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RESEARCH ARTICLE

Facile Extraction and Characterization of Silica Nanopowder from Marine National Park beach sand via Alkali Fusion Route

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ABSTRACT:
The current study showed utilization of locally available beach sand from Marine National Park in facile extraction of highly amorphous silica via a simple alkali fusion method. The purification of the silica sand was done using 6 N HCl solution to increase its purity. The method entailed formation of sodium silicate (Na_2SiO_3) solution from silica sand, precipitation using HCl acid to form tetraortosilicate acid, $Si(OH)_4$ (silica gel) which is then heated to form amorphous silica (SiO_2). The percentage yield of the extracted silica was 35.0139±0.11%. The extracted silica was characterized using X-Ray Fluorescence Spectrometer (XRF), X-Ray Diffractometer (XRD) and Fourier Transform Infrared Spectrophotometer (FT-IR). The XRF characterization revealed that the extracted silica content was 94.16±0.47 % which increased from 81.32±0.81% (Silica sand). The XRD results revealed a highly crystalline quartz as the main component of silica sand. The XRD spectra of extracted silica showed a broad diffraction peak at $2\theta = 21.76^{o}$ revealing its amorphous nature. The average particle size of the extracted silica was 45.15nm. The FT-IR characterization of the extracted silica showed hydroxyl (-OH) in silanol (Si-OH) and siloxane (Si-O-Si) as important functional groups. The results showed a low cost technique for the production of highly pure amorphous nanosized silica as a potential mineral that can be employed in vast industrial fields.

KEYWORDS: Marine National Park, Alkali Fusion, extracted silica, amorphous, silica sand.

1. INTRODUCTION:
Silica (SiO_2) is obtained naturally from minerals, biogenic marine organisms and agricultural wastes[1]. It is found in mainly in crystalline, gel or amorphous forms[2]. In the industrial fields, highly amorphous silica is widely used in vast industries such as electronics, cement, textiles, cosmetics, rubber, glass, waste water treatment, toothpaste, paint, concrete, healthcare, paper, ceramics amongst others[3,4]. The emerging technological inventions has heightened the demand for various forms of silica such as powder silica, precipitated silica, silica gel, fumed silica and silica sol[5]. This has been due to their desired features such as chemically stable, friendly to the environment, easily biocompatible, easily fabricated and highly pure for use in different industries[3,6]. Amorphous silica can be extracted from natural minerals and agricultural wastes such as quartz sand[7], rice husk[2], siliceous sands[8], sugarcane bagasse[9], Douiret sand[10], flying ash sludge[11] and mud[12] amongst others.

The natural sand is among the most abundant materials found in beaches, seas, coastal oceans and some of the fresh shallow lakes[13]. It is formed mainly from weathering and erosion resulting to finer and cleaner grains of the sand[14]. The aggregates consist of mainly silica - based quartz (SiO_2) with some crystalline such as tridymite and cristobalite[15], micro- and cryptocrystalline polymorphs[16], strained quartz polymorphs[17] with others glassy volcanic materials[18,19]. Apart from the non - reactive crystalline quartz, other quartz polymorphs (opal, granite, quartzite, phyllite, quartzite, gneiss, granodiorite, chert, chalsedony and siltstone amongst others) are reported to contain active silica from silica - silicate minerals which are potential for chemical dissolution via alkali - silica reactions[19]. The

silica sand is also reported to contain amorphous structured silica materials[20] from biogenic decomposition of siliceous organisms such as diatomaceous earth[21] and siliceous sponges[22]. The silica sand is not found in pure form but as a mixture of other oxides such as Iron (III) oxide (Fe_2O_3), Aluminium (III) oxide (Al_2O_3), Titanium (IV) oxide (TiO_2), Calcium (II) oxide (CaO), Magnesium (II) oxide (MgO) and Potassium oxide (K_2O) among others[15].

The quartz polymorphs (partly crystalline) lose their crystal structure when heated in strongly concentrated alkali solutions (activating agents) forming soluble silicates which are then employed to synthesize obtain pure amorphous silica[23,24]. This is due to their change in oxygen bridge of the siloxane (Si-O-Si) bond energies, hence allowing the bond angles to rotate freely and easily to form disordered structure with different shapes[25,24]. Amorphous silica has hydrophilic properties because of their attached hydroxyl group on the surface[26]. Various methods of extraction of highly pure amorphous silica from the natural silica sand such as electrocoagulation[27], sol-gel[28], hydrothermal[29] and alkaline fusion[30] have been reported.

The principle of alkali fusion extraction route is to break the chemical bonds in the silica sand using an alkaline solution such as KOH, NaOH and Na_2CO_3 at a certain temperature followed by the binding of silicon with oxygen to form nanosized amorphous silica[30]. In this research, an alkaline fusion chemical extraction method was used to obtain a nanosized amorphous silica.

2. MATERIALS AND METHODS:

2.1 Materials:

Hydrochloric acid (HCl) and sodium hydroxide (NaOH) analytical grade chemicals (Purity > 99.5 %), all sourced from Kobian limited, Nairobi (outlet of Sigma Aldrich), were used in the study. The solutions were prepared using distilled water at a room temperature (298 K). The equipment and instruments used in this research were Fourier Transform Infrared Spectrophotometer (IR Tracer - 100, Japan), Automated X-Ray Fluorescence Spectrometer (Bruker S1 Titan 600, Tracer 5/CTX), Distiller (WSB 14), X-Ray Diffractometer (XRD, Rigaku MiniFlex II; Tokyo, Japan), Grinding mill (Retsch SR 200), Drying oven (WTC binder FD53), Pulveriser rock grinding machine (Retsch RS 200), Magnetic stirrer with hot plate (WH240-HT) and Analytical weighing balance (ATX224 Shimadzu).

2.2 Sample collection and pre-treatment:

The procedure of sample collection was as described by[31] with slight modifications. The sand samples were collected from the Malindi Marine National Park in Kilifi county, Kenya. The samples were obtained from a composite by mixing sub-samples (3) from a site of 0 - 15cm depth at a 5 × 5km grid sampling. A 500.000g of this mixed composite was stored in cleaned polythene bags and tightly closed and transported to Kenyatta University laboratories. The sand was allowed to dry and visible physical impurities removed, sieved and oven - dried at 80 ^{o}C for 12hours. The samples were then grinded into a very fine powder and kept in an airtight - labelled containers.

2.3 Silica extraction:

The procedure of silica extraction was performed as adopted from [32] with slight modifications. A 100.000 g of the silica sand powder was soaked in 6 N HCl solution in a glass beaker for 24 hours. The mixture was the filtrated, the residue washed with distilled water until there is no yellowish color and then dried at 105 °C to a constant weight. A 400 mL of 10 N NaOH solution was then added to the sand residue and heated at 150 ^{o}C while stirring for 4 hours. The filtrate (sodium silicate) was separated from the unreacted sand residues using Whatmann filter paper N_o. 42 and 6N HCl solution slowly added to form a white gel (pH 7). The reaction mixture was left overnight at room temperature, filtered and rinsed with distilled water. The gel was then dried at 105 °C to a constant weight and stored awaiting subsequent experiments. The percentage yield of silica extracted was calculated using equation 1.

$$\% \text{ Yield} = \frac{\text{Amount of extracted silica (g)}}{\text{Mass of the Silica sand sample (g)}} \times 100 \quad (1)$$

The extracted silica was then characterized using XRF, XRD and FT-IR.

3. RESULTS AND DISCUSSION:

3.1 Silica extraction mechanisms:

The alkali fusion silica extraction involved preparation of sodium silicate (Na_2SiO_3) from silica sand using NaOH solution. This is as summarized by the equation 2.

$$SiO_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2SiO_{3(aq)} + H_2O_{(l)} \quad (2)$$

The reaction mechanism of formation of sodium silicate is shown in Figure 1 below.

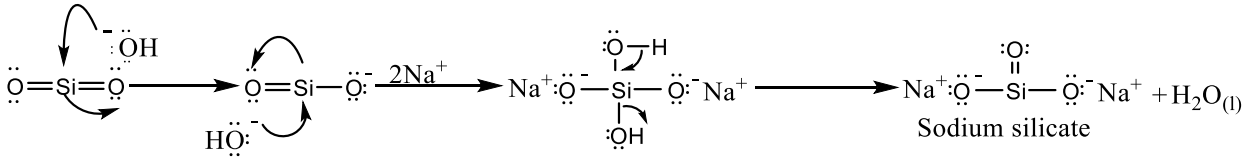

Figure 1: Reaction mechanism of sodium silicate formation

Sodium silicate is then reacted with HCl solution (precipitation agent) to form a precipitated tetraortosilicate acid, $Si(OH)_4$ (silica gel) and NaCl residue which is then separated out. This is summarized by equation 3 and mechanism in Figure 2.

$$Na_2SiO_{3(aq)} + H_2O_{(l)} + 2HCl_{(aq)} \longrightarrow Si(OH)_{4(s)} + 2NaCl_{(aq)} \quad (3)$$

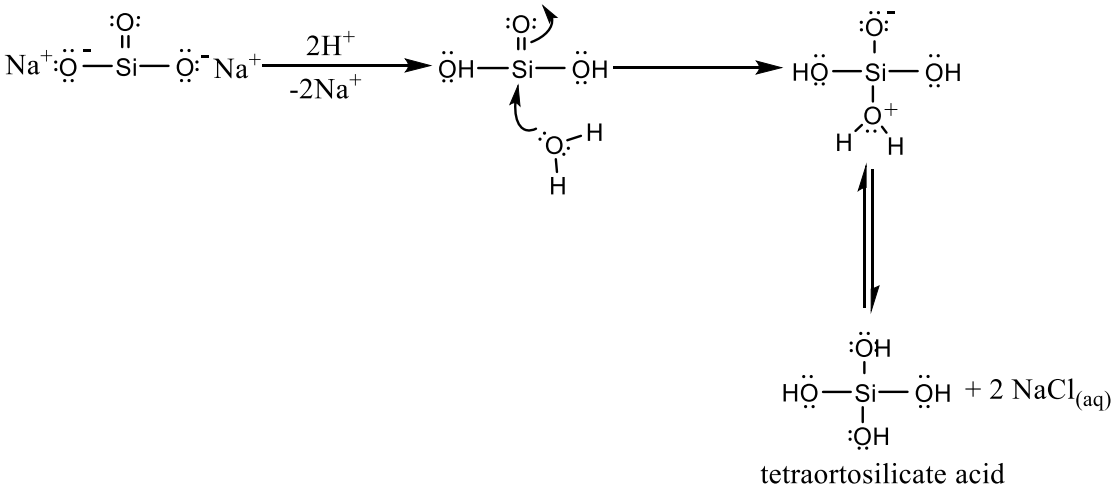

Figure 2: Reaction mechanism of tetraortosilicate acid (silica gel) formation

The silica gel is then heated to form amorphous silica as shown by the equation 4.

$$Si(OH)_{4\ (s)} \longrightarrow SiO_{2\ (s)} + 2H_2O_{\ (l)} \quad (4)$$

The reaction mechanism for the formation of amorphous silica is shown below (Figure 3).

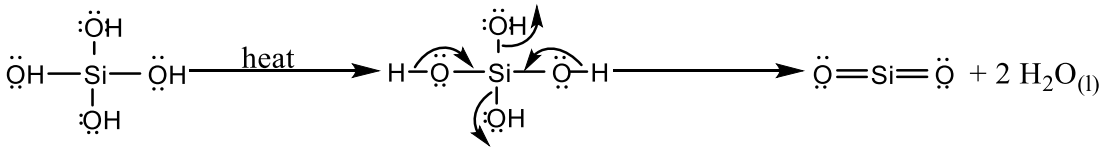

Figure 3: Mechanism of silica gel heating

3.2 Percentage yield:

The percentage yield of the extracted silica (ES) is shown in table 1.

Table 1: Percentage yield of extracted silica

% Yield
(Mean ± S.D)
35.0139 ± 0.11

3.3 XRF analysis:

The XRF spectrometer (SI Titan) was used to determine the chemical composition of natural silica sand (MNPS) and extracted silica (ES) powder and results are presented in Table 2.

Table 2: Mean percentage of chemical composition of natural silica sand and extracted silica

Sample	Oxide (%)						
	SiO_2	Fe_2O_3	ZrO_2	TiO_2	Al_2O_3	MnO_2	ZnO
MNPS	81.32 ± 0.81	5.13 ± 0.25	0.89 ± 0.16	0.33 ± 0.45	2.06 ± 0.01	0.17 ± 0.06	0.08 ± 0.01
ES	94.16 ± 0.47	0.21 ± 0.09	0.34 ± 0.14	nd ± 0.34	0.05 ± 0.68	nd ± 0.04	nd ± 0.01

*nd – not detected

From the results in Table 2, the percentage of SiO_2 in the extracted silica was 94.16 ± 0.47 %, which increased from 81.32 ± 0.81 % after alkali fusion. All the other oxides were below 1 %. This showed that alkali fusion increased not only the content of amorphous silica but also eliminated the impurities present in the silica sand[7]. These results are in in tandem with data reported by [30] on the extraction of silica from Bengkulu beach sand using alkali fusion method.

3.4 XRD analysis:

The XRD spectra for silica sand (before and after acid treatment) and extracted silica is shown by Figure 4.

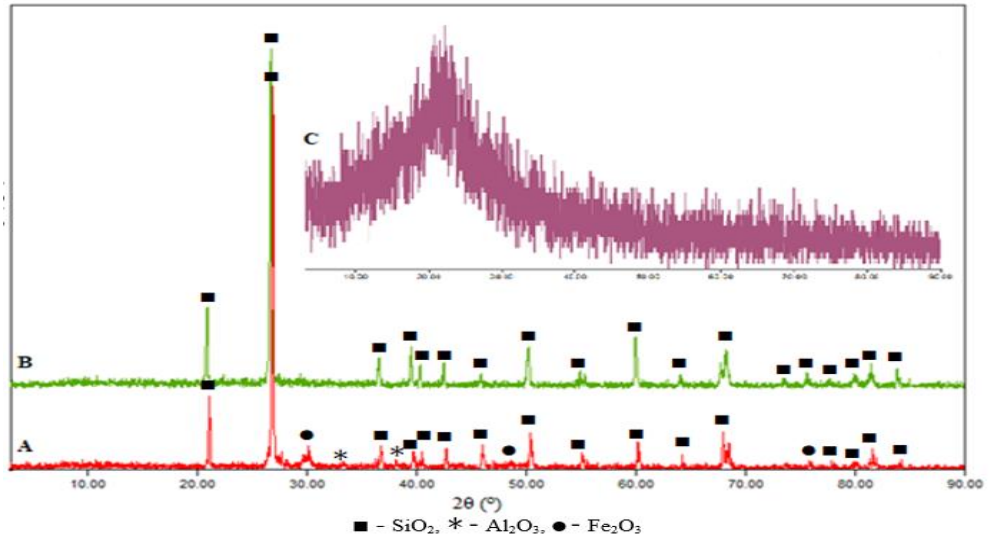

Figure 4: The XRD pattern of MNPS before (A) and after (B) acid treatment and ES (C)

The X-ray diffractogram (A) in Figure 5 exhibit narrow peaks, indicating a high degree of crystallinity of the respective samples. The presence of the quartz phase in the highest relative intensity, Al_2O_3, Fe_2O_3 and ZrO_2 impurities as minor phases was suggested by Match! software version 3.14 Build 238. The presence of amorphous silica materials from siliceous organisms in the silica sand is not evident in the XRD spectra when other crystalline, microcrystalline and cryptocrystalline phases are present[33]. All the diffraction peaks for Al_2O_3, Fe_2O_3 and ZrO_2 have disappeared after acid treatment (diffractogram B) showing that acid leaching eliminated all the impurities that were present in the natural silica sand[34].

The X-ray diffraction pattern of (diffractogram C) exhibits a broad characteristic diffraction peak at $2\theta = 21.76^{o}$ with low intensity which indicated amorphous nature of the extracted silica[35,26]. No crystalline phases or other peaks for

oxides were observed in all the XRD spectra, confirming a high purity silica structure[36]. This proved the effectiveness of the alkali fusion extraction process. The average particle size was 45.15 nm showing that the amorphous silica was powder was in nanometer scale[37]. These results are coherent to findings reported by [7] during their research study on the synthesis of silica nanopowder from Indonesian natural sand via alkali fusion route.

3.5 FT-IR analysis:

The extracted silica was characterized by FT-IR and results are shown by the Figure 5.

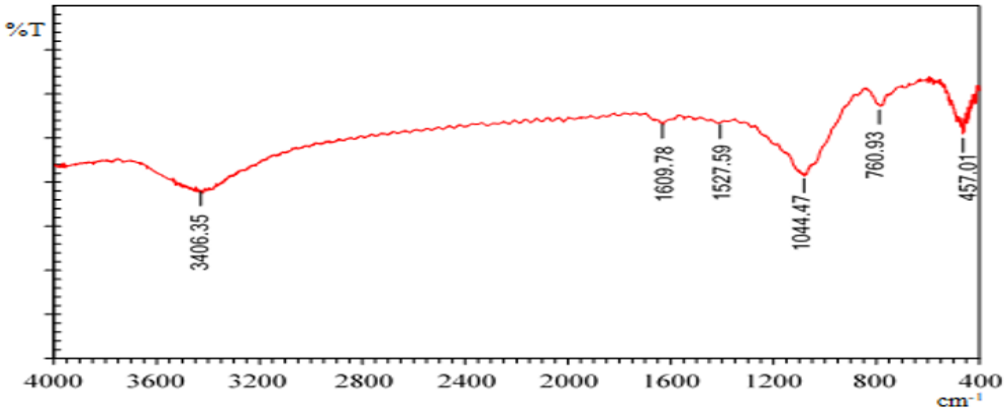

Figure 5: FT-IR spectra of extracted silica (ES)

The results in Figure 5 showed broad spectrum band at 3406.35 cm^{-1} characterized by (-OH) stretching vibrations of the silanol (Si-OH) or adsorbed water molecules on the surface of the extracted silica which could not be completely removed by heating[34]. This is confirmed by peak at 1609.78 cm^{-1} which are ascribed their bending vibrations[30]. The predominant bands 1044.47 cm^{-1} and 760.93 cm^{-1} corresponds to the asymmetric and symmetric stretching vibrations of the siloxane (Si-O-Si) bond[38,39]. The band observed at 457.01 cm^{-1} is due to bending vibrations of Si-O-Si bond in amorphous phase[37].

CONCLUSIONS:

Natural silica sand from marine national park sand contain silica (SO_2) as the main component with main impurities of Al_2O_3, Fe_2O_3 and ZrO_2 as shown by the XRF and XRD results. Acid treatment of the silica sand eliminated the oxide impurities to < 1 %. The percentage yield of extracted silica (ES) via alkali fusion route was 35.0139 ± 0.11 %. The percentage of SiO_2 in the extracted silica increased to 94.16 ± 0.47 % from 81.32 ± 0.81 %. The XRD spectra showed that the extracted silica was highly amorphous. The FT-IR results showed hydroxyl (-OH) in silanol and siloxane (Si-O-Si) as important functional groups in extracted silica.

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REFERENCES:

1. Setyoningrum TM, Murni SW, Nandari W, Nur M. Effect of sodium hydroxide concentrations and particle sizes on silica extraction from mineral rock obtained in Kalirejo village, Kokap, Kulonprogo, Yogyakarta. Eksergi. 2021; 18 (1): 29 - 31.
2. Todkar B, Deorukhkar O, Deshmukh S. Extraction of silica from rice husk. International Journal of Engineering Research and Development. 2016; 12 (3): 69 - 74.
3. Wahyudi A, Amalia D, Sariman. Preparation of nano silica from silica sand through alkali fusion process. Indonesian Mining Journal. 2013; 16 (3): 149 - 153.
4. Setyoningrum T, Murni S, Nandari W. Extraction of Silica from Kalirejo Minerals, Kokap, Kulonprogo, Yogyakarta. LPPM UPN "Veteran" Yogyakarta Conference Series Proceeding on Engineering and Science Series. 2020; 1 (1): 269 - 276.
5. Arunmetha S, Karthik A, Srither R, Vinoth M, Suriyaprabha R, Manivasakan P, Rajendran V. Size-dependent physicochemical properties of mesoporous nanosilica produced from natural quartz sand using three different methods. RSC Advances. 2015; 5 (59): 47390 - 47397.
6. El-Sawy A, Gemeay AH, Helal AS, Salem MA. Catalytic degradation of methylene blue in aqueous solution by H2O2 and SiO2-NH2-Cu(II)@SiO2 nanoparticles as catalyst. Journal of Molecular Liquids. 2021; 341: 1 - 15.
7. Munasir, Sulton A, Triwikantoro, Zainuri M, Darminto. Synthesis of silica nanopowder produced from Indonesian natural sand via alkali fusion route. American Institute of Physics. 2013; 1555 (1): 28-31.
8. Sdiri A, Higashi T, Bouaziz S, Benzina M. Synthesis and characterization of silica gel from siliceous sands of southern Tunisia. Arabian Journal of Chemistry. 2014; 7 (4): 486 - 493.

9. Chindaprasirt P, Rattanasak U. Eco-production of silica from sugarcane bagasse ash for use as a photochromic pigment filler. Scientific reports. 2020; 10 (1): 1 - 7.
10. Trabelsi W, Benzina M, Bouaziz S. Physico-chemical characterisation of the Douiret sand (Southern Tunisia): Valorisation for the production of Silica Gel. Physics Procedia. 2009; 2 (3): 1461 - 1467.
11. Cheng Y, Luo F, Jiang Y, Li F, Wei C. The effect of calcination temperature on the structure and activity of TiO2/SiO2 composite catalysts derived from titanium sulfate and fly ash acid sludge. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2018; 554:81- 85.
12. Rahmayanti A, A'yuni Q, Hartati H, Purkan P, Romanza IG. Synthesis and characterization of silica gel from Lapindo mud Sidoarjo. IOP Conf. Series: Earth and Environmental Science. 2020; 456: 1 - 7.
13. Ismail A, Widyaningtyas AL, Susanto BH, Nasikin M. Facile synthesis silica nanoparticles from Indonesia silica sand and their physico-chemical properties. Key Engineering Materials. 2020; 862: 35-39.
14. Gallop S, Kennedy D, Loureiro C, Naylor L, Muñoz-Pérez J, Jackson D, Fellowes T. Geologically controlled sandy beaches: Their geomorphology, morphodynamics and classification. Science of the Total Environment. 2020; 731: 1 - 96.
15. Munasir, Supardi Z, Mashadi, Nisa Z, Kusumawati DR, Putri N, Taufiq A, Sunaryono, Hidayat N, Darminto. Phase transition of SiO2 nanoparticles prepared from natural sand: The calcination temperature effect. IOP Conf. Series: Journal of Physics: Conference Series. 2018; 1093: 1-10.
16. Antolik A, Daria J. Assessment of the alkali-silica reactivity potential in granitic rocks. Construction and Building Materials. 2021; 295: 1 - 12.
17. Moreira K, Oliveira P, de Deus Ê, Cabral A. Alkali-silica reaction: understanding the phenomenon. Journal of Building Pathology and Rehabilitation. 2021; 6 (5): 1-10.
18. White RJ, Spinelli GA, Mozley PS, Dunbar NW. Importance of volcanic glass alteration to sediment stabilization: offshore Japan. Sedimentology. 2011; 58 (5):1138 - 1154.
19. Hasdemir S, Tug˘rul A, Yilmaz M. Evaluation of alkali reactivity of natural sands. Construction and Building Materials. 2012; 29: 378–385.
20. Qadri SB, Rath BB, Gorzkowski EP, Wollmershauser JA, Feng CR. Nanostructured silicon nitride from wheat and rice husks. Journal of Applied Physics. 2016; 119 (13): 1-7.
21. Kemp EJ, Roseburrough RR, Elliott EA, Krause JW. Spatial variability of sediment amorphous silica and its reactivity in a northern Gulf of Mexico estuary and coastal zone. Gulf and Caribbean Research. 2021; 32 (1): 1-8.
22. Drozdov AL, Zemnukhova LA, Panasenko A, Polyakova N, Slobodyuk A, Ustinov A, Didenko N, Tyurin S. Silicon compounds in sponges. Applied sciences. 2021; 11 (14): 6587-6609.
23. Lin H, Chen T, Yan B, Huang Z, Zhou Y, Huang J, Xiao X. A functionalized silicate adsorbent and exploration of its adsorption mechanism. Molecules. 2020; 25 (8): 1820-1833.
24. Luthfiah A, Deawati Y, Firdaus ML, Rahayu I, Eddy DR. Silica from natural sources: A review on the extraction and potential application as a supporting photocatalytic material for antibacterial activity. Science and Technology Indonesia. 2021; 6 (3): 144-155.
25. Sun J, Xu Z, Li W, Shen X. Effect of nano- SiO2 on the early hydration of alite-sulphoaluminate cement. Nanomaterials. 2017; 7 (5): 102-116.
26. Ismail A, Saputri N, Dwiatmoko AA, Susanto BH, Nasikin M. A facile approach to synthesis of silica nanoparticles from silica sand and their application as superhydrophobic material. Journal of Asian Ceramic Societies. 2021; 9 (2): 665–672.
27. Zhang X, Lu M, Idrus MAM, Crombie C, Jegatheesan V. Performance of precipitation and electrocoagulation as pretreatment of silica removal in brackish water and seawater. Process Safety and Environmental Protection. 2019; 126: 18-24.
28. Zulfiqar U, Subhani T, Husain SW. Synthesis of silica nanoparticles from sodium silicate under alkaline conditions. Journal of Sol-Gel Science and Technology. 2016; 77 (3):753-758.
29. Tahir R, Wahab AW, Nafie NL, Raya I. Synthesis of mesoporous silica SBA-15 through surfactant set-up and hydrothermal process. Rasayan Journal of Chemistry. 2019; 12 (3): 1117 - 1126.
30. Ishmah SN, Permana M, Firdaus ML, Eddy DR. Extraction of silica from Bengkulu beach sand using alkali fusion method. PENDIPA Journal of Science Education. 2020; 4 (2): 1 - 5.
31. Olando G, Olaka L, Okinda PO, Abuom P. Heavy metals in surface sediments of Lake Naivasha, Kenya: spatial distribution, source identification and ecological risk assessment. SN Applied Sciences. 2020; 2 (2): 279-292.
32. Andriayani, Muis Y, Nasution DY. Chemical reduction of silica into silicon from extracted quartz sand using sodium hydroxide and hydrochloric acid solutions. AIP Conference Proceedings. 2021; 2342 (1): 1-6.
33. Mustoe GE. Late tertiary petrified wood from Nevada, USA: evidence of multiple silicification pathways. Geosciences. 2015; 5 (4): 286-309.
34. Boualem A, Leontie L, Lopera SAG, Hamzaoui S. Synthesis and characterization of mesoporous silica from Algerian river sand for solar grade silicon: Effect of alkaline concentration on the porosity and purity of silica powder. Silicon. 2021; 14 (10): 5231-5240.
35. Biswas RK, Khan P, Mukherjee S, Mukhopadhyay AK, Ghosh J, Muraleedharan K. Study of short range structure of amorphous silica from PDF using Ag radiation in laboratory XRD system, RAMAN and NEXAFS. Journal of Non-Crystalline Solids. 2018; 488: 1–9.
36. Nayak P, Datta A. Synthesis of SiO2-nanoparticles from rice husk ash and its comparison with commercial amorphous silica through material characterization. Silicon. 2020; 13 (4): 1209-1214.
37. El-Didamony H, El-Fadaly E, Amer A, Abazeed I. Synthesis and characterization of low cost nanosilica from sodium silicate solution and their applications in ceramic engobes. Journal of the Spanish Ceramic and Glass Society. 2020; 59 (1): 31-43.
38. Mourhly A, Khachani M, Hamidi AE, Kacimi M, Halim M, Arsalane S. The synthesis and characterization of low-cost mesoporous silica SiO2 from local pumice rock. Nanomaterials and Nanotechnology. 2015; 5: 35-42.
39. Thahir R, Wahab AW, Nafie NL, Raya I. Synthesis of mesoporous silica SBA-15 through surfactant set-up and hydrothermal process. Rasayan Journal of Chemistry. 2019; 12 (3): 1117-1126.

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