagasse are approximately 731, 354, 203, and 180 million tons, respectively. The generation of agricultural wastes is increasing at an average yearly rate of 5-10% (Riseh et al. 2024), resulting in detrimental environmental consequences. Burning these wastes contributes to pollution of water, soil, and air (Debnath *et al.*, 2021; Riseh *et al.*, 2024). Hence, it is imperative to implement sustainable waste management practices (Li and Chen, 2020; Riseh *et al.*, 2024). In addition, the accumulation of agricultural wastes represents economic and environmental burdens (Gontard *et al.*, 2018). Thus, it is necessary to optimally exploit and maximize the use of all agricultural production inputs, especially rice wastes. Most investigators like (Abdelhady et al. 2021) indicated that the amount of agricultural wastes was about 40 Tg (teragram). Some easy low-cost extractants i.e. KOH and NaOH were tried to extract silica from rice waste herein. Silica serves many

human (Sadowska and Świderski, 2020) and agricultural purposes (Majumdar and Prakash, 2020b; Majumdar and Prakash, 2020a; Prakash *et al.*, 2020;Prakash *et al.*, 2021).

Although Si is ubiquitous in Earth's crust, its significance for higher plants remains controversial (Majumdar and Prakash, 2020b; Majumdar and Prakash, 2020a; Prakash *et al.*, 2021). It is a metalloid element, occurs naturally in the form of silica and silicate minerals that make up about 95% of the Earth's crust. Silica is a polymer network of anhydride silicic acid molecules. Silica consists of interconnected SiO_4 tetrahedral units by sharing their four oxygen atoms in the three–dimensions (Jal *et al.*, 2004). Silica is present in rocks, sediments and soils. Moreover, SiO_2 is also abundant in everything from water to plants and animals. Despite its massive amount, the soluble portion of Si in the soil solutions is very small. Monomeric silicic acid H_4SiO_4 is the predominant species of Si in natural water and soil solutions. In addition, the H_4SiO_4 concentration is not linked to the total soil Si (Kaushik and Saini, 2019). The concentration of H_4SiO_4 in soil solutions ranges from 0.1 to 0.6 mmol L^{-1} (Sakurai *et al.*, 2017). Plants uptake Si as dissolved or hydrated silica (H_4SiO_4) at the pH levels of most agricultural soils, after which it polymerizes and precipitates as amorphous silica nanoparticles, the so-called phytoliths (Guntzer*et al.*, 2012). The optimum plant-available Si level ($CaCl_2$–extractable Si) is 80 mg Si kg^{-1} soil (Datnoff*et al.*, 2001). The key reasons for plant-available Si deficiency are successive intensive soil cultivation, natural weathering or inherently deficient soils (Epstein, 2001).

Si is not included in the list of essential plant nutrients (Marschner, 1995). However, it has been reported that Si is crucial for plants, especially for *Gramineae* (monocot) plants that include rice, maize, wheat, sugarcane, barley and many grass types (Liang *et al.*, 2015). Si has been proven to boost plant's growth (Janmohammadi *et al.*, 2016; Rastogi *et al.*, 2019), productivity (Suciaty *et al.*, 2018; El-naggar *et al.*, 2020) and stress tolerance (Epstein, 2001; Kaushik and Saini, 2019). It was repeatedly confirmed that nano fertilizers are superior to conventional ones in improving crop productivity, nutrient use efficiency and environmental health (Panpatte and Jhala, 2019). Use of nano–SiO_2 as Si–NF for specific (monocots) crops is one of its novel applications. Yuvakkumar *et al.* (2014), Siddiqui and Al-whaibi (2014), Suciaty *et al.* (2018) and El-naggar *et al.* (2020) agreed that Si–NF in the form of nano–SiO_2 had a better effect on increasing seed germination, plant's growth, productivity, pest resistance and drought and salinity tolerance compared to traditional Si fertilizers or bulk silica. The use of nano–SiO_2 as fertilizer does not require it to be so pure as long as it contains no toxic elements. The majority of preparation methods of bulk silica and nano–SiO_2 currently available depend on chemical precursors of silica. For example, the sol-gel method uses sol of sodium silicate Na_2SiO_3 or Si alkoxides $Si(OR)_4$ or halides $(SiX)_n$ that are converted to a polymeric network of nano–SiO_2 gel. This method involves a three-step reaction with the use of alkoxide according to the following equations (Eqs 1-3):

Hydrolysis	$\equiv Si–OR + H_2O \rightleftharpoons \equiv Si–OH + ROH$	[1]
Water condensation	$\equiv Si–OH + HO–Si\equiv \rightleftharpoons \equiv Si–O–Si\equiv + H_2O$	[2]
Alcohol condensation	$\equiv Si–OR + RO–Si\equiv \rightleftharpoons \equiv Si–O–Si\equiv + ROH$	[3]

R = alkyl group such as CH_3, C_2H_4, …etc.

Although this method and similar ones are efficient, they are expensive, energy-consuming, hygienic, and polluting. (Yuvakkumar *et al.*, 2014; Soltani *et al.*, 2015). Therefore, the use of environmentally safe, cheap, and widely obtainable biogenic silica precursors is necessary.

Rice husk (RH) is rich in silica (20%), cheap, and available in large quantities in rice-producing countries (157 million ton annually), it has become a good biogenic source in silica preparation (FAO, 2004; Soltani *et al.*, 2015; Dizaji *et al.*, 2019). Nowadays, there are several ways to

prepare nano–SiO_2 from rise husk (RH) and RH ash (RHA), such as chemical, thermal, thermochemical, hydrothermal, and biological methods (Soltani*et al.,* 2015 Kalapathy, 2002; Liou, 2004; Liou and Yang, 2011; Rafiee *et al.,* 2012; Carmona *et al.,* 2013; Yuvakkumar *et al.*, 2014); Soltani, Bahrami and González, 2015); França *et al.*, 2017); Dizaji *et al.*, 2019).

Therefore, this paper has three interrelated aims: (1) treating rice husk waste to produce nano–SiO_2 with specifications that allow it to be used as Si–NF using a simple thermochemical technique, (2) to characterize the obtained silica product, and (3) to clarify the competency of the prepared nano–SiO_2 as a Si-source for maize (*Zea mays* L.).

2. Materials and Methods

2.1 Preparation of amorphous nano–SiO_2

We implemented the original protocol proposed by Yuvakkumar et al. (2014) with necessary modifications that were subsequently approved. Figure 1. shows the main steps involved in preparing nano–SiO2, as well as the tested purification parameters. Briefly, the production protocol can be divided into four main stages as described below.

2.2 Preparation of acid-treated RHA

RH was thoroughly washed with tap water (EC of 400 μS cm^{-1}) followed by distilled water to remove dust and water-soluble impurities, as clay and sand were also removed. The washed RH was dried in a ventilated electric drying oven at 105°C overnight, then cooled and crushed. The ground RH was burnt at 550°C for 4 h in an inert muffle furnace(Hadipramana *et al.*, 2016). After cooling, the RHA sample was dispersed in 6 M HCl solution at a mixing ratio of 8 mL acid:1 g ash and magnetically stirred for 2 h at 80°C (Alshatwi *et al.,* 2015; Sankar *et al.,* 2016). The HCl treated ash was filtered and washed with distilled water until the pH of leachates reached 7 (Nghiem *et al.*, 2017). The acid treatment aimed to removing metallic impurities from the RHA as follows:

$$RHA + HCl \xrightarrow{\Delta} SiO_2\ (ash) + H_2O + MCl \qquad [4]$$

Where, M is Al, Fe, Ca, Mg, K, Na, and so on.

2.3 Silica extraction from acid-treated RH

The HCl treated ash (incompletely purified SiO_2) was dispersed either in 3M KOH (França *et al.*, 2017) solution or 3M NaOH solution (Sankar *et al.*, 2016) at a mixing ratio of 4.0 mL alkali:1g ash at the boiling point under vigorous stirring for 1.5 h. These solutions were filtered, and the carbon residue was washed with hot boiling to extract all alkali silicates. The filtrate (silicate solution) was then allowed to cool to room temperature. This step resulted in the formation of either Na–silicate or K–silicate as shown by the following reactions:

$$SiO_2\ (ash) + NaOH \xrightarrow{\Delta} Na_2SiO_3 + H_2O \qquad [5]$$

$$SiO_2\ (ash) + KOH \xrightarrow{\Delta} K_2SiO_3 + H_2O \qquad [6]$$

2.4 Silica extraction by precipitation from alkaline silicates solutions

The nano–SiO_2 precipitates were obtained by adding concentrated H_2SO_4 dropwise to portions of K–silicate and Na–silicate solutions until the pH reached 2.0 while being stirred magnetically. The chemical precipitation reactions that took place during this chemical treatment are shown below (equations 9 and 10):

$$Na_2SiO_3 + H_2SO_4 \longrightarrow SiO_2\downarrow + Na_2SO_4 + H_2O \qquad [7]$$

$$K_2SiO_3 + H_2SO_4 \longrightarrow SiO_2\downarrow + K_2SO_4 + H_2O \qquad [8]$$

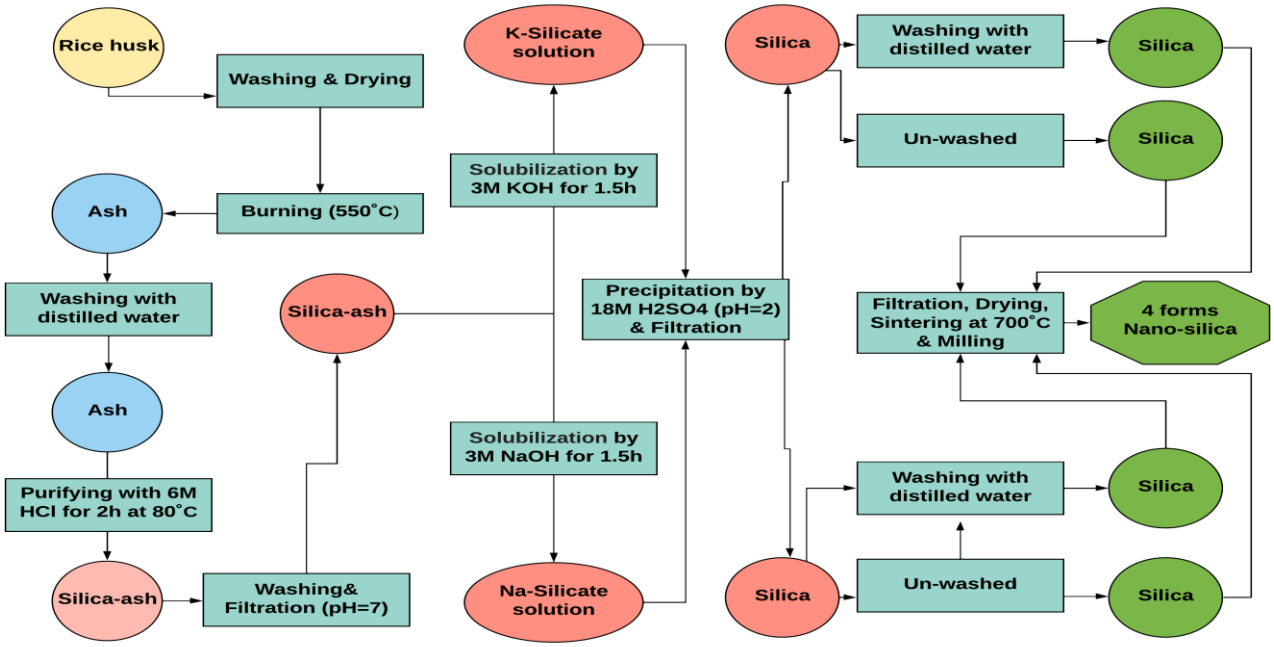

Figure 1. Scheme used to extract the four types of silica from the rice husk.

The solutions with the precipitates were set aside for 12 h to allow for the aging of the precipitated silica.

2.5 Synthesis of SiO_2

The two obtained silica precipitates (from KOH and NaOH pathways) were split into two parts. one part was washed thoroughly with warm distilled water then filtered to get rid of soluble salts and H_2SO_4 residues. The other part was filtered directly without prior aqueous washing. All four forms of silica precipitates (two from the NaOH extraction pathway and two from the KOH extraction pathway) were sintered at 700°C for 2 h. After cooling, the obtained four forms of silica were pulverized to the nano range (1–100 nm) using a mill. The produced four forms of nano–SiO_2 were stored in sealed containers so as not to absorb moisture until they were used.

2.6 Physiochemical evaluation of the produced silica product

The physiochemical characteristics of all the produced formulae of SiO_2 were examined by X-ray diffractometer (XRD) (X' Pert Pro, PANalytical, Netherland) using Cu Kα (λ = 1.5406 Å) as a radiation source over the 2θ range of 10°–80° at 293 K to explore the crystalline nature of the silica produced. The peaks of silica functional groups from Fourier transform infrared spectra (FTIR) were obtained in the wave number region of 4,000–400 cm^{-1} using FTIR spectrometer (Spectrum 100, Perkin Elmer, USA). The scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM–EDAX) (JEOL JSM–6390LV, Japan) was used to determine the chemical composition of the prepared nano–SiO_2. The morphology and size of the synthesized nano–SiO_2 were examined by transmission electron microscopy (TEM) (CM 200, Philips, USA). The specific surface area (SSA) of the prepared nano–SiO_2 via KOH synthetic pathway was analyzed using the BET surface area analyzer (Autosorb AS–1MP, Quantachrome, USA). The physical sorption analysis was done with N_2 adsorption-desorption measurements at liquid N_2 temperature (–196 °C).

2.7 Competence of produced nano-SiO_2 as Si nano fertilizers (Si–NF)

2.7.1 The studied soil

The response of maize (*Zea mays* L.) to soil application of produced nano–SiO_2 was evaluated in a pot experiment. The experiment was conducted in a wired greenhouse under local weather conditions at the Faculty of Technology & Development Experimental Station, Zagazig University (30.5897827° N, 31.4824883° E), Zagazig City, Sharkia Governorate, Egypt. The used soil is classified as Entisol, it is sandy textured (87% sand, 9% silt and 4% clay), with an average $CaCO_3$ content of 17.23 g kg^{-1}, organic matter 5.53 g kg^{-1}, cation exchange capacity 7.01 $cmol_c$ kg^{-1}, pH 7.32 (in 1:2.5 soil-water suspension), EC 1.34 dS m^{-1} (in 1:2 soil water extract), KCl–extractable N 12.12 mg kg^{-1}, Olsen–P 15.23 mg kg^{-1}, NH_4OAc–extractable K 44.65 mg kg^{-1} and $CaCl_2$–extractable Si 34.27 mg kg^{-1}. The soil was sampled to a depth of 0–30 cm and the composite soil samples were air-dried, gently crushed, and passed through a 2–mm mesh sieve.

2.7.2 Experimental design and implementation

A simple and completely randomized experimental design with a single factor and three replicates was employed. The treatments included the application of the unwashed nano–SiO_2 produced by KOH at 3 rates of 0, 50, and 100 mg Si kg^{-1}. Some properties of the produced nano–SiO_2 are presented in Table 1. All recorded properties of the soil and nano–SiO_2 were determined according to ICARDA methods (Estefan*et al.,* 2013).

Table (1): Some properties of the produced nano–SiO_2.

Silica	EC of 1:10, (dS m^{-1})	pH of 1:10 suspension	Soluble Si, (g kg^{-1})	$CaCl_2$–Si, (g kg^{-1})	Soluble -Na (mg kg^{-1})
Washed-SiO_2 by NaOH	6.32	7.33	3.27	9.67	215
Unwashed-SiO_2 by NaOH	8.12	8.47	5.22	18.24	426
Washed-SiO_2 by KOH	6.21	7.42	5.74	16.23	7
Unwashed-SiO_2 by KOH	7.15	6.43	6.12	25.23	11

Plastic pots were filled with portions of prepared sandy soil samples. Equivalent quantities of nano–SiO_2 were mixed thoroughly with soil samples before the sowing of maize seeds. Maize seeds (*Zea mays* L. CV. 166) were obtained from the Maize Research Department, Crops Research Institute, Agriculture Research Centre, Giza, Egypt. On 10th May 2019, two seeds were sown in each pot. Uniform levels of mineral fertilizers of the required essential nutrients were applied to all pots. The soil moisture was maintained near field capacity by weighing every 5 days. After full germination, the seedlings were thinned to one in each pot. After 30 days of seed germination, maize plants were genteelly taken off from pots.

2.7.3 Plant sampling and analytical techniques

The plants were cleaned, then separated into shoots and roots. The plant growth traits were measured in terms of plant height and root length in cm as well as the dry weights of shoots and roots in g pot^{-1}. The content of leaf chlorophyll was determined by a chlorophyll meter before the take-off of plants (Model SPAD-502, Minolta Corp, Ramsey, N.J.). The contents of N, P, K and Si in the plant tissues were also measured. The maize shoots and roots were oven-dried at 70˚C for 48 h. Samples of the dried matters were ground in a stainless–steel blade blender. Set powders of the plant matter powders were wet–digested in H_2SO_4–H_2O_2 mixture at 420˚C according to Parkinson & Allen (1975). The acidic solutions of the digested plant tissues were analyzed for N, P, K and Si according to ICARDA methods (Estefan*et al.*,2013).

2.8 Statistical analysis

All data were statistically analyzed according to the variance analysis technique for the simple design using the MSTATC software package. The significant differences between the mean values of treatments were achieved by the LSD method.

3 RESULTS & DISCUSSION

3.1 Physicochemical evaluation

3.1.1 Energy-dispersive X-ray spectroscopy (EDS) analysis

Fig. 2 (a–d) reveals the EDAX peaks and chemical composition of the prepared types of silica whether those extracted with NaOH or KOH. Generally, most of the elements present in the four silica products are Si and O, with K, Na, S, and C impurities. Both NaOH and KOH at a concentration of 3 M were almost similar in extracting nano–SiO_2 from RHA, regardless of water washing treatment. When aqueous leaching was adopted, the Si content in the obtained silica was 37.92 %w/w upon the extraction with NaOH corresponding to 35.72 %w/w upon extraction with KOH. In contrast, the percentages of the produced silica were 20.40 %w/w upon extraction with KOH treatment and only 14.46 %w/w upon extraction with NaOH treatment in absence of the water leaching. The Na and K appeared as impurities in the acquired silica either with the water leaching step or without it. Unexpectedly, Na and K contents exceeded the Si content in the absence of water leaching treatment (Fig. 2 b, 2d). Fig. 2d shows that carbon impurities reached 8.11 %w/w in the synthesized SiO_2 through the NaOH pathway without aqueous leaching treatment. No trace of carbon was seen in the product obtained from the KOH pathway. This means that KOH was superior to NaOH in extracting silica products.

EDS analysis (Fig. 2, a–d) indicates that leaching of SiO_2 precipitates with hot distilled water is a crucial purification step. When applying water washing for the precipitated SiO_2 before calcination, the impurities of S and C were completely removed from the final silica product. Also, water leaching treatment lowered Na and K impurities from 18.86 %w/w and 30.84 %w/w to 2.47 %w/w and 1.36 %w/w, respectively. Moreover, under our preparation condition of nano–SiO_2, the water wash treatment failed to completely remove Na and K from the silica product. This may be attributed to the strongly adhered K and Na on the silica surfaces or due to their incorporation within the silica surfaces during its partial melting.

The observed peaks of Si and O confirmed the presence of silica in the four silica products. Water leaching of SiO_2 residues prior to the calcination step, however, was not adequate to get a highly pure product as reported by Yuvakkumar *et al.* (2014). The highest purity of 82.43% SiO_2 was obtained with NaOH and aqueous washing treatment. The purity of 77.65% SiO_2 was attained by the KOH and water washing pathway of nano-silica synthesis. These purity percentages were calculated on the basis that 100% pure silica contains 46% Si. However, the corresponding stoichiometric ratios of Si:O were 1:1.76 and 1:1.57 for KOH and NaOH synthesis pathways, respectively. Nghiem *et al.* (2017) prepared nano silica from RHA at stoichiometric ratio of Si:O equals to 1:1.50 and reported that this product can be used for agricultural purposes, especially as Si nano fertilizer.

3.1.2 FTIR analysis

Samples of the four types of the prepared silica were analyzed with the FTIR technique to determine the prescience and densities of the major surface chemical groups (Fig. 3 (a–d)). It can be seen from FTIR spectra that the broad, intensity and positions of the absorption peaks varied according to the type of the alkaline purifying agent and the water washing treatment. In general, absorption peaks indicate the presence of surface groups belonging to silica structures (470–1150 cm^{-1}) and others due to the existing impurities and/or O–H groups and adsorbed H_2O (1640–3440 cm^{-1}).

A large number of researchers, including Sankar *et al.* (2016) and Nghiem et al. (2017) agreed to allocate the absorption peaks in the range of 438–475 cm^{-1} to Si–O^- bond rocking, 796–805 cm^{-1} to symmetric Si–O^- bending (silanol), 1050–1150 cm^{-1} to asymmetric Si–O–Si (siloxane) stretching in SiO_4 tetrahedra, 1633–1643 cm^{-1} to O–H bending, and 3437–3456 cm^{-1} to O–H

stretching and adsorbed water. Nevertheless, Yuvakkumar *et al.* (2014) assigned the absorption beaks of 497, 623, and 795 cm^{-1} for Si–O–Si bending, Si–H, and symmetric Si–O–Si stretching modes of vibrations, respectively. Also, they attributed the absorption beaks in the range of 1281–2428 cm^{-1} to impurities such as Na and CO_3^{2-} groups.

It is also evident that the failure to wash salts formed during SiO_2 precipitation from Na and K silicate solutions with H_2SO_4 before calcination affects the surface properties of the resulting silica, the type and the density of surface groups. For instance, the absorption peak that appeared at 600 cm^{-1} in the NaOH purification treatment disappeared when water washing treatment was applied (Fig. 3 c and d). The peaks of silica structures (silanol and siloxane groups) were stronger and broader in the case of synthesis across the KOH pathway. Hence, the use of KOH in conjunction with water washing is the right way to get silica suitable for use as Si–NF.

3.1.3 XRD analysis

The XRD patterns of the obtained four silica forms are shown in Figure 4 (a–d). A broad diffuse peak appears at $2\theta \sim 22^{\circ}$, confirming the amorphous nature of the silica produced. This only occurs when acid–precipitated silica was washed with distilled water prior to its calcination (Fig. 4 a and c). Moreover, this was observed for both KOH and NaOH synthesis routes. The absence of any sharp peaks for these treatments indicates the absence of silica crystalline phases. In contrast, Figure 4 (b and d) shows a different XRD without applying the water wash step. This disturbance in the silica structure nature and the presence of the narrow sharp peaks can be attributed to the crystalline structures of both Na_2SO_4 and K_2SO_4 salts formed during silica precipitation from the silicate solutions by sulfuric acid. Failure to wash these salts led to their crystallization and growth with or inside the silica matrix during the calcination process at 700 °C (Premaratne *et al.*, 2014). Therefore, it can be concluded that nano–SiO_2 synthesized from RH via the supposed technique, especially in conjunction with water leaching treatment, is a purely amorphous type.

3.1.4 TEM analysis

TEM studies have been carried out on the obtained silica samples to verify particle morphology and size. Generally, the obtained SiO_2 particles are uniform and slightly lumpy regardless of the alkaline purification type or treatment of water wash (Fig. 5 a – d). The TEM images show that the shapes of the SiO_2 particles are spherical without clear boundaries because they are present in the amorphous and agglomerate form.

Moreover, the particle size distribution is homogeneous and narrow with an average of about 16.1–24.3 nm upon leaching with water and 29.1–51.2 nm without water leaching. According to Benzon *et al*. (2015) and Husen & Iqbal (2019), nano fertilizers can directly enter to plant tissues through the cell wall pores when the particle sizes are in the range of 5–20 nm. Because nano–SiO_2 produced via the KOH route contains a reasonable percentage of granules with diameters < 20 nm, it can be used as a Si–NF, whether by adding it to the soil or spraying it on the plant vegetative system. For this reason, this was the only product subjected to a study of the specific surface area and then tested as a nano–Si fertilizer. Differentiate among the four numbers.

3.1.5 The specific surface area and particle sizes

The specific surface area (SSA) of silica produced by NaOH was found to be 276.12, 266.41, and KOH was 361.92, 322.12$m^2\ g^{-1}$, for washed and unwashed silica, respectively. This finding confirm and corroborate the results of the TEM image.

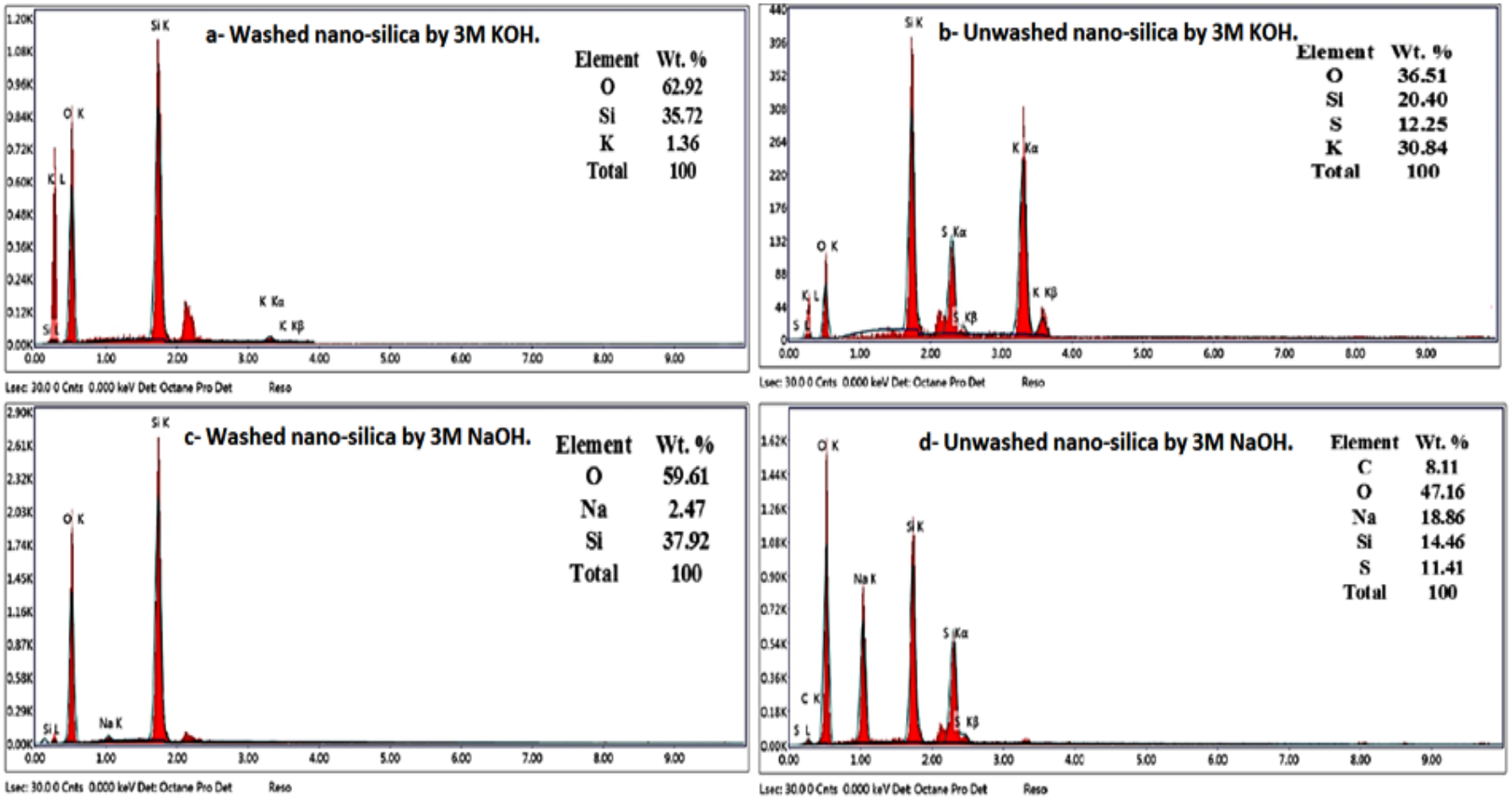

Figure 2. EDAX peaks and chemical composition of the prepared types of silica.

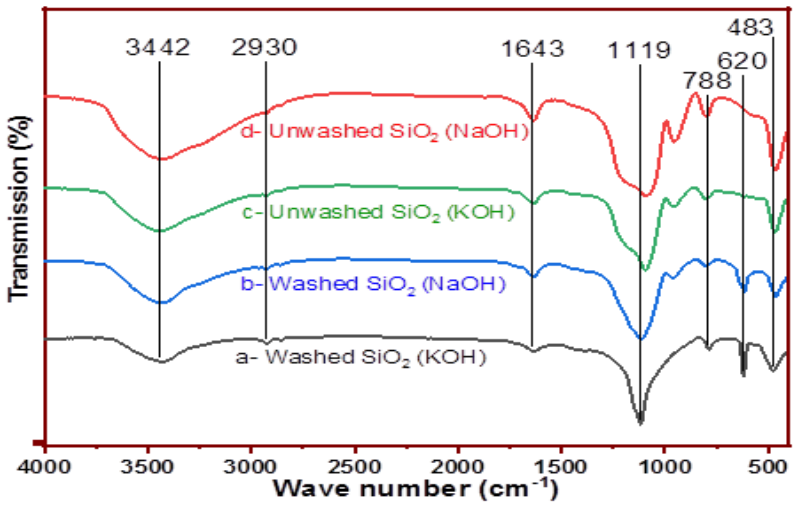

Figure 3. FTIR curves of the four produced silica types.

In addition, the high value of the SSA of these silica products suggests that these products contain external and internal surfaces, and they are of porous tissues, and hence they are highly reactive. Therefore, the results of this analysis, in conjunction with its predecessor, indicate the suitability of this product for use as Si–NF fertilizer. Moreover, the average silica diameters were largely in agreement with the previously presented TEM images, and the silica produced with NaOH and KOH which were30, 37, 18, 16nm without and with leaching by distilled water purification processes. Therefore, washed nano-SiO_2 produced by KOH effect was tried on maize plants as will be shown in the following paragraph.

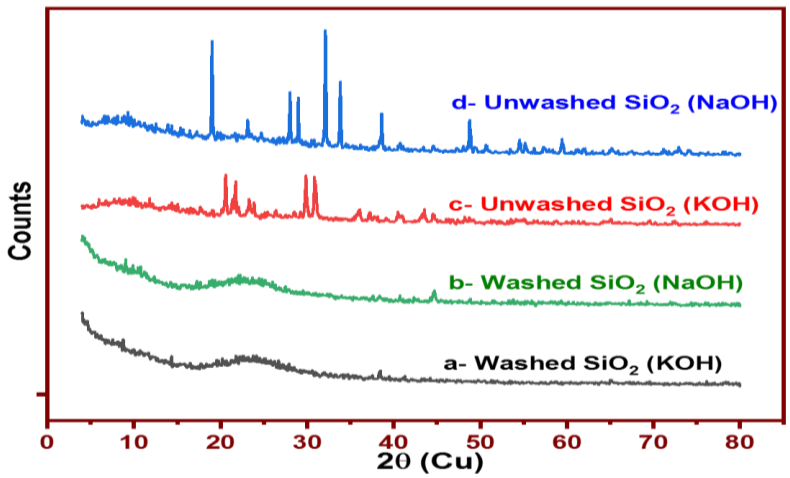

Figure 4. XRD patterns of the four produced silica types.

3.2 Maize response to the synthesized nano–SiO_2

In this experiment application of synthesized nano–SiO_2 enhanced plant growth traits including shoot, root, and total dry weights, root length, and shoot height (Table 2.). All tested parameters of plant growth were significantly increased with increasing application level of nano–SiO_2, produced by KOH except for the length of the root length where the change was not significant. The highest values were obtained for all growth parameters using nano-SiO_2. Likewise, the effect of nano-SiO_2 on the chlorophyll contents in plant leaves gave promising

results indicating its use as Si-NF. The results stand in well agreement with those of Suriyaprabha *et al.* (2012a), Suriyaprabha *et al.* (2012b), Siddiqui & Al-whaibi (2014) and El-naggar et al. (2020) who observed better seed germination and growth traits, and yield of plants in the presence of silica nanoparticles and porous silica nanoparticles compared with bulk silica and other conventional Si fertilizers. In addition, nano-SiO_2 significantly boosted plant dry weight and enhanced the contents of organic compounds such as proteins, chlorophyll, and phenols in nano silica-treated maize plants.

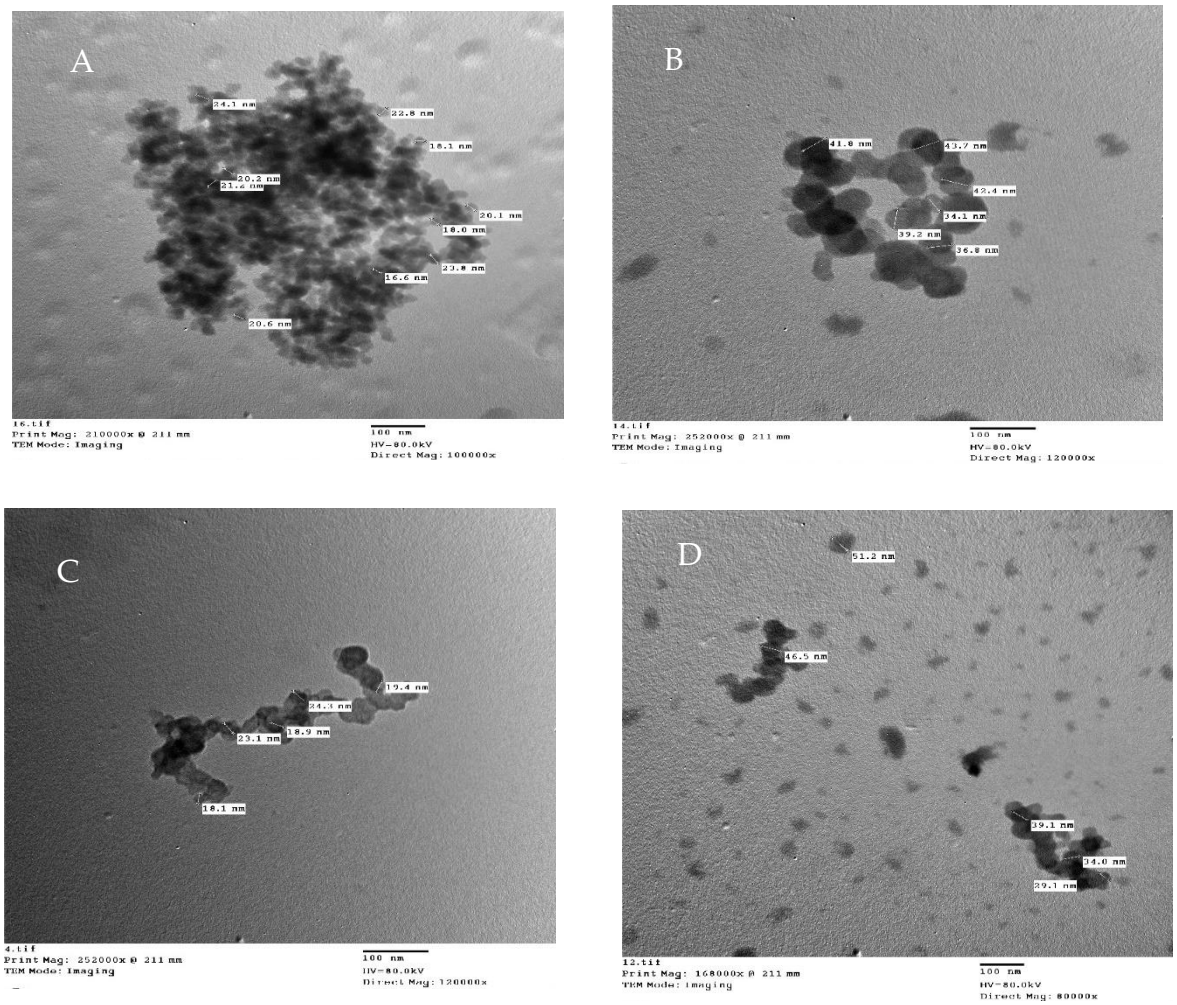

Figure 5. TEM of the produced silica (a; washed silica extracted by KOH, b; unwashed silica extracted by KOH, c; washed silica extracted by NaOH, d; unwashed silica extracted by NaOH)

Table (2): Effect of nano–SiO_2 applications on some growth traits of maize plants.

Si–level, mg kg^{-1}	Dry weights, (g $plant^{-1}$)			Root length and shoot height, cm		Chlorophyll content
	shoot	root	total	Root	Shoot	%
0	2.77^{c}	0.43^{c}	3.12^{c}	8.23^{c}	15.00^{b}	15.25^{c}
50	2.88^{b}	0.48^{b}	3.36^{b}	14.00^{b}	19.60^{a}	21.12^{b}
100	3.06^{a}	0.51^{a}	3.57^{a}	17.67^{a}	21.10^{a}	23.00^{a}

Means with the same letter within column are not significantly different.

The nano-SiO_2 participation in root and shoot growth can be related to their ability to improve the seed germination properties, hence a strong root system (Suciaty *et al.*, 2018). The treatment of nano-silica fertilizer portrayed the best results for plant growth parameters and yield components of soybean plants.

Additionally, results presented in Table 3 reveal that the application of nano-SiO_2 had a noteworthy effect on N, P, K, and Si concentrations in shoots and roots of maize plants. The N, P, K, and Si concentrations were increased with increasing levels of nano-SiO_2 from 0 up to 100 mg Si kg^{-1}. The increase in concentrations was significant for N and Si in shoots and roots and K in shoots only. The improvement in plant absorption of nutrients in the presence of nano-SiO_2 may be due to its positive effect on the chemical and biological environment of the soil and the vigor growth of the root system. In this context, Karunakaran *et al.* (2013) reported that nano-silica has a positive effect on several beneficial bacteria and the nutritional value of the soil. Siam *et al.* (2018) found that N, P, and K content and uptake by rice shoots, and grains were increased by Si addition as compared to those without Si addition.

Table (3): Effect of nano–SiO_2 applications on N, P, K and Si concentrations in maize shoots and roots.

Si–level mg kg^{-1}	N		P		K		Si	
	%							
	roots	shoots	roots	shoots	roots	shoots	roots	shoots
0	1.99^{c}	1.92^{c}	0.07^{a}	0.07^{a}	0.74^{b}	3.95^{c}	0.13^{b}	0.01^{c}
50	2.03^{b}	2.26^{b}	0.07^{a}	0.08^{a}	0.78^{a}	4.01^{b}	0.58^{a}	0.99^{b}
100	2.06^{a}	2.85^{a}	0.06^{a}	0.08^{a}	0.79^{a}	4.02^{a}	1.46^{a}	1.72^{a}

Means with the same letter within column are not significantly different.

4 Conclusion

In conclusion, agricultural-natural wastes, including rice husk or straw, can be used to make SiO_2 by using NaOH or KOH based on the specific purposes of their use. Therefore, through an applicable, ease, and low-cost protocol, nano-SiO_2 can be manufactured to specifications suitable for use as a Si-fertilizer. Based on results, the purity of nano-SiO_2 purity produced by KOH was 35.72% according to EDS analysis, with K being the only impurity, which is necessary for plants. Also, plant available-Si extracted by $CaCl_2$ was 16.23g kg^{-1}, which is considered a suitable level for fertilization. Moreover, these prepared products are characterized by highly-specific surface area and low particle size diameters i.e.361.92m^2 g^{-1}, 16 nm, respectively. Thus, acidic silica should be washed with warm distilled water before the calcination stage. Additionally, a KOH solution was more effective at extracting silica from rice husks, making it a better alternative to NaOH in this study for fertilizer purposes. Based on application, maize plants significantly respond to nano-SiO_2 produced through KOH compared to the control treatment. Finally, we suggested use of this protocol for the manufacture of silica fertilizer from agricultural wastes rich in silica, like rice and sugarcane waste, etc., using different concentrations of KOH.

Author Contributions

Conceptualization, and supervision Sh.M.M, M.H.E, and A.A.H; methodology, M.A, M.H.E and Sh.M.M,; software, Sh.M.M.; validation, Sh.M.M and A.A.H.; formal analysis, investigation,

resources, data curation, writing -initial draft preparation, writing, reviewing and editing, M.A, Sh.M.M, and M.H.E. The final paper has been reviewed and approved by all authors.

Acknowledgments

There is no acknowledgment

Conflicts of Interest

The authors declare no conflict of interest.

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