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L. Bazzi, P. Hesemann, S. Laassiri, S. El Hankari. Alternative approaches for the synthesis of nano silica particles and their hybrid composites: synthesis, properties, and applications. *International Journal of Environmental Science and Technology*, 2023, 20 (10), pp.11575-11614. 10.1007/s13762-023-04845-5 . hal-04090016

HAL Id: hal-04090016

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Alternative approaches for the synthesis of nano silica particles and their hybrid composites:
Synthesis, properties, and application

Loubna BAZZI^a, Peter Hesemann^b, Said LAASSIRI^a and Samir EL HANKARI^{*a}

^a Mohammed VI Polytechnic University (UM6P), Morocco, Chemical and Biochemical Sciences Green Process Engineering (CBS).

^b ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France.

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Abstract

Developing more sustainable and economical viable strategies to access high value-added products from alternative and less costly sources is currently a challenge in the chemical industry. Silica is among the most used chemicals and is widely used in many industrial applications such as toothpastes as a cleansing agent, rubber industry as a reinforcing agent, as an anticaking agent in cosmetics, in salts and so on. This review summarizes alternative approaches for the synthesis of porous and hybrid silica as well as silica composites. So far, these phases are mostly synthesized from molecular silane precursors via hydrolytic sol-gel chemistry or via combustion processes of chlorosilanes, and therefore indirectly from quartz sand. However, quartz sand is a non-renewable resource, and the actual sand shortage becomes more and more problematic for various processes in the chemical industry. Indeed, quartz sand is the world's second most consumed raw material after water and its availability has high impact on numerous production processes, e.g. in healthcare or in electronics. In the actual context of sand shortage, the elaboration of silica-based materials from alternative sources attracts more and more interest. This review article describes new ways to access silica-based materials from alternative sources such as bio sourced and renewable feedstocks, waste electrical & electronic equipment (WEEE) or from fluorosilicic acid (FSA), a by-product of the phosphate industry. We show that silica must be considered as a valuable raw material, and that alternative production processes from renewable resources as well as cyclic lifetime assessment and valuable recycling strategies of these materials should be considered in view of the elaboration of more sustainable and cyclic production processes. A comparative study between different sources will be given regarding the silica extraction methods, the types of silica, stability, and performance of the as-obtained nanosilica materials. Perspectives regarding the potential large-scale production of nanosilica and their hybrid or composite materials from these alternative sources will be also discussed.

1. Introduction

Silicon (Si) is the second most abundant element in the earth's crust. Silicon is present in natural silicates in various modifications such as tridymite, cristobalite or quartz (del Pozo et al. 2011). It is also the major component in non-natural silicates that attracted considerable attention in the last few years. The chemistry of silicon allows smart processing procedures and the formation of silica based materials with ordered architectures on the mesoscopic level, such as the well-known mesoporous silicas MCM-41 (Sayari and Yang 2000), MCM-48 (Kaneda et al. 2002; Shao et al. 2005), SBA-15 (Wu et al. 2006). These types of silica materials are

recognized as extremely important nano-porous inorganic materials that have been extensively studied for a wide range of applications such as adsorption (Bhagiyalakshmi et al. 2010; Yantasee et al. 2010), drug delivery (Singh et al. 2014), fillers (Frost and Meyerhoff 2004; Boonmee and Jarukumjorn 2020), catalysis (Bahia et al. 2020; Russell et al. 2020), sensing (Baumgartner et al. 2020; Qi et al. 2020), water purification (Zhu et al. 2019; Kalash et al. 2020), and electronic applications (Jain et al. 2001; Laskowski et al. 2019). Silica gels, silicon chips, silica-carbon composites and functionalized silica hybrids organic inorganic materials have been also introduced to target specific applications (Singh et al. 2014; Liou and Jheng 2018; Shusuke Sato et al. 2020). Silica is also the major component in ceramics (Zhou et al. 2009), zeolites (Jiang et al. 2020) etc, mostly in combination with other metal oxides such as alumina.

Overall, porous inorganic oxides such as silica are of great interest as low density and thermally stable microstructures, and as mechanically resistant encapsulation particles. Among these oxides, silica has an outstanding position due to its chemical and morphological polyvalence, allowing accessing a large panel of materials with defined textures, architectures, and morphologies (Mebert et al. 2017). However, the chemical synthesis of silica materials is not only relatively expensive and eco-hazardous, but also requires strict synthesis conditions (Shen 2017a). Generally, the most known silica precursors that are employed in the synthesis of structured mesoporous silica materials are alkoxysilanes such as tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS), and the synthesis of mesoporous silica phases usually follows soft templating approaches involving cationic or nonionic surfactants (Bhuiyan et al. 2013; Tsai et al. 2016). Sodium silicate has been also used for the synthesis of nano-silica gel which unfortunately has a negative impact on health (Gonçalves 2018). However, scientists and industries have investigated different approaches to find safer, cheaper, more abundant and sustainable silica sources to access porous silica phases. In this context, natural minerals containing silica, biomass or industrial waste and industrial by-products or electronic wastes have been identified as alternative sources to produce structured silica-based phases.

On the other hand, the industrial and agricultural solid waste management is becoming a growing challenge. The uncontrolled growth of population and the urbanization is leading to a complex waste management system (Hannan et al. 2020). These challenges are mainly associated with waste generation, inadequate waste collection, transport, disposal and treatment processes (Das et al. 2019), representing a serious threat for both society and environment. Hence, the valorisation of waste can not only reduce the problem of waste production, but also

make waste an alternative resource to replace raw materials in the main streams of production (Boukayouht et al. 2023).

An example of this waste management is the harnessing of solid or liquid by-products of agricultural or industrial industries such as rice husk, electronic waste or fluorosilicic acid (FSA) for the fabrication of nanostructured silica materials and hybrid organic–inorganic silica based composite materials (Rajarao et al. 2014; Liu et al. 2017; Wang et al. 2017). Nano-porous structured silica materials and composites represent a special type of materials that has been employed in several applications over a half century ago (Jeelani et al. 2020), but the use of mineral silicas, industrial or agricultural waste as alternative routes for the fabrication of these materials is still in its infancy (Krysztafkiewicz et al. 1995).

Several publications already reported the extraction of silica from mineral rocks, agricultural, electronic wastes, and industrial by-products for the fabrication of silica-based materials (Shen 2017a, b; Hossain et al. 2018, 2022; Abdul Razak et al. 2022; Yadav et al. 2022; Gebretatios et al. 2023). However, very recently, the use of different biomass, electronic and industrial by-products silica resources for the synthesis of mesoporous silica such as MCM and SBA type materials has been reported (Arumugam and Ponnusami 2013a; Yan et al. 2016; Kamari and Ghorbani 2020; Costa and Paranhos 2020; Costa et al. 2021).

The previously published reviews related to nanosilica particles from waste had discussed this topic with different approaches. While some of these works chose to focus on one type of waste i.e., agro-waste (Yadav et al. 2022), other recent reviews concentrated on only one or two types of agricultural and industrial waste-derived mesoporous (Abdul Razak et al. 2022; Hossain et al. 2022). Regarding the type of silica-based materials, some reviews focused on specific silica families such as M41S and SBA-n (Costa and Paranhos 2020; Costa et al. 2021). This review treats all types of waste and fabricated silica materials, with an extension to almost all types of waste including mineral waste, agricultural, electronic and industrial waste and different silica based materials displaying particular textures, architectures and morphologies such as mesoporous silica, silica nanoparticles including gel together with much focus on the functionalization or the hybridization of silica with a second component such as carbon, yielding silica-based composites. We also discuss their synthesis after the extraction of silica, their properties and applications. Moreover, we discuss in detail the use of the industrial waste fluorosilicic acid as source for silica and dedicated a section for this interesting by-product of the phosphate industry.

Thus, as shown in Fig. 1, this article gives an overview over recent developments in the field of structured silica materials, nano-silica gel and hybrid silica-based composites from alternative sources: agricultural and industrial by-products, waste electrical & electronic equipment and others. We will summarise the last progress in the valorisation of different raw products and by-products. We discuss in detail the use of industrial by-products such as fluorosilicic acid that is a large-scale by-product of the phosphate industry. FSA is currently considered to be a basic alternative source of fluorine for the chemical industry and an interesting source for silica. Other sources such as fly ash which is generated during the combustion of coal for energy production and mentioning the electronic waste (E-waste) used in the synthesis of photonic waste, electrolytic slag, waste glass bottles, coal slag will also be discussed. Finally, a comparative overview will be established between different silica sources with respect to the extraction and fabrication procedures as well as the production costs. This review will provide new perspectives and opportunities in the field for potential scale-up fabrication of functional silica-based materials from alternative silica sources.

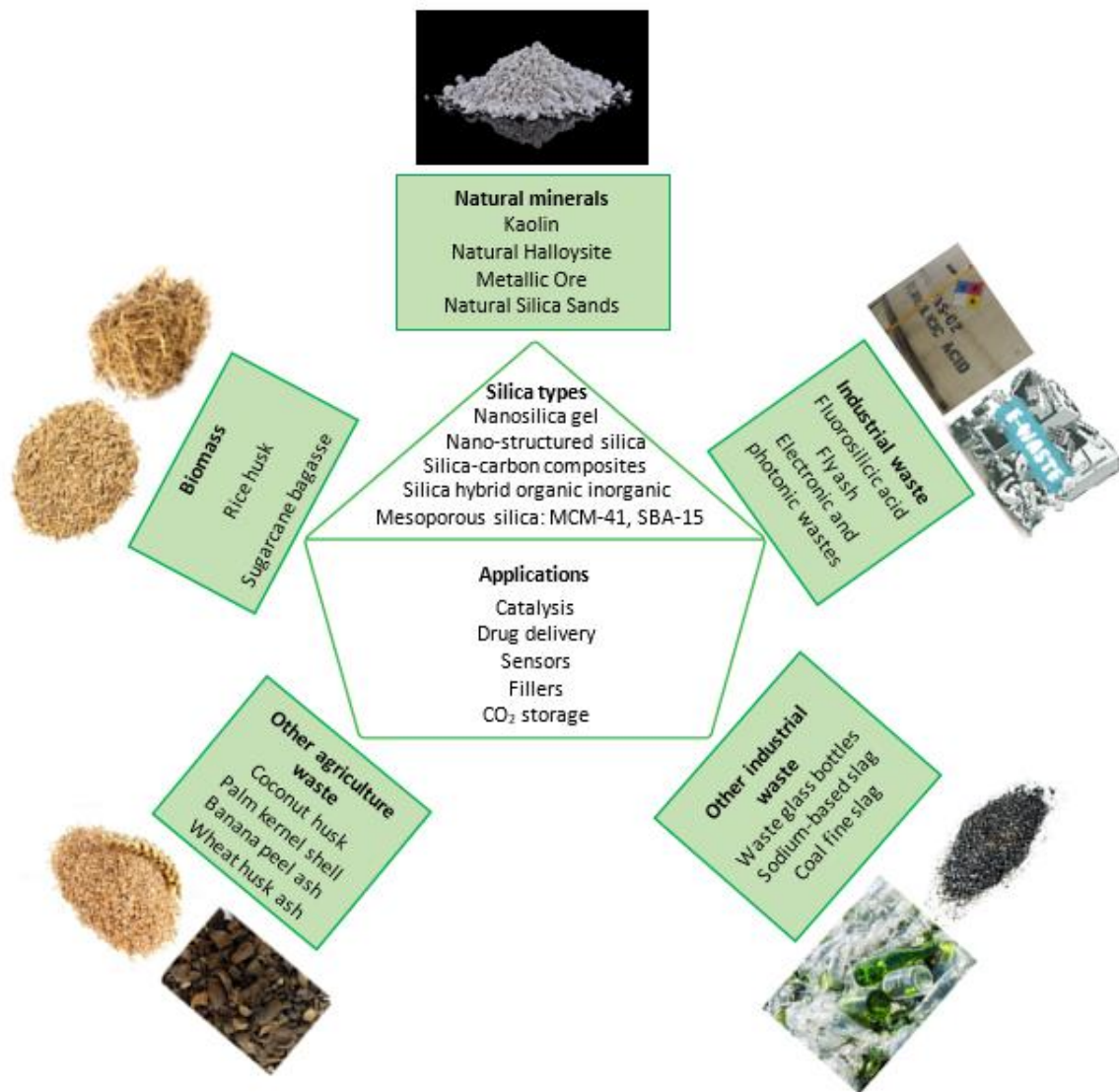


Fig. 1. A schematic diagram of different silica types from different natural and industrial wastes and their applications.

2. Silica minerals and natural rocks rich in silica

So far, the large scale production of nano-silica, nanostructured silica materials and their hybrid composites is limited due to the economic and environmental impacts of the commercial organosilicates (TEOS, MEOS...) (Meléndez-Ortiz et al. 2012). Recently, many attempts have been realized for their synthesis by replacing these toxic precursors with inorganic silicate minerals or mineral wastes as cheap silicon sources (Gaydhankar et al. 2006; Okada et al. 2007; Taralkar et al. 2007; Kimura and Kuroda 2009; Kim et al. 2011; Yu et al. 2012).

Clay minerals belong to the family of phyllosilicate or sheet silicate minerals, which are characterized by layered structures composed of polymeric sheets of SiO_4 tetrahedra linked into sheets of $(\text{Al, Mg, Fe})(\text{O,OH})_6$ octahedra. The high silica content of natural clay minerals

together with their low cost, abundancy, and environmental friendliness makes them a good alternative and sustainable sources for the fabrication of nanostructured silica materials and their hybrid composites via sol-gel method. With high silicon content, uniform nano-sized architectures, low price, and natural abundance, clay mineral recently has been regarded as one of the most attractive precursors for the synthesis of nanostructured silica via magnesiothermic reduction which is occurring upon the exposure of SiO_2 to Mg vapor, leading to its reduction by Mg and Mg_2Si , producing Si and MgO (Tan et al. 2021). As the metal ions (especially Al) in clay minerals may easily react with other oxides to form high temperature by-products (e.g., spinel) during the heavily exothermic reaction, previous studies always first transformed clay minerals to amorphous SiO_2 by strong acid etching (Ismadji et al. 2015; Chen et al. 2018).

In 1990, kanemite ($\text{NaHSi}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$) was transformed into mesoporous materials through a pillaring method upon calcination (Yanagisawa et al. 1990). An acidic leaching of vermiculite with HCl was proposed for the synthesis of porous materials (Maqueda et al. 2007). Later, the grinding of kaolin (Du and Yang 2012) and attapulgite (Yang et al. 2010b) as a pre-treatment allowed the synthesis of Al-MCM-41. Grinding and calcination with K_2CO_3 were combined for the synthesis of Al-MCM-41 molecular sieve from K-feldspar (Miao et al. 2005). Calcination with NaOH was performed to synthesis Al-MCM-41 from bentonite (Yang et al. 2010a). Highly porous MCM-41 and SBA-15 were obtained from the conversion of coal fly ash after calcination with NaOH (Kumar et al. 2001). Microwave irradiation was also used for the preparation of highly stable mesoporous materials from bentonites after adding sodium silicate and aluminium chloride (Tang et al. 2008). Therefore, four pre-treatment methods, including acid-leaching, grinding, calcination and microwave irradiation, have been used for the transformation of silica minerals to mesoporous materials (Fig. 2). In the following, we will give more details on different strategies reported for the extraction of silica from inorganic minerals and their transformation into nano-silica and porous structured silica as well as their hybrid composites from various inorganic minerals, including kaolin, natural halloysite, metallic ore, natural silica sands, bentonite, natural clay, diatomite, natural equisetum ramosissimum, natural perlite, natural sediment, rectorite minera, volcanic minerals and sepiolite.

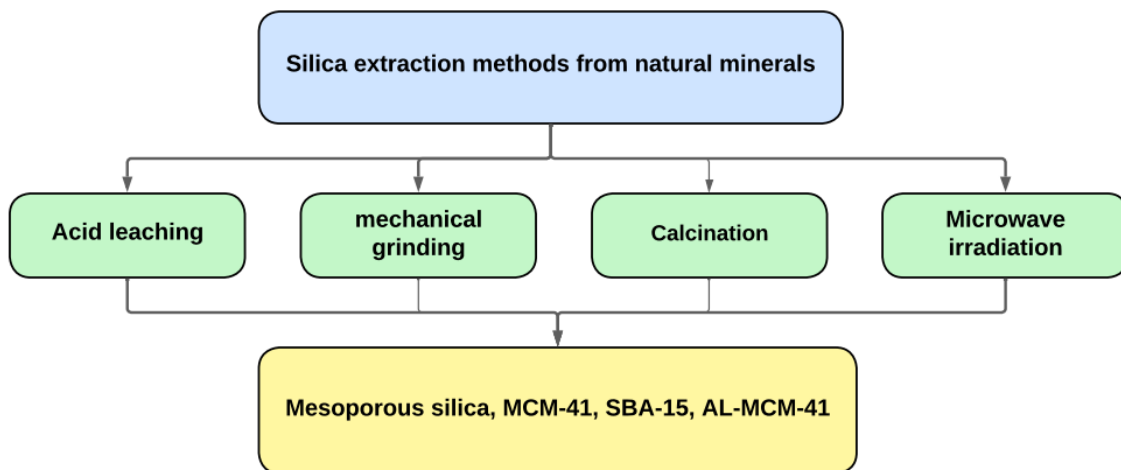


Fig. 2. Schematic illustration for different silica extraction methods from minerals and their subsequent transformation into porous silica-based materials.

Kaolin

Kaolin is a fine clay mineral with the chemical composition of $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, composed of two crystal layers: a silicon–oxygen based on SiO_4 tetrahedra and a second layer based on alumina octahedra. Kaolinite is the main ingredient of kaolin of chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (theoretically 39.8 % alumina + 46.3 % silica + 13.9 % impurities) (Ullah et al. 2014). The raw natural clay kaolin can be used for different purposes. For instance, a calcination pre-treatment allows the transformation of Kaolin into metakaolin. After leaching with hydrochloric acid and a second calcination step, mesoporous phases were formed by hydrothermal treatment of the resulting solid in the presence of a surfactant mixture consisting of the fluorocarbon surfactant FSO-100 and P123. This material was finally used for Fe/BiOCl loading. The composite showed excellent efficiency for degradation of 2-nitrophenol in a Fenton-like reaction (Zhao et al. 2015).

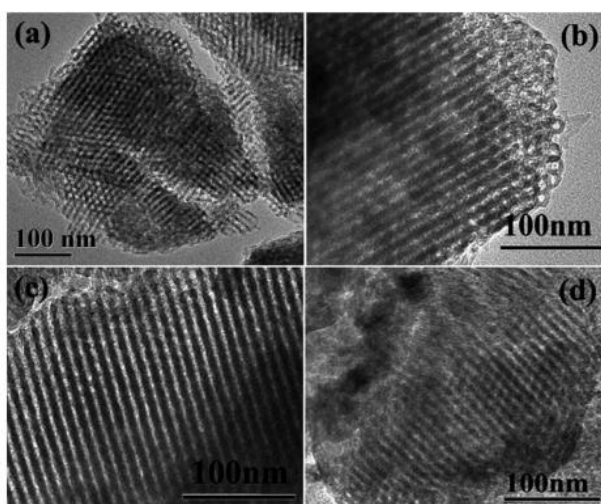


Fig. 3. TEM images of FCSBA-15 (a) and SBA-15 (b) and counterparts after hydrothermal treatment (c and d) (Zhao et al. 2015).

Metakaolin appears as a universal source for the formation of porous silica based phases (Kang et al. 2005; Madhusoodana et al. 2006; Wang et al. 2009; Slatni et al. 2020). As an example, mesoporous silica could be obtained via the addition of dissolved Pluronic L35, by aging at high temperature, drying and calcination. The resulting material show good efficiency for the removal of acid red dye in a real industrial textile effluent (Slatni et al. 2020). Finally, the addition of cetyltrimethylammonium bromide CTAB to the pre-treated metakaolin allowed the formation of a mesoporous Al-MCM-41 material by hydrothermal treatment under static conditions followed by calcination at 550 °C (Kang et al. 2005).

Finally, rare earth doped porous Ln-ZSM-5/MCM-41 composites were prepared under hydrothermal condition using kaolin as silica and alumina sources. For this purpose, a metakaolin dispersion was mixed with tetraethyl orthosilicate (Wang et al. 2009; Li et al. 2010) which, after adding CTAB, forms highly regular mesoporous Al-MCM-41 materials (Wang et al. 2009). The addition of tetrabutylammonium bromide and Ln = La, Ce species to this mixture and removal of the ammonium salt by calcination gave rise to the formation of zeolite@MCM-41 composites with encapsulated rare earth species Ln = La, Ce (Ln-ZSM-5/MCM-41, Ln = La, Ce) (Li et al. 2010).

In the context of developing more sustainable strategies for the formation of porous silica phases from kaolin, and in particular to avoid calcination steps, Du and Yang reported the formation of a highly porous Al-MCM-41 phases by grinding followed by hydrothermal treatment under basic conditions. The mesoporous and highly regular Al-MCM-41 material (Fig. 4) was obtained in the presence of CTAB, followed by calcination (Du and Yang 2012).

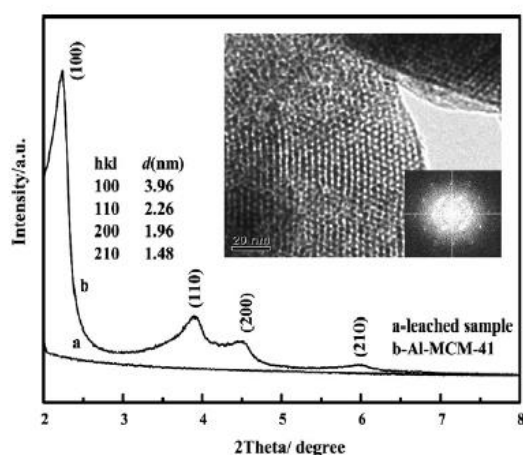


Fig. 4. SAXRD patterns and HRTEM image of the samples (inset: HRTEM image for Al-MCM-41) (Du and Yang 2012).

Kaolin clay can also directly be used for the preparation of amorphous mesoporous aluminosilicate, without prior treatment. For instance, Qoniah *et al.* reported the treatment of kaolin in NaOH solution without pre-calcination. A gradual addition of LUDOX colloidal silica was used as a seed (Qoniah et al. 2015). Thus, different treatments were employed for the transformation of Kaolin to porous structured silica materials by using either two steps, one step calcination or grinding followed by a leaching in an acidic medium. Direct leaching of kaolin in alkaline solution without any treatment was also employed.

Natural Halloysite

The mineral clay of halloysite which was described first as a mineral of the kaolin group (Li et al. 2017) with chemical composition and structure similar to those of kaolinite, dickite and nacrite (G. J. Churchman; R. M. Carr 1972; G. J. Churchman & R. M. Carr 1975; Yushan Liu, Haiming Nan, Qiang Cai 2012; Zengjiang Wei Chaoyang Wang Hao Liu Shengwen Zou Zhen Tong 2012). The ideal unit formula for halloysite is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ where $n = 0$ and 2. However, the chemical composition is subject to little variation with the common presence of impurities (Joussein et al. 2005). The main characteristics of Halloysite is its nanotube morphology. Halloysite can be used for pseudomorphic transformations to mesoporous silica based materials either directly after acidic treatment or after calcinations followed by acidic treatment (Amin 1996; Yang et al. 2007; Panda et al. 2010). The nanotube morphology was used as precursor for the synthesis of porous nanotube materials. For instance, Zhang reported the synthesis of silica nanotubes (SiNTs) by simple acid-leaching of natural halloysite nanotubes (HNT) (Zhang et al. 2012). Importantly, as shown in Fig. 5, short cylindrical hollow tubes of silica were obtained, displaying similar morphology like the original HNTs (Zhang et al. 2012). A pre-treatment of the halloysite clay via emulsion dispersion was applied before the acidic leaching.

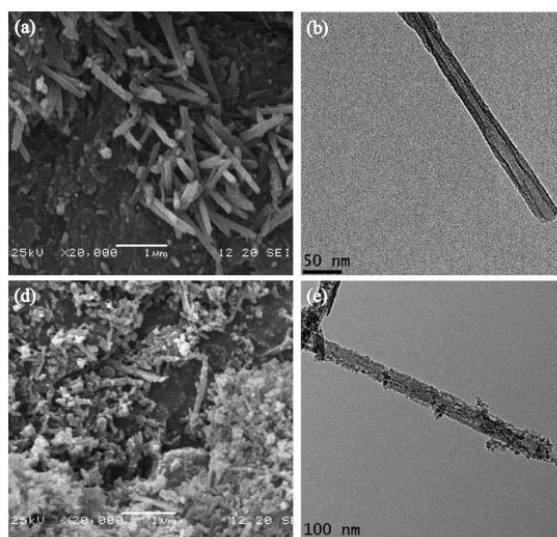


Fig. 5. (a, d) SEM, (b, e) TEM images and (c, f) EDAX spectra of HNTs (a–c) and SiNTs (d–f) samples (Zhang et al. 2012).

A hydrothermal treatment in the presence of CTAB allowed the synthesis of nanotubes with a tunable mesoporous silica inner shell with preserved outer shell after the acidic leaching as described in Fig. 6 and 7 and shown in Fig.8 (Fu et al. 2017).

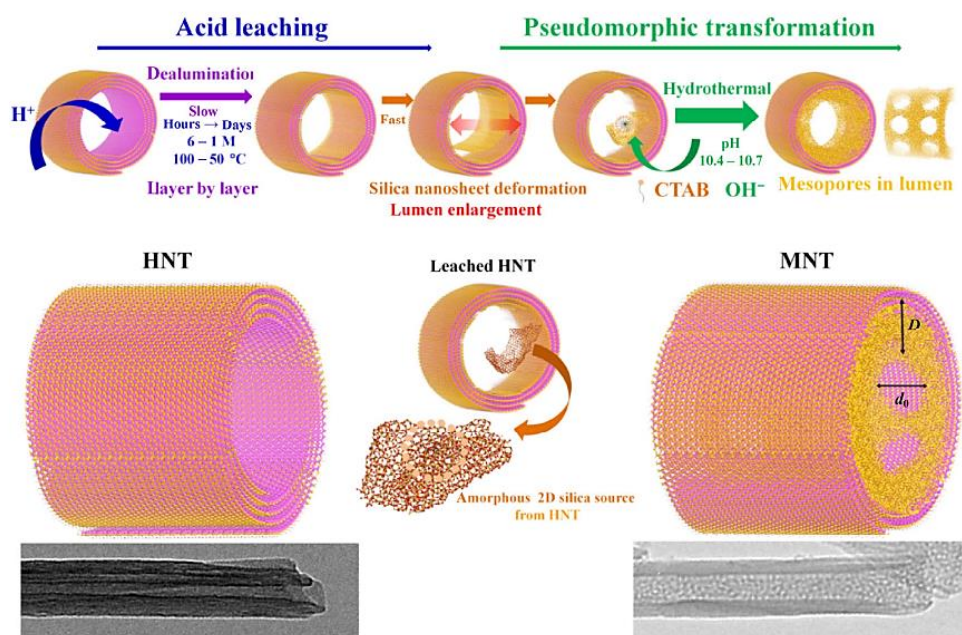


Fig. 6. Illustration of the synthesis strategy from HNT to MNT. The lumen enlargement of HNT after the dealumination process of acid leaching, the formation of the amorphous 2D silica source from the deformation of the 2D silica nanosheet, and the formation of the mesoporous nanotube structure are illustrated. The inner-shell thickness (D) of the nanotube wall and the mesopore size (d_0) were tuned by changing the acid-leaching and pseudomorphic-transformation conditions (Fu et al. 2017).

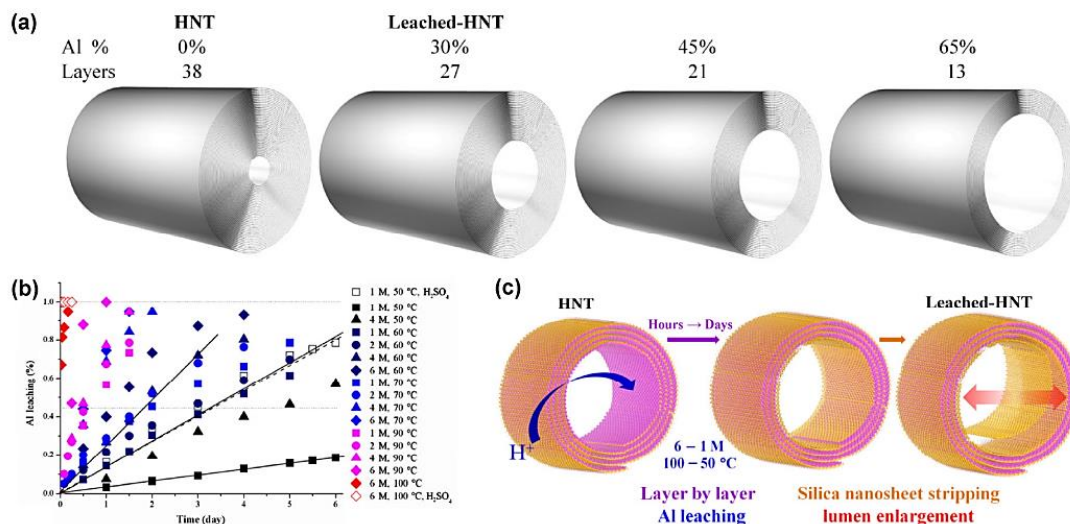


Fig. 7. The decrease of the number of layers and Al content in HNT after acid leaching. (a) Tubular structure of pristine HNT and leached HNT with different layers. The corresponding leached Al content and numbers of residual HNT layers are indicated. (b) Al leaching content of halloysites with respect to time in an aqueous suspension at different temperatures and acid concentrations. The aluminum concentration was normalized with respect to the maximum, and the estimated error of the concentration determination was $\pm 4\%$. The leaching content for 1 M acid at 50, 60, and 70 °C is fitted with a solid line. (c) Schematic of the acid-leaching process (Fu et al. 2017).

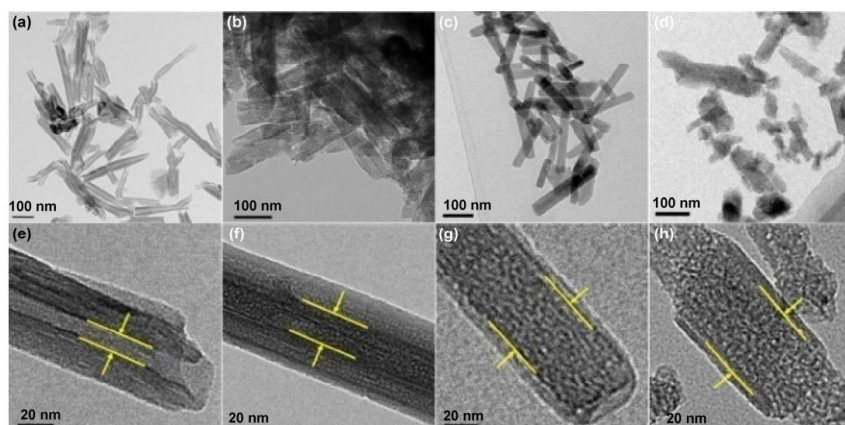


Fig. 8. TEM images of pristine HNTs and MNTs. (a)–(d) Low- and (e)–(h) high-magnification TEM images of (a) and (e) pristine HNTs, (b) and (f) MNTs-2h, (c) and (g) MNTs-4h, and (d) and (h) MNTs-6h (Fu et al. 2017).

Ordered mesoporous aluminosilicates were also prepared from natural halloysite following a basic or acidic leaching (Xie et al. 2014, 2015; Zhou et al. 2014). For instance, the treatment of calcined halloysite with NaOH forms an alkali-leached white powder, used in the presence of P123 for the preparation of mesoporous aluminosilicate molecular sieves, the mechanism is illustrated in Fig. 9 (Zhou et al. 2014).

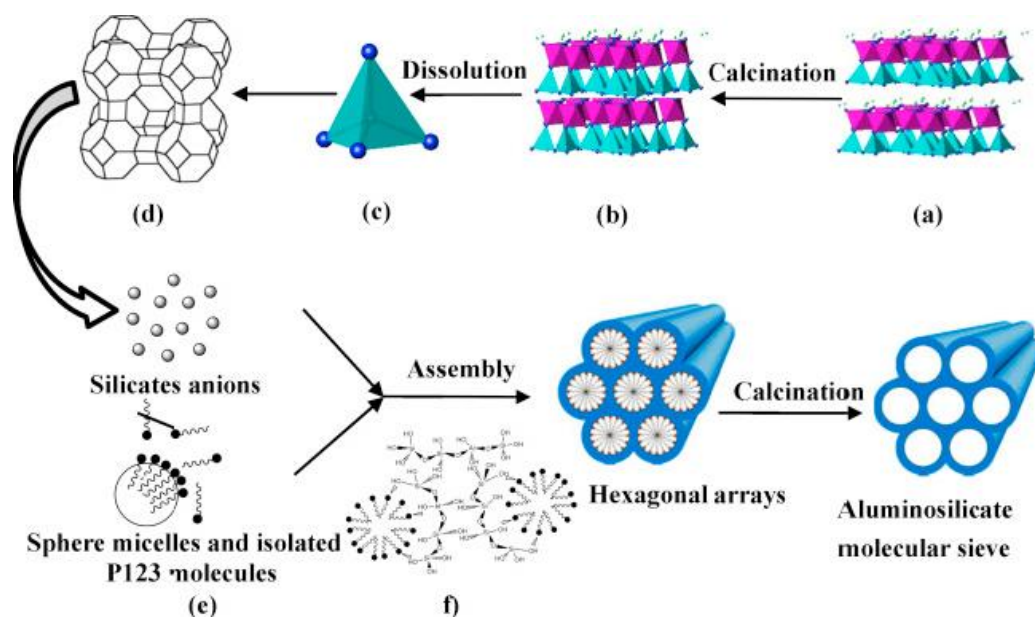


Fig. 9. Possible mechanism from natural halloysite to mesoporous aluminosilicate molecular sieve: (a) original halloysite; (b) calcined halloysite; (c) tetrahedrons unites;(d) acid-leached sample; (e) reactants; (f) assemble process for hydrothermal synthesis; (g) as-synthesized sample; (h) calcined aluminosilicate molecular sieve sample (Zhou et al. 2014).

Recently, highly ordered Ti-containing Al-SBA-15 (Pham et al. 2020a) and Ag@AgBr/Al-SBA-15 (Pham et al. 2020b) mesostructured phases were prepared from natural halloysite. While in the first example, the Ti precursor titanium tetraisopropoxide was added to the leached halloysite dispersion (Pham et al. 2020a), the immobilization of Ag was achieved via chemical vapour deposition method using a previously synthesized SBA-15 type material in the second work (Pham et al. 2020b). Both mesoporous structured silica composites were tested in the photocatalytic oxidative desulfurization of dibenzothiophene oxidation. The leached natural halloysite can be used directly or after calcination and is not only used as silica source for the preparation of porous nanostructured silica phases, but also to achieve mesoporous silica materials with hollow tube morphology.

Metallic Ore

Metallic ores and derived metallic ore tailings produced as by-products from the mineral extraction process. Metallic ores can be used a source of silicon, aluminium, and other metallic species since they contain these components in relatively high but variable concentrations. However, different processes can be applied for the extraction of silica species from these metallic ores and subsequent transformation to porous nanostructured silica materials. For instance, sodium silicate extracted from iron ore tailings can be used as a source of silica for the fabrication of ordered mesoporous silica (Yu et al. 2009; Yang et al. 2014). In fact, pre-treatment processes involving specifically acid leaching is necessary to eliminate in the first

step Fe-containing species, yielding an insoluble residue that contains more than 80 % of SiO₂ that can finally be used as a Si source for the synthesis of MCM-41 (Yang et al. 2014) (Yang et al. 2015).

Prior to the alkaline hydrothermal reaction of this silica residue to form sodium silica, an activation at high temperature for more than 1000 K was applied to get a better dissolution of SiO₂. Finally, the sodium silicate solution was slowly added to the CTAB solution to form a mesoporous MCM-41 material either under hydrothermal conditions in alkaline (Yang et al. 2014) or acidic medium (Yang et al. 2015), followed by removal the organic surfactants via calcination (Yang et al. 2014). The obtained MCM-41 materials were tested for methylene blue (MB) removal from water (Yang et al. 2014). It is important to note that parameters such as pH, molar ratio of CTAB to SiO₂, the aging time and calcination temperature affect the synthesis of MCM-41 (Yang et al. 2015).

A non-hydrothermal gelation method for the synthesis of mesoporous MCM-41 was developed by Ortiz *et al.* described in Fig. 10 (Meléndez-Ortiz et al. 2012). The formation of the material involved much softer reaction conditions, in particular room temperature and shorter reaction time, TEM images are shown in Fig.11. Compared to the hydrothermal method, the mesoporous silica formed under these conditions possess higher specific surface areas (Lu et al. 2020).

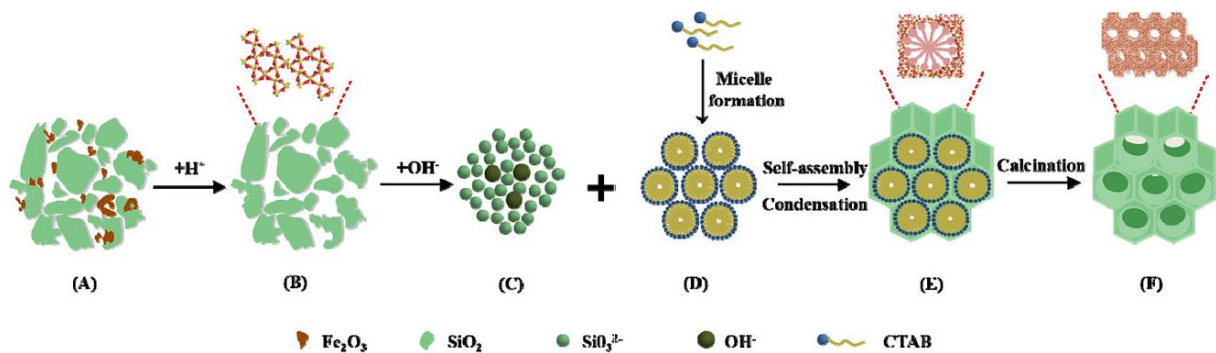


Fig. 10. Proposed mechanism from iron tailings to mesoporous silica materials: (A) iron tailings, (B) acid -insoluble residue (mainly quartz), (C) sodium silicate solution, (D) CTAB, (E) as -synthesized, (F) mesoporous silica materials (Lu et al. 2020).

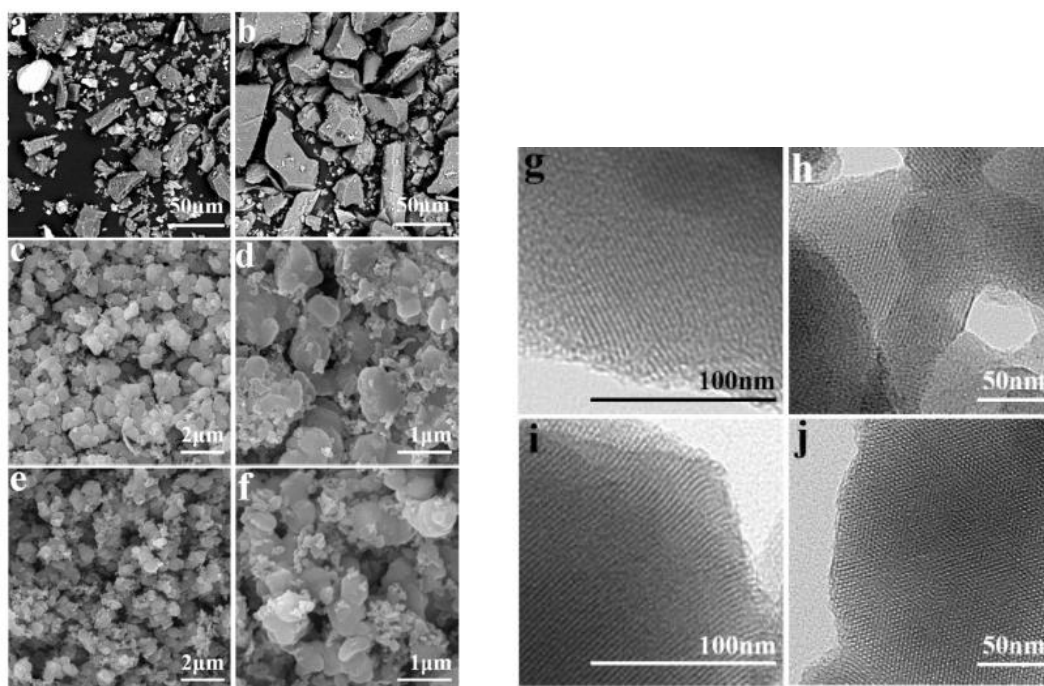


Fig. 11. SEM images of (a) iron tailings, (b) acid -insoluble residue, (c, d) as -synthesized and (e, f) mesoporous silica materials. TEM images of (g, h) as -synthesized and (i, j) mesoporous silica materials (Lu et al. 2020).

The filtrate from the acid leaching process was used as the iron source for the synthesis of Fe-doped MCM-41 (Fe/MCM-41) using the impregnation method, without adding any other Fe agents (Deng et al. 2020). The new Fe/MCM-41 composite was successfully tested in photocatalytic degradation of MB dye in aqueous media (Deng et al. 2020). Mn^{2+} promoted the structure transformation of Iron ore tailing into functional value-added mesoporous manganese silicate (MS) composites containing reactive Mn-OH groups by the assistance of sodium silicate (Fig. 12). The new composite was used to extract MB molecules from the mixed cationic dye solutions (Bai et al. 2020).

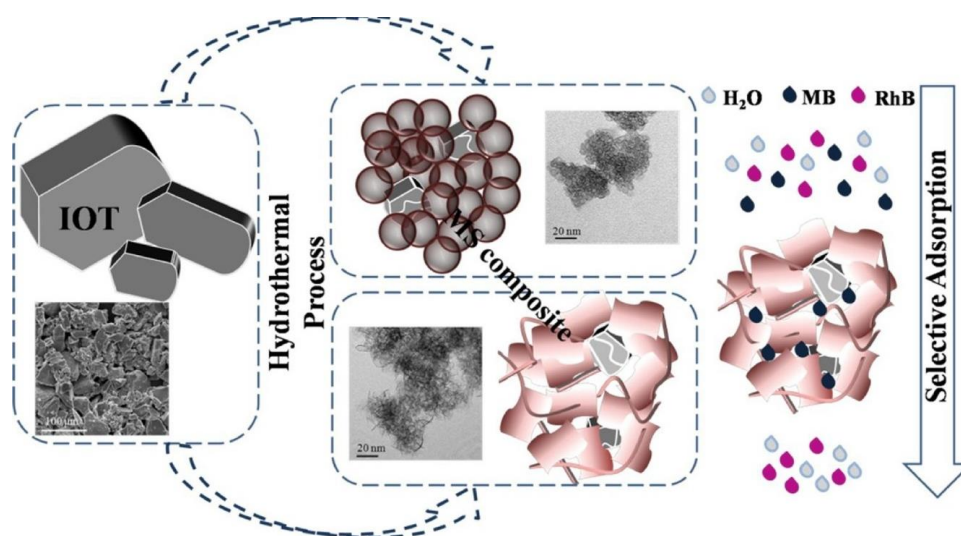


Fig. 12. Illustration of the synthesis of mesoporous manganese silicate composites and their application of the extraction of methylene blue (Bai et al. 2020).

The copper ore tailing was also used as a source of silica for the synthesis of MCM-41. In this case, an alkaline molten-salt method at 500 °C was applied to extract Na_2SiO_3 , which forms a gel after addition to the CTAB solution. Then the gel was heated under hydrothermal conditions to yield mesoporous silica MCM-41 (Fu et al. 2015). While the conversion of hematite to NaFeO_2 has been inhibited, the quartz and orthoclase are decomposed to produce soluble Na_2SiO_3 when low reaction temperature in the molten salt was used (Fu et al. 2015). Similarly, iron ore tailing was recycled into mesoporous silica by an alkali fusion treatment and acid leaching as described in Fig. 13 (Han et al. 2021). This strategy is temperature dependent as the quartz contained in the iron ore tailing is considered a stable structure. The formed mesoporous silica was further tested for MB adsorption (192 mg g^{-1}).

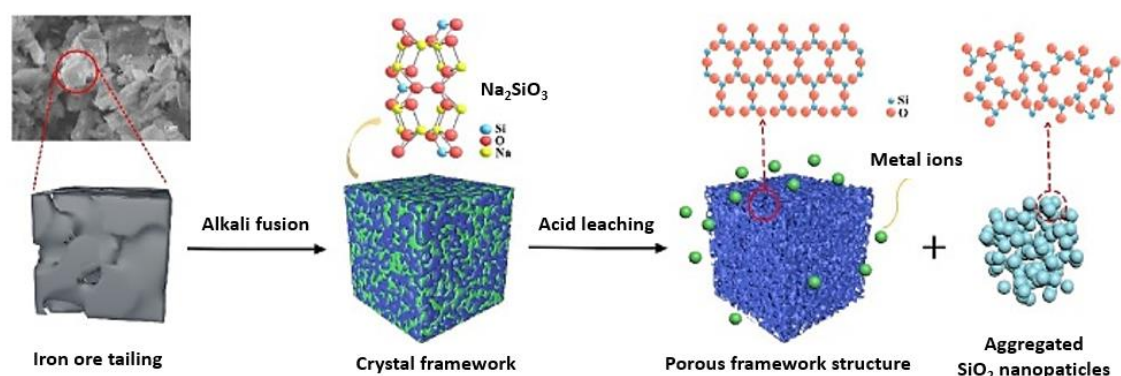


Fig. 13. Schematic diagram of the formation process of mesoporous silica from iron ore tailings (Han et al. 2021).

In summary, calcination of metallic ore tailings facilitates the leaching of silica from the inorganic residue after an alkaline treatment to form Na_2SiO_3 that can subsequently be used for the synthesis of mesoporous structured silica. The leached metallic solution can be used as a source of metal to insert another metallic species within the mesoporous material.

Natural Silica Sands

Silica sand is also crystallographically named as quartz sand. It can be produced by crushing quartz stones or taken directly from sand deposits close to water or from natural weathered desert quarries. For example, the natural silica sands used in silica glass industry contain more than 95 % of silica components, which can be an excellent and cheap silica source for the synthesis of nanoporous silica materials. For instance, white sandstone was used as silica precursor for the synthesis of silica gel nanoparticles using microwave irradiation. A sodium silica solution was first prepared by refluxing the white sandstone in alkaline solution overnight

that jellified upon acidification. The pH and the density of the mixture allow controlling the formation of sodium silica used in the preparation of silica gel. It was also demonstrated that the dissolved sands can produce a gel with lower surface area and larger average pore diameter than those obtained using commercial sodium silicate (Zaki et al. 2012).

The basic hydrothermal treatment of different sands including waste quartz sand (Hong et al. 2014; Febriana et al. 2020), crushed quartz stones, desert stone and the sea bed deposit stone (Sheng et al. 2018) with a NaOH solution allowed the extraction of silicon species for the synthesis of ordered mesoporous silica via the sol-gel method as illustrated in Fig. 14. More importantly, the surface area of the material derived from sand was higher than those originated from other silica sources such as fly ash, packaging resin waste, and sepiolite (Hong et al. 2014; Febriana et al. 2020). Moreover, while the hydrothermal treatment of different sands showed the same trends regarding the dissolution in NaOH solutions, the particle size of the sands controls dominantly their dissolution behaviour. However, all the dissolved silica can be employed in the preparation of mesoporous and microporous silicas. The best fixed-bed adsorption performance toward methylene blue was observed with silicas originated from the desert sands (Sheng et al. 2018). Moreover, mesoporous silica generated from natural sand can be used as catalyst for the production of biofuel. The catalysts are synthesized by a CTAB template method and then doped with Mo via a wet impregnation method (Alisha et al. 2022).

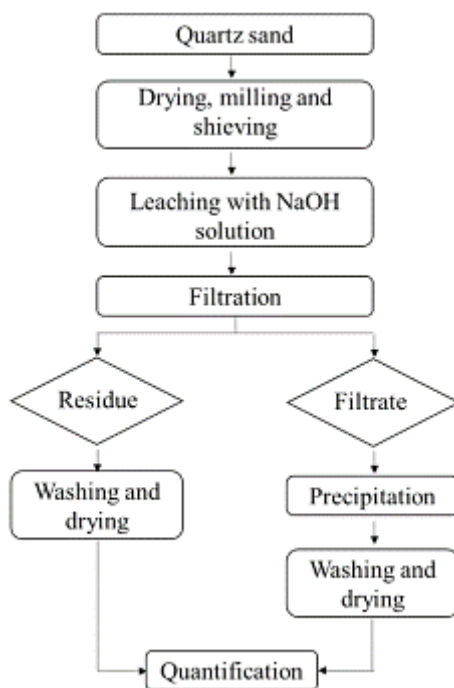


Fig. 14. Experimental chart (Febriana et al. 2020).

Many other natural minerals such as Bentonite (Torkashvand and Bagheri-Mohagheghi 2020), natural clay (Feng Zhang, Chunyan Sun, Shengfang Li, Lin Yang 2015), diatomite (Yu et al. 2014), natural Equisetum ramosissimum (Liu and Kuok 2018), natural perlite (Chen et al. 2019a), natural sediment (Boldrini et al. 2019), rectorite mineral (Chen et al. 2019b) and volcanic minerals (Adjdir et al. 2009; Guzel Kaya et al. 2019) sepiolite (Jin et al. 2012) have been used for the pseudomorphic transformation to structured mesoporous silica and silica composites as well as silica xerogels through various controlled sol-gel processes.

The mineral rock wastes and natural silica have been used extensively as a source of silica in the fabrication of various silica structured materials to target various applications. Distinct strategies have been applied for the extraction of silica elements and subsequently used for the fabrication of porous and structured silica materials after adding a structuration agent. Researchers attempted to explore new mild alternative to replace the pre-calcination step by direct leaching or applying another force to disperse the rock such as grinding. In this area, only very few examples have been reported which opens more perspective to researchers for the use of this methodology for the fabrication of structured silica materials and their composites.

3. Agricultural waste and biomass

Agricultural activities generate a large number of wastes and by-products. Generally, the burning of biomass waste is the solution used to limit the quantity of this residue. However, this method results in the pollution of air, soil and water, having a negative impact on the environment (Sarkar et al. 2021). Thus, researches showed an increased interest in the production of value-added materials from the biomass waste such as biochar (Tripathi et al. 2016), biofuels (Cho et al. 2020), organic fertilizers (Chew et al. 2019), graphene quantum dots (Abbas et al. 2018), etc. Silica is one of the main materials produced from agricultural waste as it is rich with SiO₂ content. Different biomass wastes can be used as silica precursors varying from rice husk, sugarcane bagasse, wheat straw, bamboo leaf, palm kernel shell, to corn cobs, etc (Surayah Osman and Sapawe 2019; Zamani et al. 2019; Singh et al. 2020; Sarkar et al. 2021). In this work, the synthesis of silica nanomaterials and their composites will be discussed in detail, mainly using rice husk and sugarcane bagasse as starting materials.

3.1. Rice husk

Silica-rich rice husk (RH) is an abundant and sustainable agricultural waste that have a relatively high content of inorganic compounds, representing approximately 20 % of the dry weight of the husk. Silica represents 94% of the total while the remaining 6 % are K₂O, CaO,

MgO, Al₂O₃, and P₂O₅ (Carmona et al. 2013). Silica can therefore be obtained as sodium silica or other silica based materials depending on the used process, either under combustion or chemical/hydrothermal treatment as summarized in Fig. 14 (Ding et al. 2005). Burning RH results mainly in the formation of various rice husk ash (RHA) containing 85-95 % of silica which can be extracted efficiently to yield amorphous or crystalline silica depending on the thermal treatment (Kumar et al. 2016). Otherwise, solvent extraction method can be also applied to extract sodium silica from RH (Adam et al. 2012). In general, the form of silica depends on the experimental conditions and the temperature which influence the properties and structure of the RH-derived silica (Shen 2017b).

RHA has been widely used in the manufacturing of various nano-silicas and their composites, zeolites, ceramics, cement and insulator material, etc. (Shen 2017a) (Soltani et al. 2015). The valorisation of RH and RHA attracted huge scientific interest (Kumar et al. 2016). However, approaches focusing on the elaboration of porous and structured silica and their hybrid composites from RHA remain scarce. Moreover, this chapter will give an update on the recent progresses in the synthesis of RH-derived silica materials produced from RH that have marked the field, with the focus on different types of nanoporous silica materials obtained from this biomass along with silica functionalization and their applications.

The first work explored partially the valorisation of rice husk ash in the economic cycle of agricultural waste for the fabrication of value-added silica materials. It reports different chemical and thermal procedures for the extraction of amorphous SiO₂ from RHA such as alkaline extraction followed by acid precipitation and thermal degradation method (Ding et al. 2005). Fig.15 resumes the silica extraction methods from rice husk and different types of silica prepared.

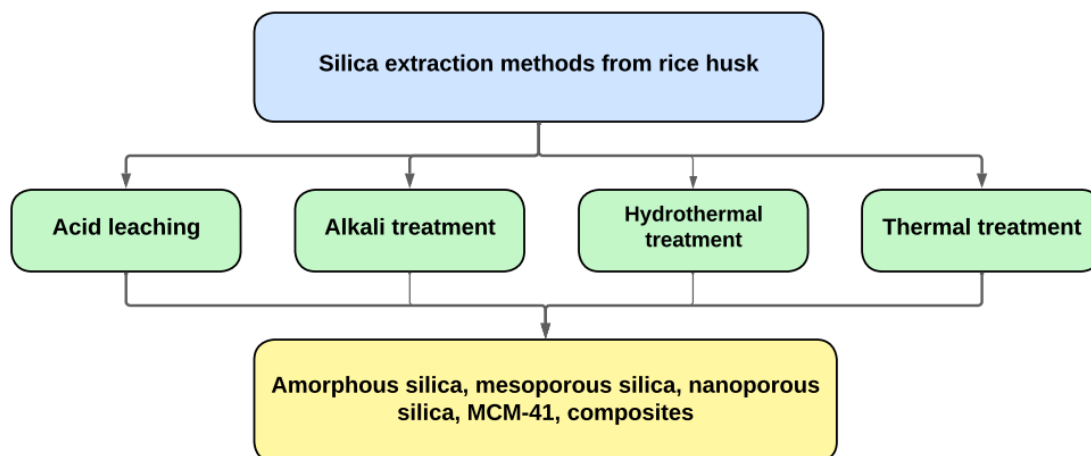
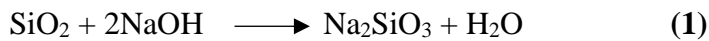


Fig. 15. Different methods for the extraction of silica species and their use in the fabrication of different silica from RH.

For example, an acidic treatment can be applied to dissolve the ash and reduce the metallic impurities to produce sodium silicate used as a silica precursor after adding suitable amount of mineral acid. In a whole, two basic reactions can be applied to produce amorphous SiO₂ as shown by the two following reactions:



Other reviews spotlighted the use of RH in the synthesis of silica derived nanomaterials for batteries (Shen 2017a), catalysis (Permatasari et al. 2016), and other sustainable applications (Shen 2017b) as well as the utilisation of RHA as an alternative source of silica in ceramics (Hossain et al. 2018).

It is obvious that researchers are getting interested in the synthesis of different form of silica from RH and RHA. Different types of silica materials were synthesized from rice husk, such as amorphous silica (Askaruly et al. 2020), nanosilica (Soemphol et al. 2020) (Carmona et al. 2013), porous and mesoporous silica (Chen et al. 2013), and hierarchical porous silica monoliths (Bahrami et al. 2017). Some of them have been processed with other materials to fit specific requirements through the fabrication of silica composites from RHA to get new properties that cannot be achieved from bare silica with a view of adding new functions to these materials. For example, photoluminescent carbon quantum dots grafted silica nanoparticles were synthesized directly from RH (Wang et al. 2017), designed with ease of surface modification, high water dispersibility, and biocompatibility of silica particles. They were synthesized by a hydrothermal treatment, followed by an acid treatment and ultrasonication (Wang et al. 2017). The same process was employed for the synthesis of amino-functionalized RH-silica-carbon nanoparticles (RH-silica-C NPs) by adding urea to the oxidized RHA before the hydrothermal reaction (Wang et al. 2017). The RH-silica-C NPs represent a new generation of silica-based photoluminescent nanomaterials that can be used in biosensors, bio-probes, diagnosis and therapy. Thus, their toxicity and biocompatibility were investigated by co-culturing them with HeLa cell suspension. Fig. 16 depicts the cell viability of HeLa cells after treatment with RH-silica-C NPs at various concentrations for 24 or 48 h (Wang et al. 2017). The tests showed that the introduction of RH-silica-C NPs caused no damage to the cells, indicating their good biocompatibility, making them promising luminescent agents for biosensors.

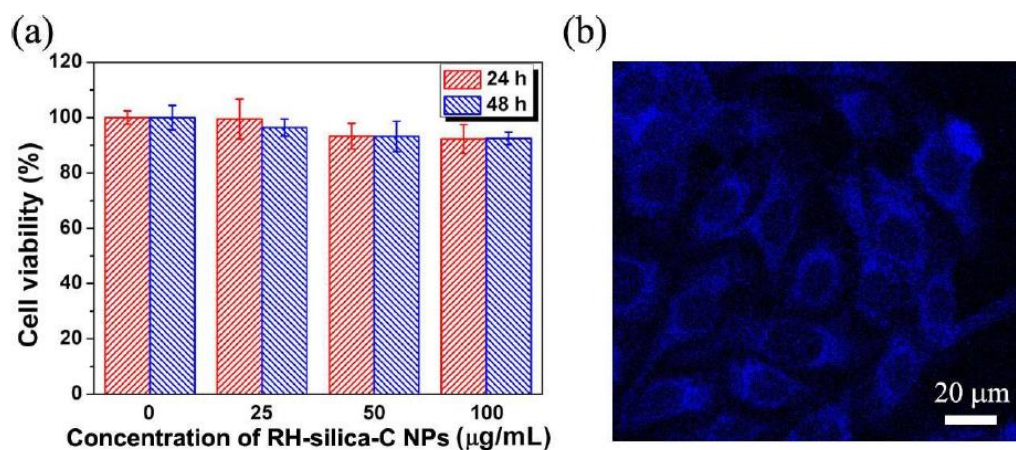


Fig. 16. (a) Viability of HeLa cells treated with different concentration of the RH-silica-C NPs for 24 and 48 h; (b) Cell imaging of HeLa cells combined with 50 µg/mL RH-silica-C NPs under excitation of 315 nm (Wang et al. 2017).

Another paper discussed the use of rice husk for the design and preparation of highly photoluminescent carbon incorporated silica (Wang et al. 2019). In this case, the rice husk underwent an acidic pretreatment first followed by a two-step calcination process. A series of localized energy levels can be created by the incorporated carbon within the band gap of silica, permitting the acceptance of excited electrons and recombination with holes, allowing the carbon incorporated silica to have photoluminescent properties.

Recent work on the biogenic silica nanopowders from RHA treated three different types of rice husk (sticky, red and brown) using a simple acid pretreatment method, followed by acid leaching and sonication steps. The material was then annealed in an oven to yield spherical particles of SiO₂ (70 nm, 20 nm and 10 nm diameter, respectively). Bacterial compatibility/toxicity tests were conducted using both gram-positive (*Escherichia coli*) and gram-negative (*Staphylococcus aureus*) microorganisms. The authors reported an enhanced antibacterial activity of the sticky rice husk nanosilica compared to the red and brown RH silica.

Using thermochemical treatment, silica nanoparticles SNPs were synthesized, then colored with concentrated pigment in ethanol. Corn starch was then added to homogenize the dispersion of pigments (Rajan et al. 2019). Subsequently, the various fluorescent SNP powders were studied for fingerprint tests. The fluorescent SNP powder exhibited a good contrast for fingerprint ridge enhancement without contributing to excess background fluorescence. Moreover, the use of natural pigment reduces the risk of toxicity to users (Rajan et al. 2019).

Another work focused on the synthesis of silica nanoparticles for the sequestration of heavy metals. Silica particles derived from RHA have been functionalized with chelating functions for the removal of heavy metals Ni(II) and Co(II) from aqueous solution. For

example, salicylaldehyde functionalized silica particles were obtained by condensation reaction between silica source (RHAPrNH₂) and salicylaldehyde which showed high efficiency in the removal and extraction of Ni(II) and Co(II) ions from their aqueous solution as shown in Fig. 17 (Mohsin and Mihsen 2020). A similar work was conducted for the extraction of Ni(II), Co(II) and Cu(II) by silica-salen derivative from RHA (Attol and Mihsen 2020).

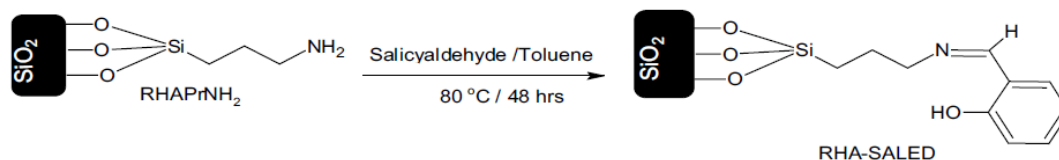


Fig. 17. Scheme of the functionalization of silica particles (Mohsin and Mihsen 2020).

The use of husk-derived silica was extended to the immobilization of enzymes to form bio-silica catalysts, more precisely for the chemoenzymatic epoxidation of limonene (Salvi and Yadav 2020). For this purpose, the silica was functionalized by grafting aminopropyl triethoxysilane (APTES) on the surface of RH-silica and cross-linked with glutaraldehyde, then calcium alginate was further used to form silica beads, for maximum recovery of the catalyst (Salvi and Yadav 2020). The bio silica was found to be a promising support for the immobilization of enzymes to form effective bio-catalyst for the chemoenzymatic epoxidation of limonene to limonene oxide, using in situ generation of peroxyacid from H₂O₂.

In addition to the functionalization to make organic hybrid silica RH silica materials, other nanosilica RH based composites with other metallic nanoparticles were also reported. For example, the formation of magnetic mesoporous MCM-41 from rice husk ash was described (Kamari and Ghorbani 2020). Silica was first extracted from rice husk by acid leaching using four acids HCl, HNO₃, H₂SO₄, and H₃PO₄, then MCM-41 was synthesized by hydrothermal method using CTAB surfactant as a structure directing agent. As for the magnetic MCM-41, hydrothermal process was used, reacting the extracted mesoporous silica with FeCl₂·4H₂O and FeCl₃·6H₂O. The characteristics of the magnetic MCM-41 were reduced in comparison with the MCM-41 due to the incorporation of Fe₃O₄, since the increase of its incorporated concentration affect the ordered structure of MCM-41 (Kamari and Ghorbani 2020). In another study, rice husk was used for the synthesis of mesoporous iron-silica composite Fe/SiO₂ applied for the removal of pollutants in banknote printing wastewater (Xiong et al. 2019). The preparation was achieved through an alkali treatment, co-precipitation and calcination. Fe/SiO₂ played both the role of flocculent and catalyst and showed the best activity under ambient temperature and pressure compared to the acidified water using H₂O₂ without Fe/SiO₂. The

prepared iron-incorporated silica mainly removed dye, acid-like substances, and microbial by-products like organics from water (Xiong et al. 2019).

Bimetallic silica composites of CoFe_2O_4 @biosilica was studied in a recent paper (Olusegun et al. 2019). Nanosilica was first extracted from rice husk, treated with NaOH and then sulfuric acid to precipitate silica gel as shown in Fig. 18 hybridizing nanosilica with CoFe_2O_4 (Olusegun et al. 2019). Furthermore, the composite was used for the removal of methylene blue, exhibiting a favourable adsorption of MB owing to the increment in ionic strength and its high surface area. Another work on the adsorption of MB made use of amino-functionalized mesoporous silica nanoparticles derived from RH (Usgodaarachchi et al. 2021). The synthesis of these materials focused on the extraction of the silica precursor via an alkali treatment of RH followed by a sol gel process. Moreover, the amine functionalization of the silica was conducted by two methods: co-synthesis and post grafting. Consequently, the prepared amino-silica were successfully applied for the removal of MB, as these materials demonstrated a negatively charged surface with a significant surface area and pore volume facilitating the adsorption of the cationic MB.

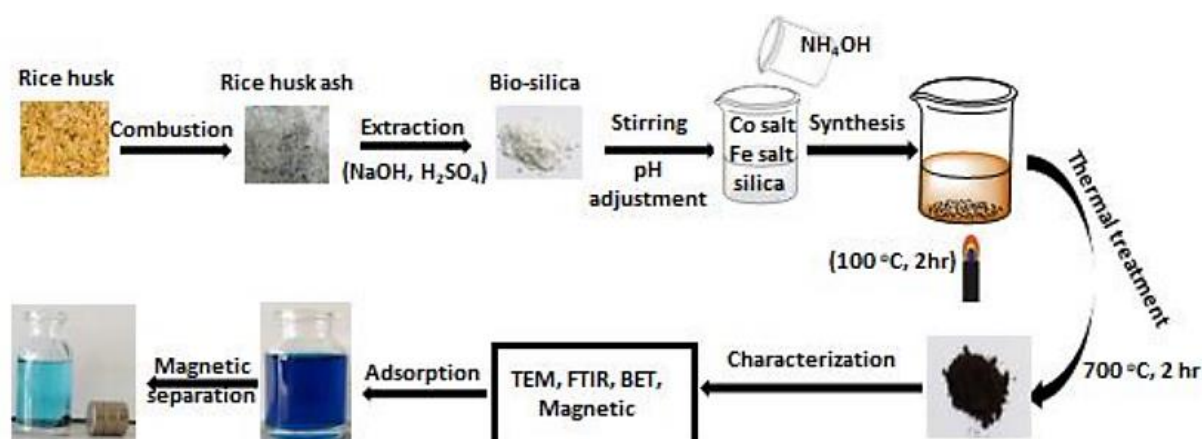


Fig. 18. Schematic description of the extraction of nanosilica to the adsorption of MB (Olusegun et al. 2019).

More recently, a study by Liou *et al.* described the preparation of SBA-15 from rice husk ash which was then used as a template for carbons mesostructured from Korea-3 (CMK-3) (Liou et al. 2022). The synthesis of SBA-15 started with an alkali extraction of sodium silicate from RHA, followed by a typical procedure with P123, then the SBA-15 was functionalized with APTES. Furthermore, the amino functionalized SBA-15 and CMK-3 were utilized for the adsorption of tannic acid. Both materials proved to be excellent adsorbents for tannic acid with maximum capacities of 209.64 and 675.67 $\text{mg}\cdot\text{g}^{-1}$. Interestingly, Park *et al.* described an alkali extraction to detoxify RH-derived silica and to increase its biocompatibility (Park et al. 2022). The preparation of the nanoporous silica was achieved either by calcination,

acid leaching or alkali treatment. Subsequently, the toxicity of these nanosilica were tested in different cells. The tests showed that both acid leaching and alkali treatment decrease the content of the nanosilica in residual carbon. While a percentage of carbon remains after the treatment, however, it is lower in the case of alkali extraction. On the other hand, in the case of calcination, which is considered as a more effective method, it was proven to be also not complete and carbon is still present, thus causing the deterioration of the biocompatibility of these materials. Another study opted for the use of a response surface methodology to optimize the extraction of silica from rice husk (Gun et al. 2022). The effect of different parameters were studied to achieve a maximum yield of 55%. The model demonstrated that KOH:RH ratio is the most influential parameters, followed by the time of the extraction and the temperature. The prepared silica were used for the adsorption of safranin dye with a removal efficiency of 78%.

3.2. Sugarcane bagasse

Sugarcane bagasse (SCBA) is a solid waste of sugarcane industry containing a high amount of silica ranging between 75-90 % (Norsuraya et al. 2016; Channoy et al. 2018). The combustion of sugarcane bagasse generates SCBA (a ton of burnt bagasse generates 25–40 kg of bagasse ash) (Sales and Lima 2010). In general, the sugarcane bagasse ash were washed several times with water (Hamad et al. 2019) or an acid (Boonmee and Jarukumjorn 2020) to remove dirt and oxides. Several protocols have been reported for the extraction of silica from SCBA, including calcination (Hamad et al. 2019), acidic leaching (Sholeh et al. 2020), or co-precipitation. For instance, calcination in the presence of sodium hydroxide assists the silicon extraction from the sugarcane bagasse ash thanks to the NaOH melting at high temperature, this process was summarized in Fig. 19 (Hamad et al. 2019).



Fig. 19. Synthesis of silica nanoparticles from sugarcane bagasse (Hamad et al. 2019).

Nanostructured silica can also be formed by direct calcination of bagasse ash followed by acidic leaching (H_2SO_4) and alkaline (NaOH) extraction (Fig. 20). Then after, nanostructured silica particles are formed upon acidic treatment (H_2SO_4), this protocol is summarized in Fig. 19 (Sholeh et al. 2020). In this approach, large particles are formed due to the collapse of the aggregated structure of the silica at high temperature and pH. However, the structure can be maintained upon adding a second sodium silicate to the solution. Modifying the reaction parameters, increasing temperature from 60 to 90 °C and decreasing pH from 11 to 8, resulted in a lower yield and reduced average particle diameter of nanosilica. The silica particles have high potential for applications as reinforcement agent for the natural rubber where well dispersed NPs are needed (Sholeh et al. 2020).

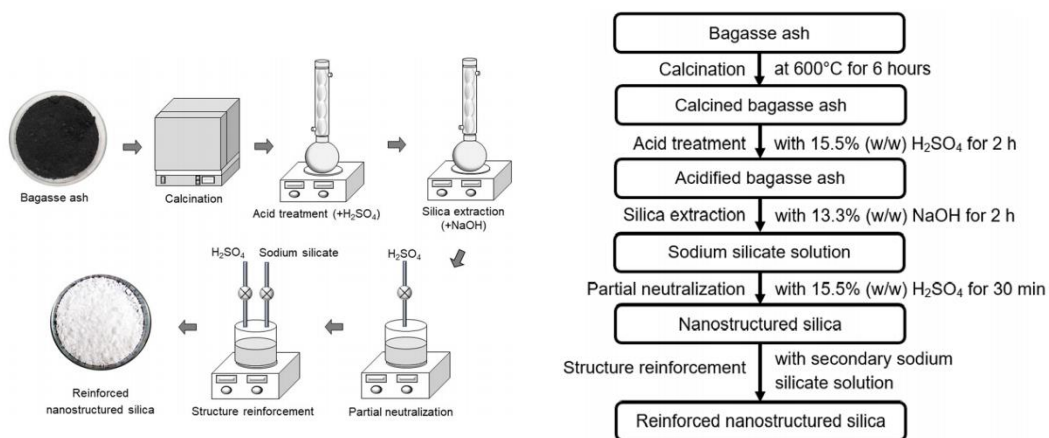


Fig. 20. Graphical Abstract and steps of the synthesis of nanostructured silica from bagasse ash (Sholeh et al. 2020).

In similar approach, Alves *et al.* reported the formation of mesoporous silica from SCBA (Alves et al. 2017). The formation of mesoporous nanosilica materials was achieved by fusion method at an aging temperature of 80 °C for 1 h. A second method based on two-step process was proposed for the production of sodium silica. First, a mixture of sugarcane waste ash and NaOH was calcined at 550 °C for 1 h. Water was then added to the resulting solid, product of the fusion reaction, to obtain a slurry. In a second step, the slurry was subject to hydrothermal treatment at 90 and 100 °C to produce sodium silicate (Alves et al. 2017).

Several parameters have been reported to affect the yield of silica recuperation and their final textural and structural properties. For instance, Megawati *et al.* maximized the yield of silica (~ 99 %) recuperated from sugarcane bagasse, by optimizing the extraction process (NaOH concentration and duration of extraction). The obtained silica powder has a surface area of 407 m².g⁻¹ and a pore diameter of 3.8 Å. The material was successfully used for the adsorptive-distillation of ethanol-water, separating the ethanol from the water and increasing the ethanol concentration from 96 to 99.3 % v/v (Megawati et al. 2018). Another key parameters for the silica synthesis is the calcination temperature (Rahmat et al. 2016). As the temperature of the calcination controls the crystallinity of the final product. At high temperature, higher crystallinity is observed which is reflected by sharper and intense XRD diffraction peaks when compared to low calcination temperature. In addition, at 1000 °C, recrystallization of cristobalite silica into quartz silica is confirmed by XRD through the changes in the relative intensity of the peaks and miller indices (hkl).

The direct calcination of sugarcane sources has several advantages. It can be used to remove the organic components and/or to remove the metallic impurities, when combined to an acidic leaching to yield high purity of silica up to 95 %. In addition, direct calcination can maintain the characteristic morphology of the original sugarcane and the biogenic structure of the source material which can be used to finely tune the characteristic of the final product (Bortolotto Teixeira et al. 2020). In addition to the spherical silica particles obtained at 550 °C, irregular aggregates, and fibrous-textured particles in the range of 10 nm, forming a three-dimensional array of nanoparticles packing around pores (hollows) are shown in Fig. 21.

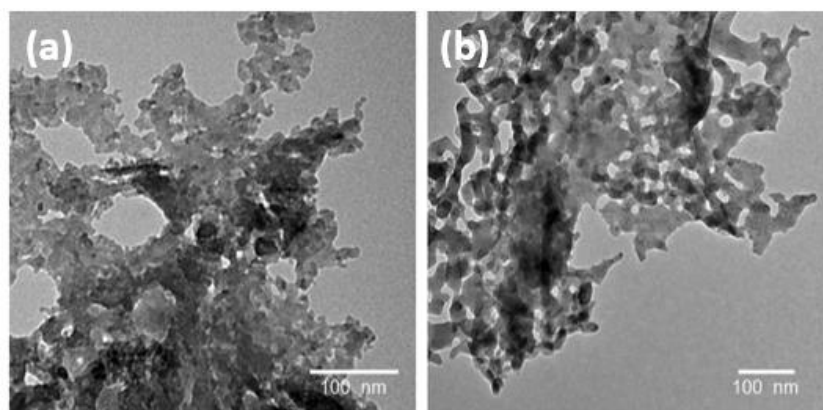
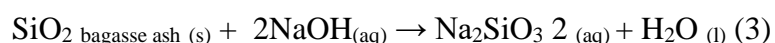


Fig. 21. Micrographs of the obtained ashes by using Route B and C: (a) TEM micrographs of SBA-L 550 (magnification: 120,000 ×), and (b) TEM micrographs SLA-L 600. (magnification: 120,000 ×) (Bortolotto Teixeira et al. 2020).

Later, two different methods for the extraction of silica using laser ablation and calcination followed by alkali treatment were described by San *et al.* (San et al. 2014). The silica particles formed by the calcination and NaOH treatment showed larger than those produced by laser ablation. Moreover, the silica nanoparticles formed by laser ablation were found to be non-toxic to *C. vulgaris* algal growth.

Alternatively, a low-chemical and low-energy consumption method based on the dissolution and acid precipitation can be used for the extraction of silica (Vaibhav et al. 2015). In this context, xerogel type silica was extracted from bagasse ash using low concentration of alkaline extraction and acid precipitation as shown in equations 3 and 4 (Chindaprasirt and Rattanasak 2020).



It should be noted that the silica yield was not significantly improved by high concentration of NaOH (> 1 M) or an increase in the HCl concentration (> 2.5 M) [140]. In the latter case, an adverse effect on silica yield can occur due to the re-dissolution of silica in high acid environment (< 2 M) (Amin et al. 2016). Importantly, the second step can be conducted in the presence of a structure directing agent such as CTAB to produce mesoporous silica gel nanoparticles (Rovani et al. 2018). Due to its intrinsic characteristics the produced mesoporous silica can be used in a variety of applications including adsorption and catalysis. In instance, mesoporous silica produced from bagasse showed high adsorption capacity for the removal of dye ($Q_{\text{ads}} = 230 \text{ mg.g}^{-1}$, acid orange 8). Plus, the materials had good regeneration ability up to five cycles (Rovani et al. 2018).

The pH and aging time are the key factors influencing the number of crystal phases of the synthesized nanosilica (Indrasti et al. 2020). The number of siloxane groups can be increased by raising the precipitation pH and aging time, allowing the creation of nano-silica with three crystal phases: tridymite, quartz and cristobalite, which affect their properties and potential applications, including filler for rubber and membranes, composite resin, and extra material in cements industry, etc. (Indrasti et al. 2020).

The choice of the filtration process was found to play an important role in controlling the purity of the end-product. In instance, when freeze drying and heat drying techniques were used to recuperate silica nanoparticles in the range of 90 ± 10 nm with high purity ≥ 98.5 %. Compared to the conventional heat drying technique, the slow removal of water in the freeze dry via sublimation process yield silica nanoparticles with porosity and higher surface area $156 \text{ m}^2.\text{g}^{-1}$ (Boonmee and Jarukumjorn 2020). The particles were used as a filler in natural rubber composites. In fact, tensile strength of the composites increased with silica content and tended to reduce at high silica nanoparticle content (Boonmee and Jarukumjorn 2020). Other filtration techniques can be used to purify the sodium silica, such as cationic exchange as shown in the flow diagram Fig. 22 (Affandi et al. 2009), and column packed with activated carbon (Farirai et al. 2020). For instance, the produced sodium silica with 99.16 % purity was jellified after adding HCl to produce a slurry transferred into high purity silica xerogel with 99.37 % of purity after drying. Interestingly, the adsorptive capacity of this mesoporous xerogel in water vapor, obtained from pure sodium silica exhibited better adsorption compared to the xerogels from low-purity one, due to the decreased impurities that can influence the surface adsorption properties (Affandi et al. 2009). In another study, a column packed with activated carbon was also employed to produce highly pure nano-silica with particle size ranging from 6 to 24 nm high specific area of $240 \text{ m}^2.\text{g}^{-1}$ (Farirai et al. 2020).

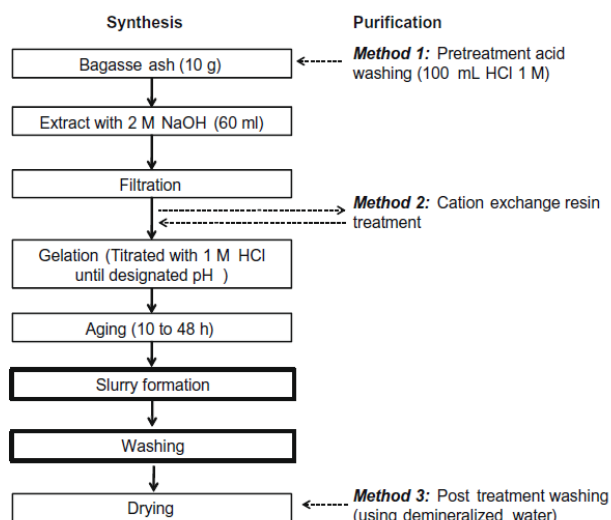


Fig. 22. Flow diagram of silica xerogel production from bagasse ash (Affandi et al. 2009).

Another strategy to increase the silica purity from sugarcane bagasse is the simple purification with HCl/NH₄F which increased the silica content from 72 % (when only HCl is used) to more than 90 %. Fig. 23 shows the comparative micrographs of untreated sample and one that underwent an HCl or HCl/NH₄F washing (Huabcharoen et al. 2017). However, this purification was an obstacle to the rubber-rubber crosslinking. In this case, the surface adhesion rubber was improved using a silane coupling agent named couplink 89 with the chemical structure of (C₂H₅O)₃-Si-(CH₂)₃-S₄-(CH₂)₃-Si-(C₂H₅O)₃ (Huabcharoen et al. 2017).

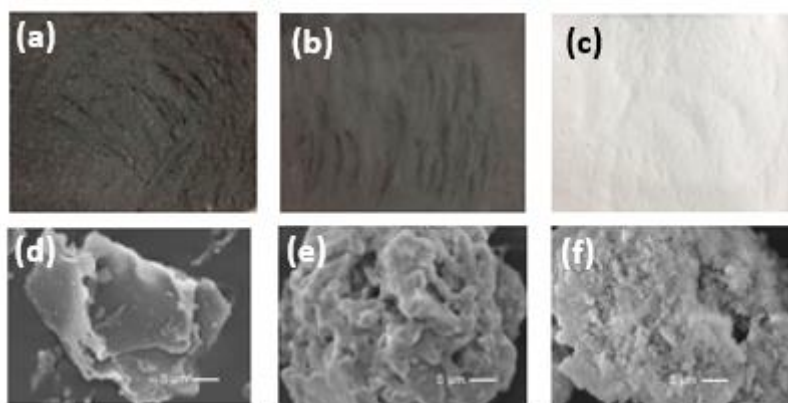


Fig. 23. Photographs and SEM images of the untreated silica (a,d) HCl-treated silica (b,e) and HCl/NH₄F-extracted silica (c,f)(Huabcharoen et al. 2017).

The recovered sodium silicate is not only used in the synthesis of nanosilica particles but can also be employed as a silica precursor for the synthesis of structured silica or silica hybrid materials. The most relevant example is the synthesis of mesoporous silica including SBA-15 (Arumugam and Ponnusami 2013a), (Arumugam and Ponnusami 2013b), (Norsuraya

et al. 2016) or SBA-16 (Boza et al. 2016). The preparation of mesoporous silica through sol-gel templating method using pluronic P123 or F127 as a structure directing agent. In general, the sugarcane leaf is first added to sodium hydroxide and thermally treated for the preparation of silica precursor solution. Then after, the precursor is added to a solution of HCl containing P123 or F123 copolymer. The obtained SBA-15 from the sugar ash displayed a typical wheat-like morphology which is identical to the conventional SBA-15 prepared from TEOS (Arumugam and Ponnusami 2013b), consisting of aggregates of uniform rope-like particles with hexagonal arrayed mesopores as shown in Fig. 24 (Arumugam and Ponnusami 2013b). The many visualized parallel stripes demonstrate regular stacking of elongated cylindrical assemblies in the synthesized fiber-like owing to the controlled conditions as shown in Fig. 25 (Arumugam and Ponnusami 2015). While the recovered sodium silica used in the synthesis of SBA-15 is optimized by controlling the sonication time, temperature and amount of sodium hydroxide added for fusion (Arumugam and Ponnusami 2015), the size of mesopores can be also tailored by the choice of synthesis temperature which dependent to some extent on the synthesis, aging temperature, and silica source. A scattered pores with pore size dimensions around 2.3 μm to 781 nm was obtained as shown in Fig. 26 (Norsuraya et al. 2016).

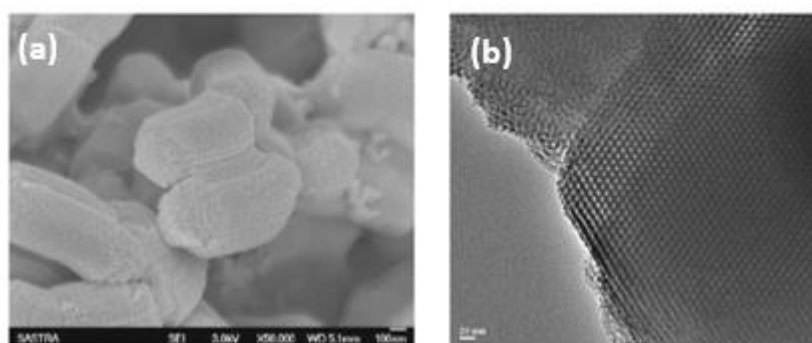


Fig. 24. (a) SEM image of SBA-15 and (b) TEM images of SBA-15 (Arumugam and Ponnusami 2013b).

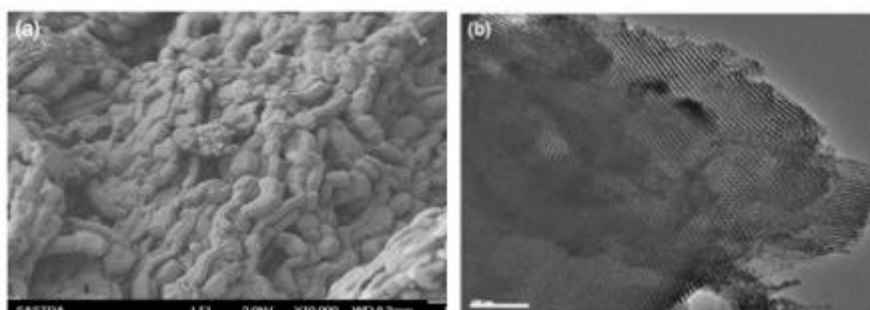


Fig. 25. SEM and TEM image of SBA-15 synthesized from sugarcane leaf ash (Arumugam and Ponnusami 2015).

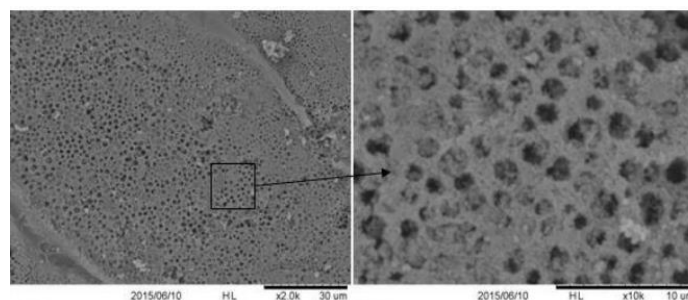


Fig. 26. The morphology of synthesised SBA-15 (Norsuraya et al. 2016).

Importantly, the obtained mesoporous SBA-15 can undergo a post functionalization with different groups or used to immobilize other species. For instance, amino, thiol, carboxyl and phenyl groups were grafted to the surface of SBA-15 originated from sugarcane leaf ash which was used in the adsorption of Ni (Arumugam and Ponnusami 2013a). It was also employed as a porous matrix to load high enzyme content for biodiesel production from renewable and non-edible feedstock (*e.i.* *C. inophyllum* oil). Advantageously, the presence of mesopores facilitated the access of oil into the loaded enzymes (Arumugam and Ponnusami 2013b).

Another work discussed the synthesis of SBA-16 by mixing the sugarcane bagasse with NaOH at 550 °C and dissolved in deionized water, then added to a mixture of HCl and the Pluronic F127 surfactant as a structure directing agent (Boza et al. 2016). A post-synthesis functionalization of the SBA-16 was carried out with thiol groups using 3-mercaptopropyltrimethoxysilane and subsequently oxidized into SO₃H. The SBA-16 and the functionalized SBA-16/SO₃H were used as catalyst for α -aminophosphonate synthesis from benzaldehyde and aniline, following the same protocol presented in Fig. 27. Where SBA-16/SO₃H showed a slightly better performance than SBA-16 due to the presence of additional acidic sites in the mesopores (Boza et al. 2016).



Fig. 27. General scope for SBA-16 and SBA-16/SO₃H catalysing the Kabachnik–Fields reaction (Boza et al. 2016).

Silica derived from sugarcane can be also used in the fabrication of other silica composites. For instance, SiO₂-CaO-Na₂O was synthesized by melting the sugarcane ash with CaO and Na₂O, then pouring the hot mixture in water to produce glass frit (Teixeira et al. 2010).

The glass transition temperature was found to be around 710 °C and the bulk crystallisation is the dominant mechanism for the crystallisation of the glass-ceramic products.

Silica from sugarcane bagasse can find applications as a photochromic pigment filler (Chindapasirt and Rattanasak 2020) or as a filler for natural rubber (NR) (Boonmee and Jarukumjorn 2020), or as an enhancer for drilling mud (Hamad et al. 2019). Respectively, increasing in silica nanoparticle content increase the modulus and hardness of the NR and the tensile strength of the composites (natural rubber-silica), which tends to decrease at high content. As for the use of silica in the drilling mud enhancing, better rheological properties, reduced fluid loss, high temperature stability and thinner filter cake were reached. Intriguingly, the preparation of mesoporous structured silica such as SBA-15 and SBA-16 extended the scope of application into other field such as catalysis by the preparation of mesoporous functionalized silica and silica composites (Arumugam and Ponnusami 2013b; Boza et al. 2016). Another application for sugarcane derived silica is the adsorption of bisphenol-A BPA (Rovani et al. 2020). The synthesized mesoporous silica nanoparticles were functionalized with CTAB to exploit the electrostatic interactions of the surfactant with BPA at higher pH, thus improving the adsorption of BPA. Moreover, silica was derived from sugarcane bagasse and pumice stone to compare the effect of the source on the quality of the silica (Nurwahid et al. 2022). The utilisation of a low-temperature alkaline extraction method and acid precipitation process permitted the synthesis of high purity silica. Furthermore, the generated silica was used as a catalyst support for silver in the 4-nitrophenol reduction reaction. Consequently, the catalyst performance showed that both sugarcane bagasse-derived silica and pumice stone-derived silica are good catalyst support. However, these waste generated silica suffered from agglomeration of the particles. In addition, the particles size was significantly bigger which led to slower reaction rate compared to the catalyst synthesized with commercial silica.

To sum up, different extraction methods were used for the extraction of silica from sugarcane bagasse, generating different silica types as shown in Fig. 28.

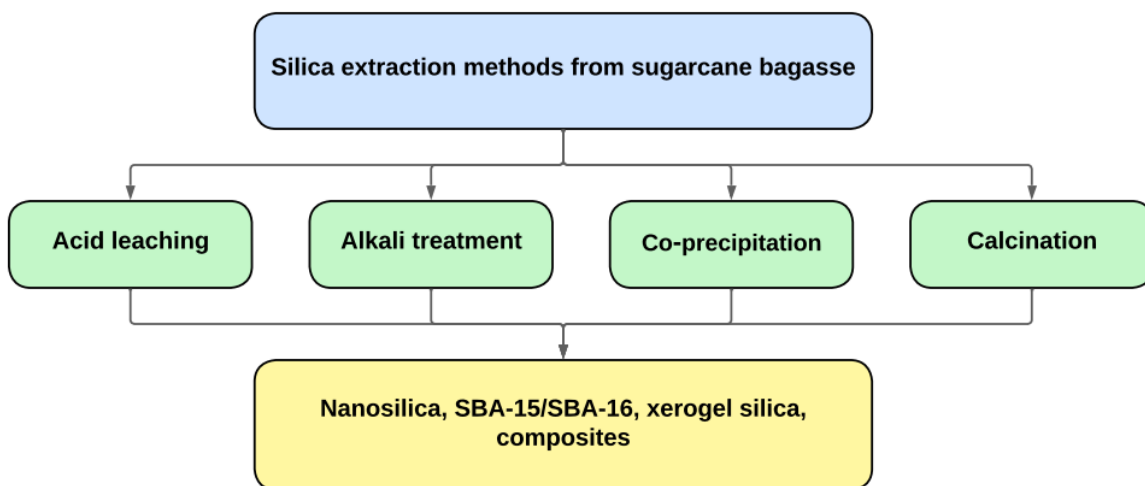


Fig. 28. Different methods for the extraction of silica and their use in the fabrication of different silica from sugarcane bagasse.

3.3. Silica synthesis from different agricultural wastes

In addition to rice husk and sugarcane, there are several different agricultural wastes that can be potentially valorised for the production of silica-based materials. In instance, coconut husk has been recently explored as a source of silica content. M. F. Anuar *et al.* conducted a study on the structural properties of coconut husk and its application as a precursor for silica synthesis (Anuar et al. 2018). Depending on the extraction method the structure and morphology of the silica varied, from amorphous using an alkali treatment to crystalline using an acid leaching. Furthermore, the physical and optical properties of crystalline silica from coconut husk ash, was found to be of high interest in optical application (band gap energy : 4.3 eV) (Anuar et al. 2020a). Further improvement of the photo-optic properties of silica was achieved upon modification with ZnO nanopowders. The ZnO-SiO₂ composite were prepared via solid state reaction and displayed a band gap of 4.05 eV (Anuar et al. 2020b).

Another interesting source of silica is palm kernel shell which is alternatively recognized as oil palm shell. P. E. Imoisili *et al.* used palm kernel shell ash (PKSA) as the starting material for the production of silica xerogels by a sol gel technique with a yield of 96.83 % (Imoisili et al. 2019). PKSA was first dissolved in NaOH solution, filtered and washed, then a silica gel precipitated by adding the filtrate into HCl solution. In the same line of work, nanosilica was obtained from palm kernel shell (Imoisili et al. 2020). After the synthesis of silica xerogel by the same process as mentioned before, a reflux of the dry silica gel in HCl was conducted and followed by a dissolution in NaOH and titration by H₂SO₄ to obtain the nanosilica (Imoisili et al. 2020).

In addition, oil palm frond was used for the synthesis of nanosilica with high purity via a sol gel method. First, the oil palm frond went through several stages of combustion and acid leaching treatment with citric acid. Then after, the acid leached palm oil frond ash (POFA) was added to a solution of NaOH. The pH of the solution was controlled with H₂SO₄ to form a silica gel with 68 % yield (Surayah Osman and Sapawe 2020). NaOH molarity and acid leached POFA concentration were found to be the main parameters controlling the sol gel process, and thus the properties of the final materials (Osman and apawe 2020; Osman and Sapawe 2020). Moreover, POFA was utilized for the synthesis of silica encapsulating metallic catalysts. For instance, Ni/SBA-15 was synthesized and then used as a catalyst for H₂ production via CO₂ reforming of CH₄. The optimum Na₂SiO₃-POFA/P123 mass ratio for SBA-15 preparation was found to be at 2.9, as it showed the best catalyst performance compared to the catalyst prepared from Na₂SiO₃ due to its well-arranged hexagonal mesoporous framework, and better metal interaction with the support (Chong et al. 2019).

Mesoporous silica nanoparticles can be synthesized using banana peel ash (BPA) as a silica precursor. First the banana peel underwent a combustion turning to ash. Second, the BPA was mixed with sodium hydroxide, then silica was precipitated by H₂SO₄ from the previously obtained sodium silicate. The prepared mesoporous nanosilica was then tested for the absorption of methyl orange and phenol, showing promising results as a low-cost adsorbent for the removal of dyes contamination in wastewater (Mohamad et al. 2019). Nanosilica was also prepared from *Equisetum arvense* plant by calcination process followed by precipitation (Washington LE 2015). Another two species of the family of horsetails (*Equisetaceae*) plants were used for the synthesis of amorphous biosilica (Neumann et al. 2010). In general, *Equisetum hyemale* and *Equisetum telmateia* are known for their high content on SiO₂ as they assimilate silicic acid from the soil and deposit it either as demobilized amorphous silica or as opal (Neumann et al. 2011). Both plants underwent an acidic pretreatment, followed by a thermal oxidative process. Upon careful control of time, temperature, and thermal gradient to obtain silica with surface area as high as 418 m².g⁻¹ (Neumann et al. 2010).

Sedge is a type of weed, used in a study as a source for highly pure silica which was then used for the production of mesoporous MCM-41 (Ghorbani et al. 2013). Three different treatments were tested for the silica recovery, leaching process, refluxing process, and the combination of both. As for the MCM-41 synthesis, CTAB was used as the directing agent, added to the sodium silicate solution, followed by a calcination to remove the surfactant. The resulted MCM-41 was defined by pore size of ~ 4.1 nm and high surface area up to 1174 m².g⁻¹

¹ (Ghorbani et al. 2013). Synthesis of silica nanoparticles from *Bambusa vulgaris* leaves ashes, was also reported using sol-gel methods (Durairaj et al. 2019). The prepared silica was then used for the removal of Cd and Cr with an adsorption capacity of 133 and 172 mg.g⁻¹ respectively. Another recent study reported the extraction of silica from bamboo leaves (Joshi et al. 2022). The extracted silica was functionalized with alginate. Subsequently, the alginate-silica was used for methylene blue removal, and the incorporation of silica particle in the alginate matrix offered more adsorption sites for the dye which was proved by the DFT calculations. Besides, bamboo-derived silica was used for the synthesis of a cobalt silica composite (Pei et al. 2022). First, 3D C/SiO₂ composite was obtained by the carbonization of the bamboo leaves, followed by and acid treatment. Second, the C/CoSi composite was synthesized by a hydrothermal method using the 3D C/SiO₂, which was then converted to Co-rich C/CoSi by adsorption, as summarized in Fig.29. Consequently, the prepared composites were used for the fabrication of electrodes, which displayed excellent oxygen evolution reaction (OER) activity, thanks to the layered structure and the increase of active sites with the incorporated Co.

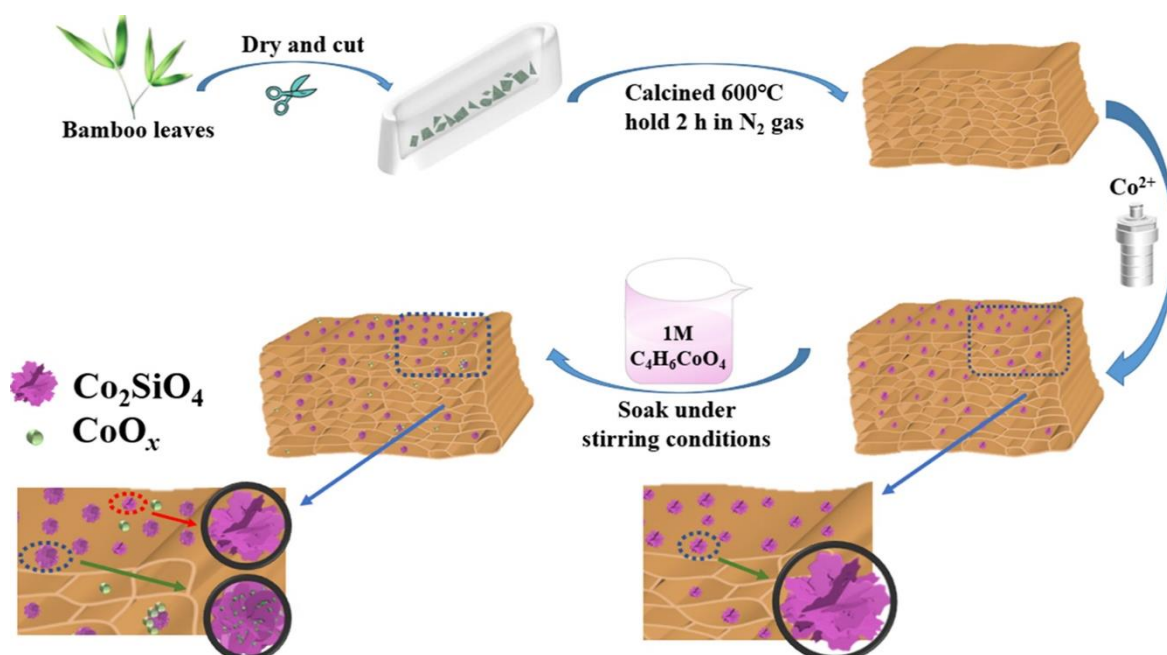


Fig. 29. Synthetic route and SEM images of C/CoSi and Co-rich C/CoSi: (a) Synthetic route of C/CoSi and Co-rich C/CoSi (Pei et al. 2022).

Crystalline silicon (Si) has been also synthesized from wheat husk ash (WHA). The WHA was first subjected to thermal annealing. The silica was then recovered by an alkaline leaching process and precipitated with HCl. The as precipitated silica was grounded and put into contact with vaporized Mg in an inert atmosphere at different temperatures (550 °C, 650 °C and 750

°C). Finally, the product was washed with HCl and HF to remove Mg, yielding silicon materials with the highest crystallinity at 550 °C. Energy cells is a potential application for the synthesized silicon (Rodríguez-félix and Wong-corrall 2020). Liu *et al.* used wheat husk ash for the synthesis of hydrophobic silica aerogel (Liu et al. 2016). First, silica was extracted from wheat husk ash by sodium hydroxide to form sodium silicate, then silica aerogels were prepared following a sol-gel method using an acidic ion exchange resin process. Second, a surface modification was conducted, by a solvent exchange method, washing the silica gels and immersing it in a solvent mixture of trimethyl-chlorosilane, ethanol and hexane. The last step of the process was drying the silica gels under an ambient pressure for 1h at 200 °C. The hydrophobic property was tested with a water contact angle exhibiting an angle of $147 \pm 0.1^\circ$ (Liu et al. 2016).

4. Silica recovery from industrial waste

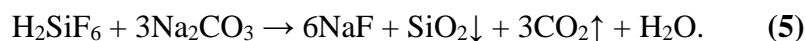
4.1. Silica from fluorosilicic acid

Fluorosilicic acid (FSA) or hexafluorosilicic acid as one of the major hazardous by-products of phosphate fertilizer industry (Yu et al. 2000) can be used as the starting material for fluorochemicals as it can be the precursor for many silicon-based compounds. Advantageously, wet chemistry has been used for the valorisation of the silicon from FSA compared to other mineral and agricultural wastes that involve most of the time solid state reactions such as calcination and grinding followed by acidic or alkaline leaching for the production of silica showing the potential importance of such by-products in the silica industry.

In view of the importance of the solar cell application the recovery of solar grade Si from fluorosilicic acid offers a tantalizing approach for the development of affordable low-cost solar cell. The process is based on the reduction of SiF_4 by alkaline earth metal (preferably Na), resulting in the formation of Silicon and sodium fluoride (Sanjurjo et al. 1984). In addition to inventions concerning Si, many researchers studied the silica recovery from FSA. For example, a procedure is presented for the use of waste silica from hydrogen fluoride synthesis and aluminium fluoride production from fluorosilicic acid. The waste silica was first washed from any fluorine impurities by HCl solution or hot water washing on a battery of filters then hydroxides of alkaline earth metals were added to form sodium and potassium metasilicate. Subsequently, the obtained silica was modified with silane and titanate coupling agents in carbon tetrachloride. The unmodified and modified silica were then tested in rubber mixtures, and used as polyurethane fillers, showing later that the unmodified silica had a small

improvement of tensile strength and activity compared to the modified silica that showed considerable improvement in the physico-chemical parameters (Krysztalkiewicz et al. 1995).

A similar work discussed the synthesis and the modification of nanosilica particles from FSA with p-tolyltriethoxy silane (PTTES) and bis-(γ -triethoxysilylpropyl)-tetrasulfide (Si-69) silane coupling agents (Bach et al. 2020). The nanosilica particles were extracted via direct precipitation after adding NH_3 solution. The co-silanized silica was then used for the modification of natural rubber and styrene-butadiene rubber blend to enhance their thermal and mechanical properties. (Bach et al. 2020). Recently, unmodified amorphous silica nanoparticles extracted from FSA was achieved via the same precipitation process, which was adopted as reinforcement material to enhance the tensile strength and decrease the elongation rate for a natural rubber (Nguyen et al.). Controlling the ammoniation of H_2SiF_6 by controlling the addition of ammonia, the rate and speed of agitation and the pH allowed the synthesis of mesoporous silica nanoparticles that have great potential in the synthesis of aerogels, bio-sensing and drug delivery (Abburi et al. 2020). In fact, the FSA was reacted first with ammonia to form a soluble ammonium fluorosilicate, which then was reacted with additional ammonia to precipitate the silica (Abburi et al. 2020). In addition, silicon dioxide was prepared using the same method while controlling and analyzing the fluorine ions content, by the direct potentiometry in a two-electrode cell containing a fluoride-selective electrode with a crystal membrane (Panasyuk et al. 2018). Others opted for the two-step ammoniation method for the synthesis of amorphous silica with high quality. In this work, the first step consisted of adding NH_3 to the H_2SiF_6 solution, and the obtained slurry was filtered, then the filtrate was recovered for the subsequent second step, wherein the same procedure for the 1st-step ammoniation was applied. As above, the ammoniation fluorosilicate molar ratio, the flowrate, pH, and temperature are key variables for the reaction (Yu et al. 2000). This two-step ammoniation was also used for the synthesis of ZSM-5 zeolite after the recovery of high-quality silica. In this process fluorine impurity helped increasing the growth of zeolite crystal (Jin et al. 2017). However, the method was tedious and non-economical due to low silica yield and the impossibility of ammonia recycling. These challenges motivated other researchers to pursue other alternative, by reacting FSA with Na_2CO_3 or a second silica precursor of sodium silicate to form unstable monomeric silicic acid, which underwent condensation and polymerization (Sarawade et al. 2010; Hilonga et al. 2012; Elineema et al. 2013; Xu et al. 2014). For instance, the reaction of hexafluorosilicic acid with Na_2CO_3 under reflux and controlled pH to generate an alkaline aqueous slurry containing small silica particles follow the equation:



While filtration was used to separate silica from the slurry and form mesoporous silica particles, the evaporation method was employed to extract the sodium fluoride from the aqueous solution (Sarawade et al. 2010). After drying, mesoporous silica nanoparticles with high surface area up to $800 \text{ m}^2 \text{ g}^{-1}$ were formed, the SEM image and N_2 adsorption/desorption isotherms of the synthesized silica is displayed in Fig. 30 (Sarawade et al. 2010).

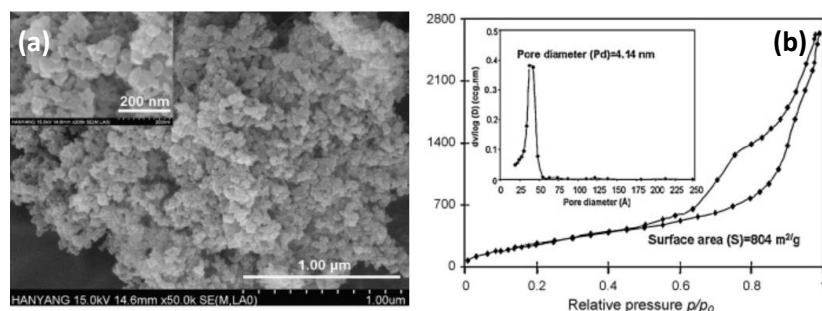
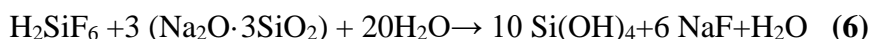


Fig. 30. (a) FE-SEM image of the mesoporous silica and (b) N_2 adsorption/desorption isotherms and pore size distribution (PSD) of the mesoporous silica (Sarawade et al. 2010).

Moreover, two studies reported the synthesis of mesoporous silica by reacting FSA with sodium silicate ($\text{Na}_2\text{O} \cdot \text{SiO}_2$) with the same polycondensation polymerization reaction for the formation of aggregated silica clusters with three-dimensional mesoporous porous network following the reactions (Hilonga et al. 2012; Elineema et al. 2013).



The use of two silicon sources improved the silica yield (Elineema et al. 2013) and the synthesized mesoporous silica was used as inorganic filler suitable for tires (Hilonga et al. 2012).

In addition to mesoporous silica NPs, nanostructured mesoporous silica such as MCM-41 was synthesized from hexafluorosilicic acid using CTAB as a structure directing agent under an alkaline environment using $\text{NH}_3 \cdot \text{H}_2\text{O}$ under a hydrothermal treatment at 323-363 K. In this work, titanium precursor was added to yield mesoporous molecular sieves catalyst of Si/Ti-MCM-41 with the highest ordered hexagonal lamellar structure at CTAB/Si molar ratio 0.81 after an optimization of the CTAB:silicon ratio. Moreover, the reaction time and the hydrothermal temperature were found to be key parameters to control. The calcined materials showed a well-defined hexagonal arrangement with a fairly uniform pore structure as shown in Fig. 31 (Liu et al. 2017). Another recent paper compared the MCM-41 prepared from FSA in

the presence of CTAB and the one prepared from the commonly used precursor TEOS (Vacca et al. 2020). The MCM-41 synthesized from FSA possessed thicker walls indicating higher thermal stability compared to the TEOS-derived MCM with similar hydrothermal stability. In addition, the generated samples were used as template for the synthesis of Fe₂O₃-nanocomposites, which were tested for the removal of H₂S from sour syngas showing similar performance for both FSA- and TEOS-derived samples with easier removal in the case of FSA-MCM-41 (Vacca et al. 2020).

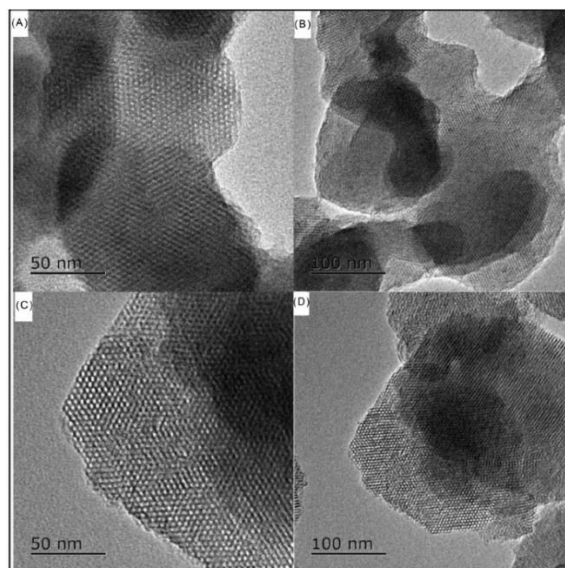


Fig. 31. TEM micrographs of different samples prepared by changing xSi/Ti-MCM-41TTe1 (A) & (B) for x=10, (C) & (D) for x=60 (Liu et al. 2017).

Mesoporous silica MS was also prepared using a nonionic surfactant templated gelation method (Kim et al. 2019). A mixture of an aqueous solution of Na₂SiO₃, H₂SiF₆ and polyoxyethylene (12) nonylphenol ether PN12 resulted in a white precipitate, which was then dried and calcined to remove the surfactant, this process is summarized in Fig. 32. The mesoporous silica was subsequently impregnated with Ni and Rh, then used as a catalyst for the partial oxidation of methane. The results showed that the specific surface areas of MS using nonionic surfactant varied in the range of 959-1135 m².g⁻¹, as for the cationic surfactant, the surface area is lower at 371 m².g⁻¹ (Kim et al. 2019).

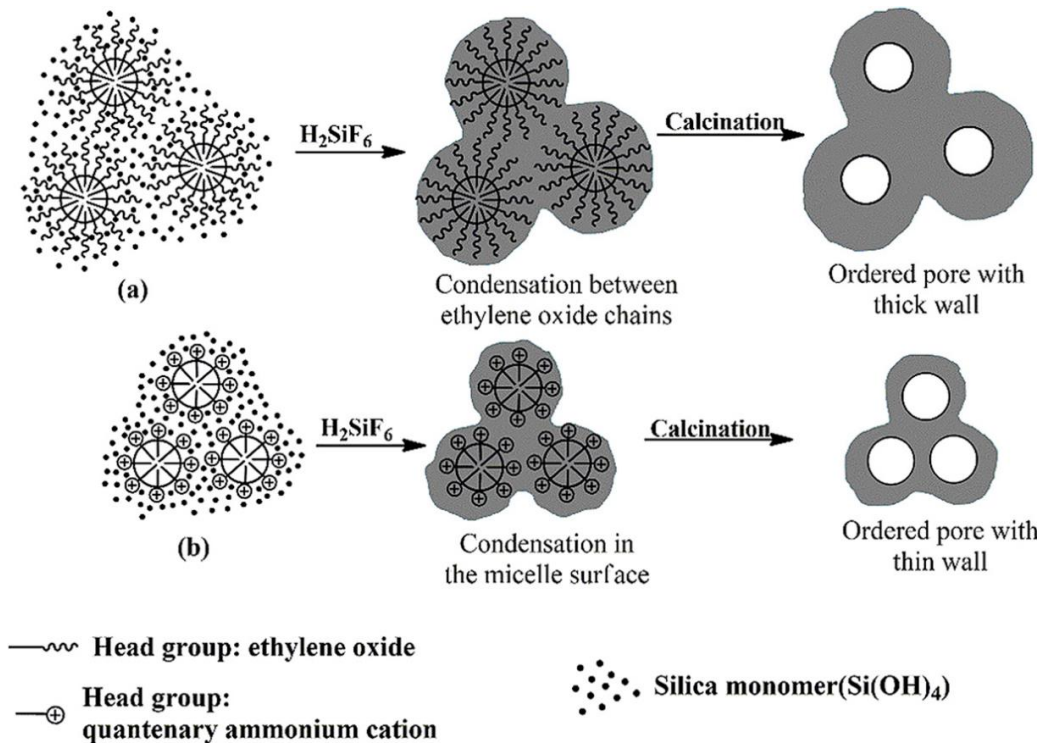


Fig. 32. Schematic illustration showing the formation of MS samples via cationic and nonionic surfactant templating (Kim et al. 2019).

Accordingly, the valorization of this by-product into valuable nanomaterials could be viewed as a promising strategy for the synthesis of sustainable mesoporous silica-based materials, usually using wet chemistry in contrary to the aforementioned silica sources. The different silica extraction methods from FSA and the different silica types synthesized are mentioned in Fig. 33.

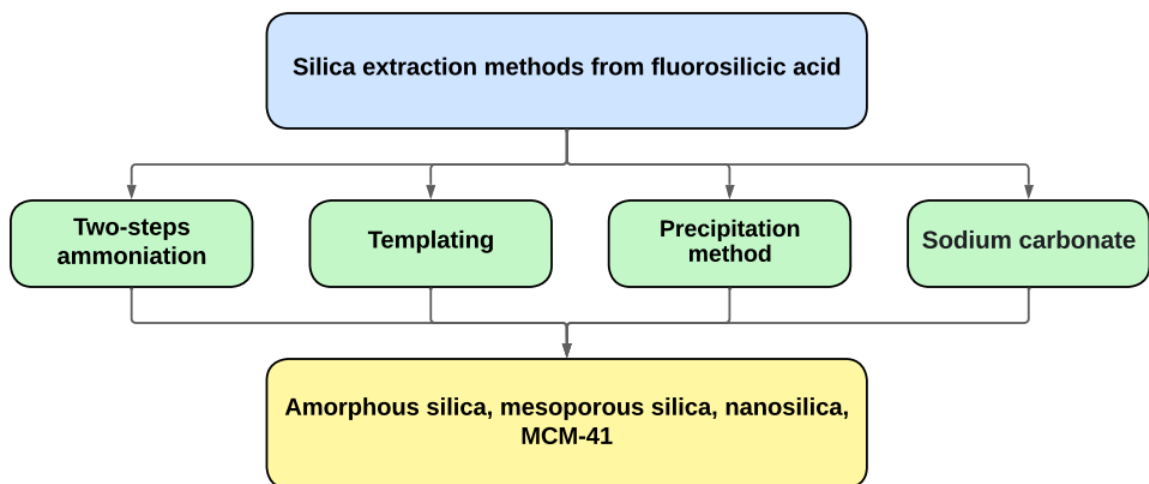


Fig. 33. Different silica extraction methods and their use in the synthesis of different silica from fluorosilicic acid.

4.2. Fly ash derived silica

Coal fly ash (CFA) is another cheap, abundant, and silicon-rich industrial by-product derived from coal combustion in thermal power plants (Yao et al. 2015), having variable components of SiO₂ (both amorphous and crystalline) and Al₂O₃ depending on the composition and source of the coal being burned, which was harnessed for instance in the synthesis of different types of silica materials including amorphous silica (Kumar Yadav et al. 2020)(Yadav and Fulekar 2019), mesoporous structured materials such as SBA-15, MCM-41 and Al-MCM-41 with hexagonal structure (Kumar et al. 2001). For instance, using a two steps method, involving the extraction of sodium silicate by NaOH treatment, followed by the formation of silica gel after a neutralization with hydrochloric acid allowed the synthesis of nano sized silica particles of 20-70 nm from fly ash tiles and fly ash, with a purity of 90-96 % (Kumar Yadav et al. 2020)(Yadav and Fulekar 2019). Coal fly ash was also transformed to ordered mesoporous nanosilica by introducing a green simple method based on an alkali-dissolution process and a precipitation of the nanosilica assisted by a simulated flue gas and surfactant with a twice-carbonation process. Subsequently, the obtained mesoporous nanosilica was used as a support to immobilize CaO for CO₂ capture (Yan et al. 2017). In fact, the nanosilica enhanced the cyclic stability and the sorption kinetics of CaO as shown in Fig. 34, mainly attributed to the formation of larnite (Ca₂SiO₄) and the nanostructure of silica (Yan et al. 2016).

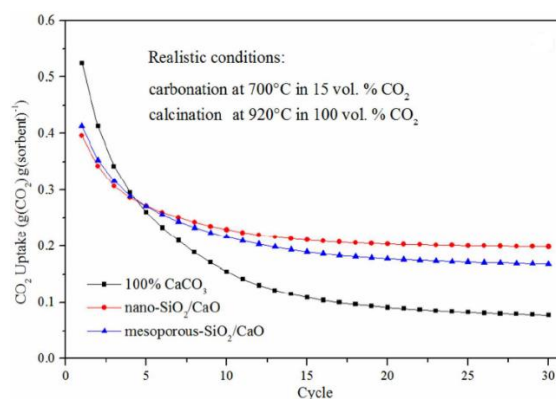


Fig. 34. CO₂ uptake as a function of cycle for “100%CaCO₃”, “nano-SiO₂/CaO” and “mesoporous-SiO₂/CaO” under realistic conditions (Yan et al. 2016).

A recent study investigated the synthesis of micro- and mesoporous silica from coal fly ash at different pH values (De Oliveira et al. 2020). The silica was extracted from coal ash by an acid leaching. Second, a mixture of silicon oxide /NaOH /CTAB /H₂O was aged and heated in a Teflon lined stainless steel autoclave at 110 °C to yield micro- and mesoporous silica used in parabens adsorption (De Oliveira et al. 2020).

Importantly, the valorisation of this industrial waste extended to the fabrication of mesoporous structured silica materials such as MCM-41 and SBA-15. In this case, high

temperature was used to dissolve the coal fly ash in the presence of sodium hydroxide to obtain a fused mass, which was cooled, milled overnight and then mixed with water to have a supernatant containing silica species after filtration. Combining the supernatant with CTAB in NH_4OH under hydrothermal lead to the formation of MCM-41. While SBA-15 was prepared after adding surfactant P123 to the supernatant together with sodium metasilicate. All the obtained materials were washed, dried, and calcined at $550\text{ }^\circ\text{C}$ to form mesoporous materials as the TEM images show in Fig. 35 (Kumar et al. 2001). Another study discussed the use of CFA for the preparation of SBA-15 (Cui et al. 2022). The synthesized silica was functionalized with diethylenetriaminepentaacetic dianhydride (DTPADA, AR) amino group (APTES), which was further used for rare earth elements removal, i.e. Eu (III), Gd (III), Tb (III), Nd (III) and Sm (III) in acidic solution. The functionalized SBA-15 showed a maximum adsorption capacity of $32\text{ mg}\cdot\text{g}^{-1}$.

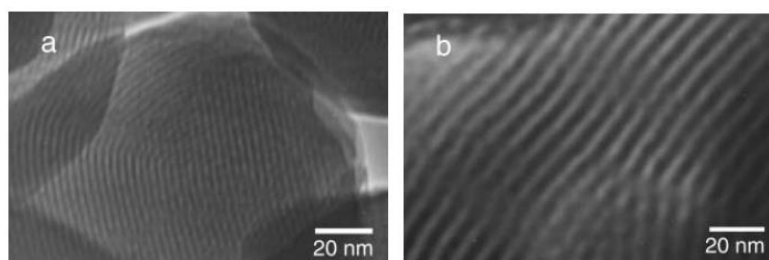


Fig. 35. TEM images of (a) Al-MCM-41 and (b) SBA-15, prepared using fly ash as the starting material (Kumar et al. 2001).

Coal fly ash contain both Si and Al, most of the work on coal fly ash has been focused on zeolite porous materials based Si and following a method based on the dissolution of Al-Si-bearing fly ash phases with alkaline solutions led to the precipitation of zeolitic materials (Alastuey et al. 2002). Moreover, a study was conducted concerning fly-ash-based geopolymers as sustainable porous aluminosilicate heterogeneous catalysts (Alzeer and MacKenzie 2018). In this case, Al_2O_3 was added to the fly ash to adjust $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. Second, ion-exchange was applied to exchange the charge-balance Na^+ ions with NH_4^+ , by adding NH_4Cl to the pristine geopolymers. Those materials demonstrated excellent catalytic reactivity in the model Friedel-Crafts, superior to other commonly used aluminosilicate catalysts such as M-zeolite, mesoporous molecular sieves, mixed oxides, and ionic liquids. More recently, a value added zeolite beta BEA product was produced from coal fly ash via an indirect hydrothermal process (Ameah et al. 2020). Si/Na, Si/Al molar ratio and hydrothermal time had was demonstrated to have a significant effect on crystallinity, crystal size and percentage yield of BEA zeolites (Ameah et al. 2020). Moreover, a comparative study was conducted regarding the direct hydrothermal and indirect fusion methods for the synthesis of zeolite from coal fly ash using a

single-mode microwave irradiation. The first process is a single-step hydrothermal alkaline treatment, mixing sodium hydroxide and CFA in deionized water at 60 °C for 12 h, then sodium aluminate was added to the mixture and subjected to microwave radiation for crystallization. As for the second method, the mixture of NaOH and CFA was first thermally treated at 550 °C for 2 h, then followed by the same steps as the first process. The results showed that hydrothermal-produced zeolites was better for heavy metal ions immobilization and showed better crystalline structure, whereas fusion products had a higher BET surface area and a slightly higher cation exchange capacity (Bukhari et al. 2014).

Different methods were used for the extraction of silica from fly ash, resulting in different types of silica as summarized in Fig. 36.

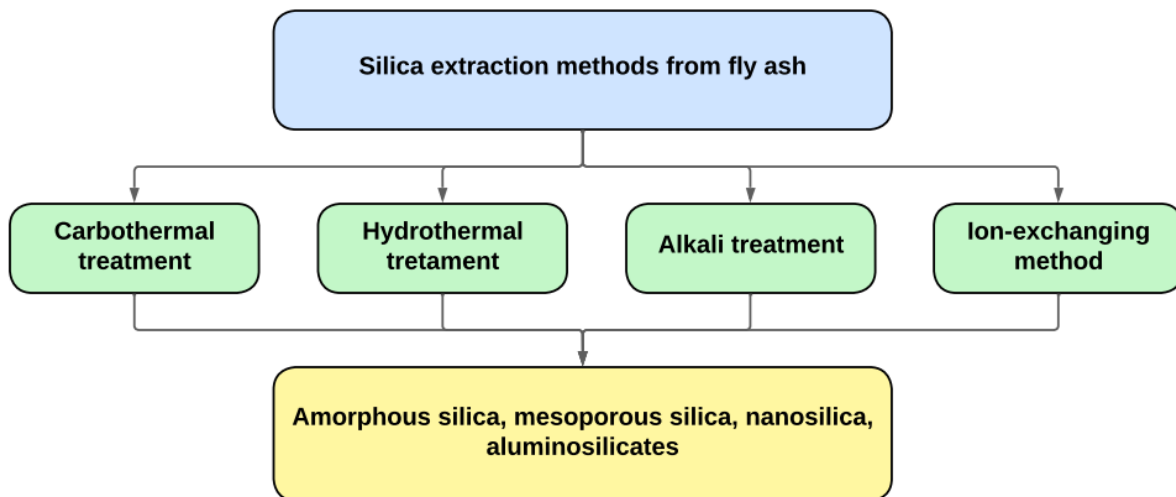


Fig. 36. Different methods for the extraction of silica and their use in the fabrication of different silica from fly ash.

4.3. Electronic and photonic wastes (e-waste)

Electronic and photonic wastes or E-wastes are serious ecological problems due to their contents of a variety of toxic substances. Thus, different management strategies were put together for their proper collection, recovery and recycling, particularly, the separation and recovery of components that can be recycled such as rare and precious metals (Kiddee et al. 2013). The recovery of silica from E-waste is another solution to mitigate the environmental problem of these wastes and use other non-expensive sources for the fabrication of silica-based materials. In this context, Liou (Liou 2011) synthesized highly ordered mesoporous silica from e-waste packaging resin waste with cationic CTAB surfactant as a structure directing agent, which was carried out by mixing the dissolved CTAB surfactant in sulfuric acid solution with sodium silicate extracted from resin ash by an alkali treatment and subjected to hydrothermal

treatment to yield hexagonal mesoporous MCM-41 with high surface area ($1033 \text{ m}^2\cdot\text{g}^{-1}$) as shown in Fig. 37, after drying and calcination to remove surfactants.

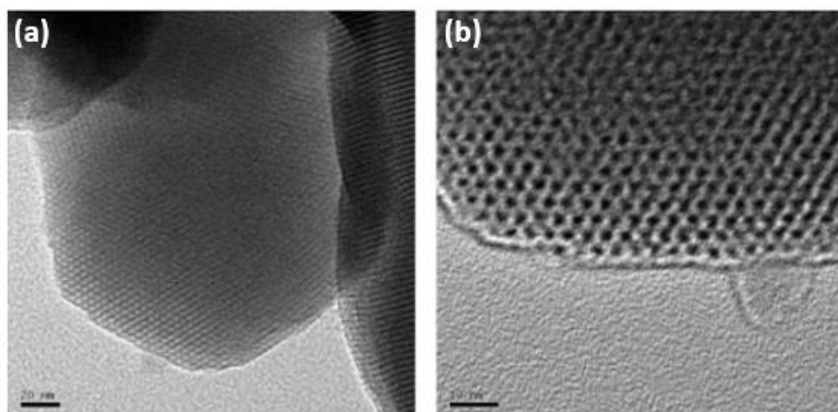


Fig. 37. HR-TEM view of silica samples produced from PRA: (a) pH 11 (scale bar: 20 nm), (b) pH 11 (scale bar: 10 nm) (Liou 2011).

Other composite based silica can be synthesized from e-waste. For instance, alkali-extracted electronic packaging resin ash provided a source of silicon for the synthesis of a photocatalyst $\text{TiO}_2/\text{MCM-48}$ after loading the TiO_2 nanoparticles within the mesoporous MCM-48 to form the photocatalyst materials combining the high adsorptive efficiency of MCM-48 along with the photocatalytic activity of TiO_2 (Liou and Lai 2012). The composites were tested for the degradation of MB, as the high surface area of MCM-48 allowed better adsorption of MB, consequently increasing the photocatalytic properties of TiO_2 (Liou and Lai 2012). Applying the same green approach, enabled the synthesis of MCM-48, employed as a template for the preparation of ordered mesoporous carbon OMC molecular sieves (Fig. 38 and 39) (Liou 2012; Liou and Jheng 2018).

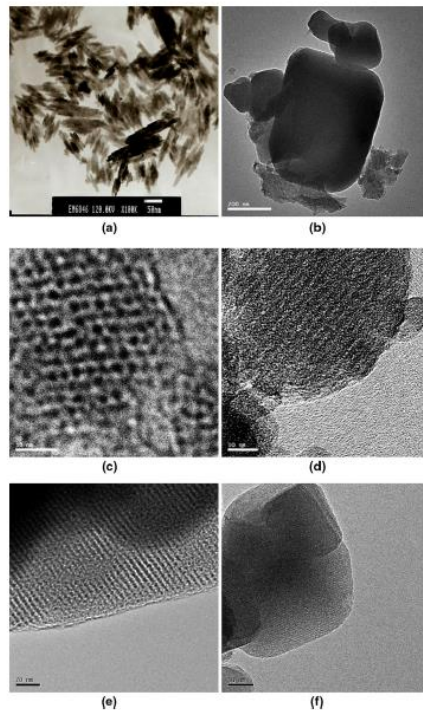


Fig. 38. High-resolution TEM images of samples: a PRA, b particle morphology of MCM-48, c, d MCM-48 synthesized at pH 11, e, f CMK-1 carbon (Liou 2012).

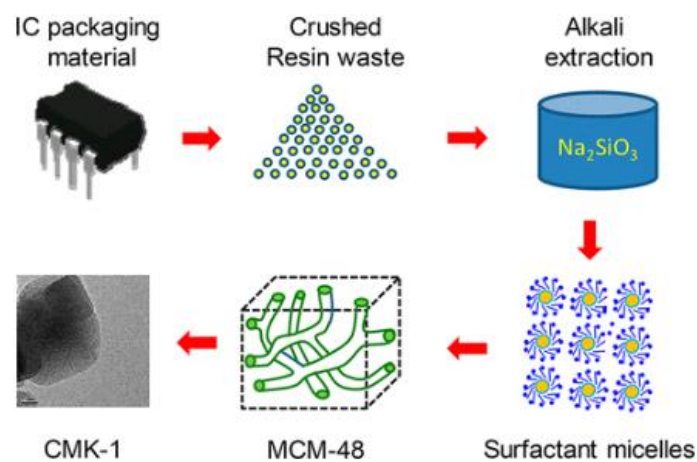


Fig. 39. A simple, green route method was employed to create CMK-1 carbon, which was obtained using cheap, recycled silica template from e-waste (Liou and Jheng 2018).

In addition to the recovery of silica from electric waste and packaging, a couple of studies showed interest in silicon carbide preparation from e-waste. For example, silicon carbide nanowires were synthesized via the carbothermal reduction combining two different e-wastes, using the glass of an obsolete computer monitor (GCM) as a silica source and the computer plastic shell (CPS) as the carbon source (Maroufi et al. 2017). The GCM was pulverized, and the CPS was subjected to a pyrolysis treatment and then the powders were mixed, pressed, and

underwent a heat treatment as summarized in Fig. 40. Nevertheless, the reaction requires a high temperature 1550 °C, which could be problematic energetic and cost wise. Another study reported the use of silicon carbide grinding sludge waste as a source for the synthesis of MCM-41 (Lin et al. 2022). Furthermore, the mesoporous silica was functionalized with APTES and tested for dehumidification application, resulting in higher moisture adsorption ($>45.75 \text{ g/m}^2$) then the Japanese Industrial Standard JISA 1470–1 standard ($>29 \text{ g/m}^2$).

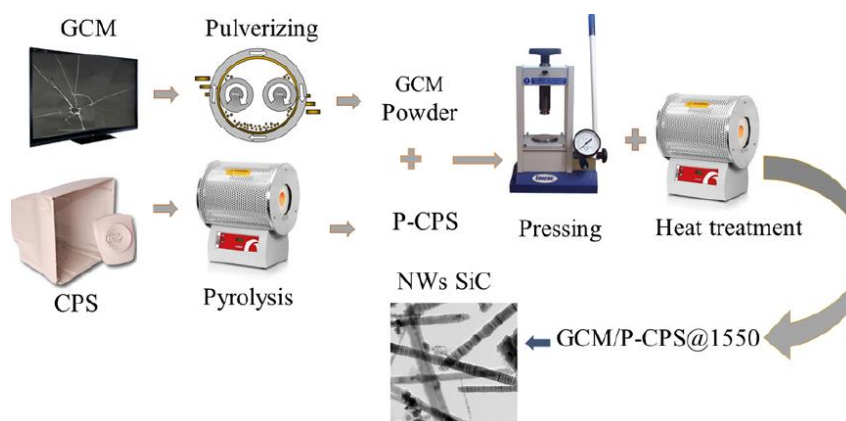


Fig. 40. Scheme of the synthesis of the silicon carbide nanowires (Maroufi et al. 2017).

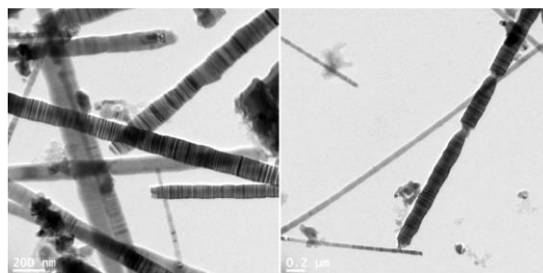


Fig. 41. High magnification of FE-SEM images of synthesized SiC at 1550 °C. and TEM images of SiC NWs (Maroufi et al. 2017).

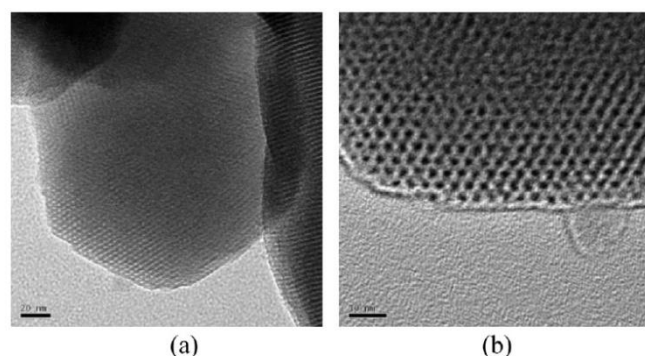


Fig. 42. High magnification of FE-SEM images of synthesized SiC at 1550 °C (Maroufi et al. 2017).

Photonic waste powder (SiCl_4) was also used as a silica alternative source for the synthesis of amine-modified MCM-41 used as adsorbent for CO_2 capture (Lin et al. 2011; Lin

and Bai 2013). The functionalized silica materials were achieved at room temperature with the assistance of hydrofluoric acid, and ammonia hydroxide in the presence of cationic surfactant, followed by the immobilization of tetraethylenepentamine (TEPA). Higher adsorption capacity was obtained compared to TEPA-MCM-41 made from pure chemicals under the same testing conditions (Fig. 43).

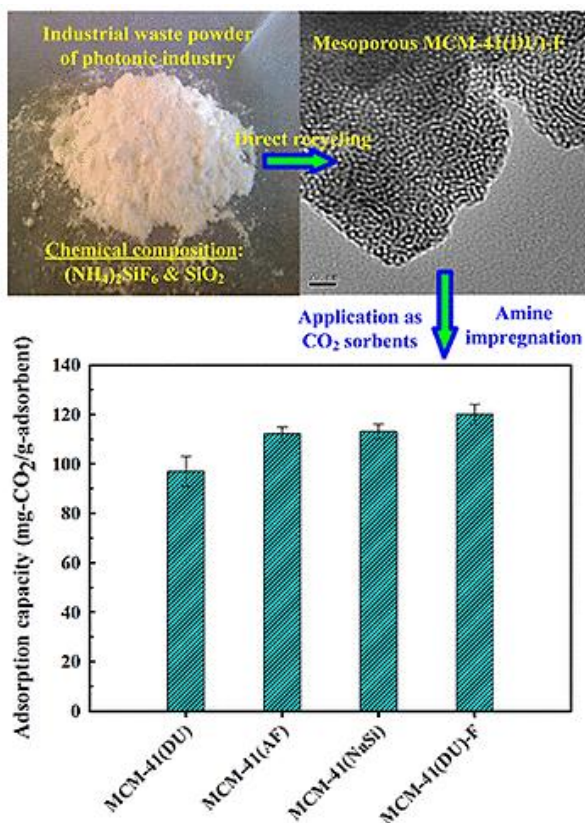


Fig. 43. Graphic abstract for recycling silica materials from waste powder of the photonic industry (Lin and Bai 2013).

As shown in Fig. 44, the silica particles derived from photonic industrial waste powder can be processed into mesoporous silica spherical particles by using the salt-templated aerosol spray approach (Lin and Bai 2012). The different approaches for silica extraction from E-wastes with different silica types are recapitulated in Fig. 45.

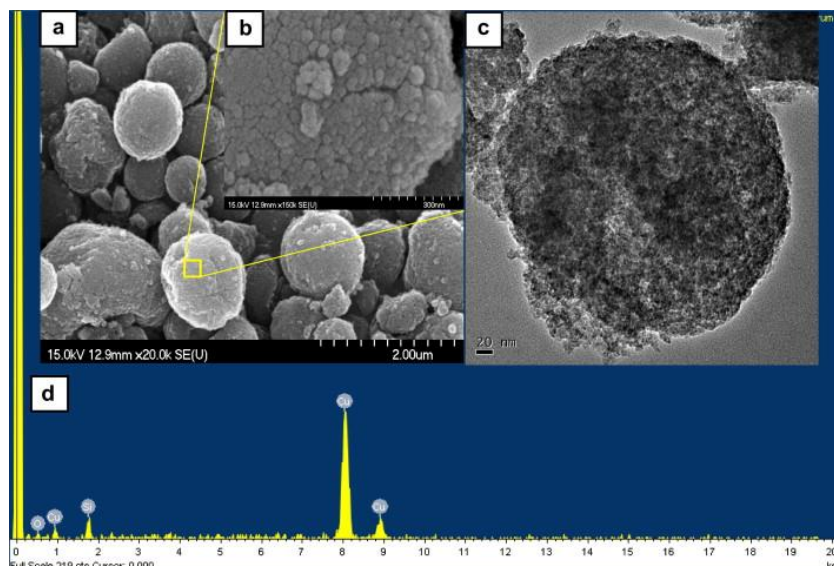


Fig. 44. SEM images (a) low-magnification, (b) high-magnification of the washed MSP (AS), (c) TEM image and (d) EDS spectrum of the washed MSP (AS) (Lin and Bai 2012).

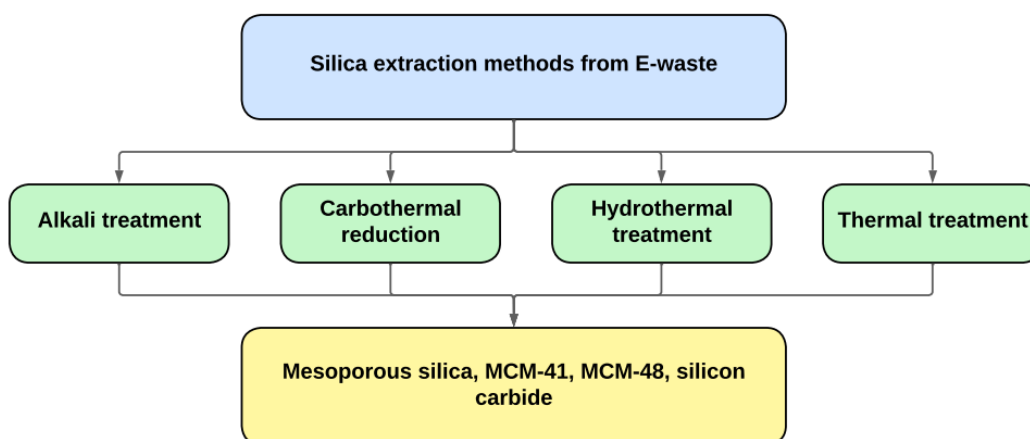


Fig. 45. Different methods for the extraction of silica and their use in the fabrication of different silica from E-waste.

4.4. Other industrial by-products

Silica production can be conducted from other different industrial wastes, such as waste powder from liquid crystal (Lin et al. 2013), automotive glass (Farzana et al. 2016). For example, waste glass bottles were used to produce silica gel particles with 85-459 nm size via a sol gel technique by changing the ratio of waste glass/NaOH to optimise the production of silica particles. The silica gel was tested for the reduction of free fatty acid FFA to refine waste cooking oil, showing an adsorption efficiency of 91 %, depending on changing patterns of the density according to the temperature and the refractive index properties (Sudjarwo and Bee 2017). The industrial waste of metallurgical silicon of sodium-based slag was also used for the synthesis of mesoporous silicon (Huang et al. 2018). Starting with the leaching of grinded slag with HCl, followed by calcination at 700 °C, and dispersion of silica in NaCl, to produce

subsequently the silicon by Mg reduction, followed by leaching with HCl, as simplified in Fig. 46. Furthermore, as shown in Fig. 47, the prepared nano-silicon possess a nanosized particles with highly mesoporous network with a surface area of $75.5 \text{ m}^2 \cdot \text{g}^{-1}$ and a pore size of 3.7.

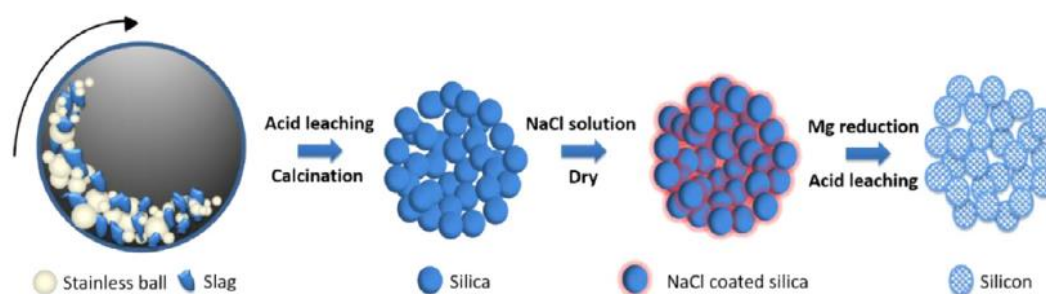


Fig. 46. Scheme of the method to prepare porous silicon from sodium slag (Huang et al. 2018).

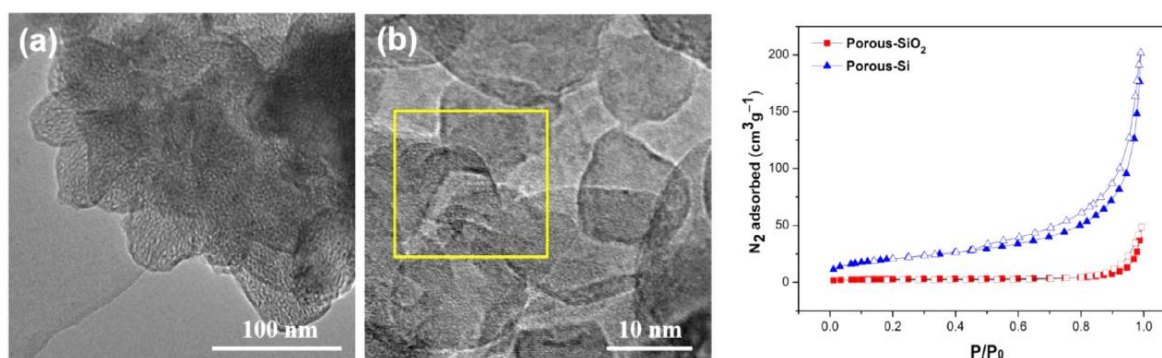


Fig. 47. (a) Low-magnification, (b) high-magnification TEM images and (c) N₂ adsorption and desorption isotherms of the prepared nano-silicon (Huang et al. 2018).

The electrolytic manganese slags EMS, the by-product of the industrial production of manganese dioxide, was also used for the synthesis of mesoporous silica using amino-ended hyperbranched polyamide AEHPA as a template (Zhang et al. 2017). The study revealed that AEHPA molecular weight is a key parameter to control the surface area and pore size of the mesoporous silica. However, the silica recovered is not totally pure, containing only 93,1 wt % of SiO₂.

Using another type of slag, mesoporous silica particles with high specific area of $1199 \text{ m}^2 \text{ g}^{-1}$ were prepared from slags after SiO₃²⁻ leaching and a hydrothermal process. The coal slag was leached by hydrochloric acid to remove iron and oxides, then reacted with aqueous NaOH to prepare the SiO₃²⁻. The mesoporous silica was prepared by a hydrothermal treatment by mixing the precursor solution with a CTAB solution, while adjusting pH by hydrochloric acid. The adsorption behavior of the prepared mesoporous silica was then tested for metal ions using Pb²⁺, Cu²⁺, Co²⁺ and Cd²⁺ (Zhang et al. 2019).

In addition, coal fine slag was used for the synthesis of mesoporous silica with a simple leaching method, (Liu et al. 2019) which was then tested in the adsorption of cationic dye methylene blue, demonstrating an adsorption capacity of 140.57 mg.g^{-1} due to the combination of electrostatic interaction and hydrogen-bonding. Another innovative work used coal slag and CO_2 storage material ($\text{CO}_2\text{-SM}$). Silicon was extracted using an acid leaching and the leached solution was then added to CTAB and the $\text{CO}_2\text{-SM}$ for a hydrothermal treatment. The obtained mesoporous silica was tested for the adsorption of phenol with a strong adsorption of 106.2 mg.g^{-1} (Yang et al. 2019). A recent study described the utilization of blast furnace slag BFS for the synthesis of mesoporous nanosilica with high surface area (Fakhar and Jiang 2020). In this case, BFS was grinded and calcined to remove organic elements, then nitric acid was used to remove metal components, afterword CTAB was used for the synthesis of the nanosilica.

To sum up, Fig. 48 illustrates the different alternatives sources that have been discussed in this review for the synthesis of nano silica particles and their hybrid composites. Several approaches were employed for the extraction of silica from low-cost and eco-friendly silica sources ranging from natural minerals and agricultural to the industrial wastes, producing different silica types used in various applications in an attempt to minimize the possible impacts on the environment and human health of inadequate disposal of these wastes, mainly because they are alternative, abundant, renewable, low-cost, and eco-friendly silica sources.

5. Challenges and prospect of research

The concept of reduce, reuse and recycle has been encouraged as a sustainable solution for the growing environmental issues caused by wastes and by-products of different industries. Thus, the valorization of waste and the recovery of high value-added products is of major environmental and economical relevance. The utilization of mineral, agricultural and industrial wastes and by-products for the production of silica derived materials is a good example for the promotion of sustainability principles. However, there are several limitation regarding the valorization process. The challenges in developing silica materials and their hybrid composites from waste are mainly related to the silica source itself, i.e. its purity. Moreover, the selected extraction method is a key operation for the recovery of these high value materials. The use of acid leaching, alkali treatments and thermal processes for the extraction of silica precursors can be highly cost and energy consuming. For instance, the production of silica gel is based on the acidification of sodium silicate solution from melting quartz sand with soda ash (sodium carbonate) at a high temperature of $1300 \text{ }^\circ\text{C}$ (John Wiley and Sons 1979; E Williams 2000). In

addition, the synthesis of several commercial silica products uses high-cost templates and surfactants. Thus, the development of ‘greener’ technologies with lower energy consumption for the production of silica is highly desirable.

Nevertheless, a major gap still present between the ideas and processes generated in the laboratory and the ones needed for up-scaling these methods and for the production of these waste-generated materials on an industrial level. This gap must be closed for the concept of the reutilization of wastes to reach full-cycle processes. One of the main challenges for the scaling of silica is the consistency of the properties and quality of the produced silica to ensure the reproducibility. Silica suffers from agglomeration of particles depending of the used synthesis process and depending on the silica sources. The degree of agglomeration is a key parameter for the control of quality for several applications, such as ceramics, composites and electronics. Typically non-agglomerated particles are made by wet chemistry. These processes tend to be costly and may give products low morphological homogeneity during large-scale manufacture as they involve many process steps (Mueller et al. 2004). Moreover, there are few works providing detailed studies guiding the design and the synthesis of mesoporous nanosilica to satisfy the specific requirements of their applications. Therefore, for a successful execution of the transition from laboratory scale to industrial production, holistic research with complete understanding of the technological route and mechanisms, followed by an exhaustive studies on the economic and environmental assessment of the product/process are crucial.

On the other hand, literature data focusing on the valorization of industrial wastes is scarce compared to the one on bio-sources such rice husk which was exhaustively studied. More particularly, there are few studies on silica from fluorosilicic acid which can open opportunities in the field for researchers to develop and advance. Hence, there are still multiple aspects that need to be elaborated and the growing concern will encourage publications in this field, extending the work on functionalized silica and their composites originated from waste and natural sources to reach different industrial and technological areas such as adsorption, catalysis and fillers.

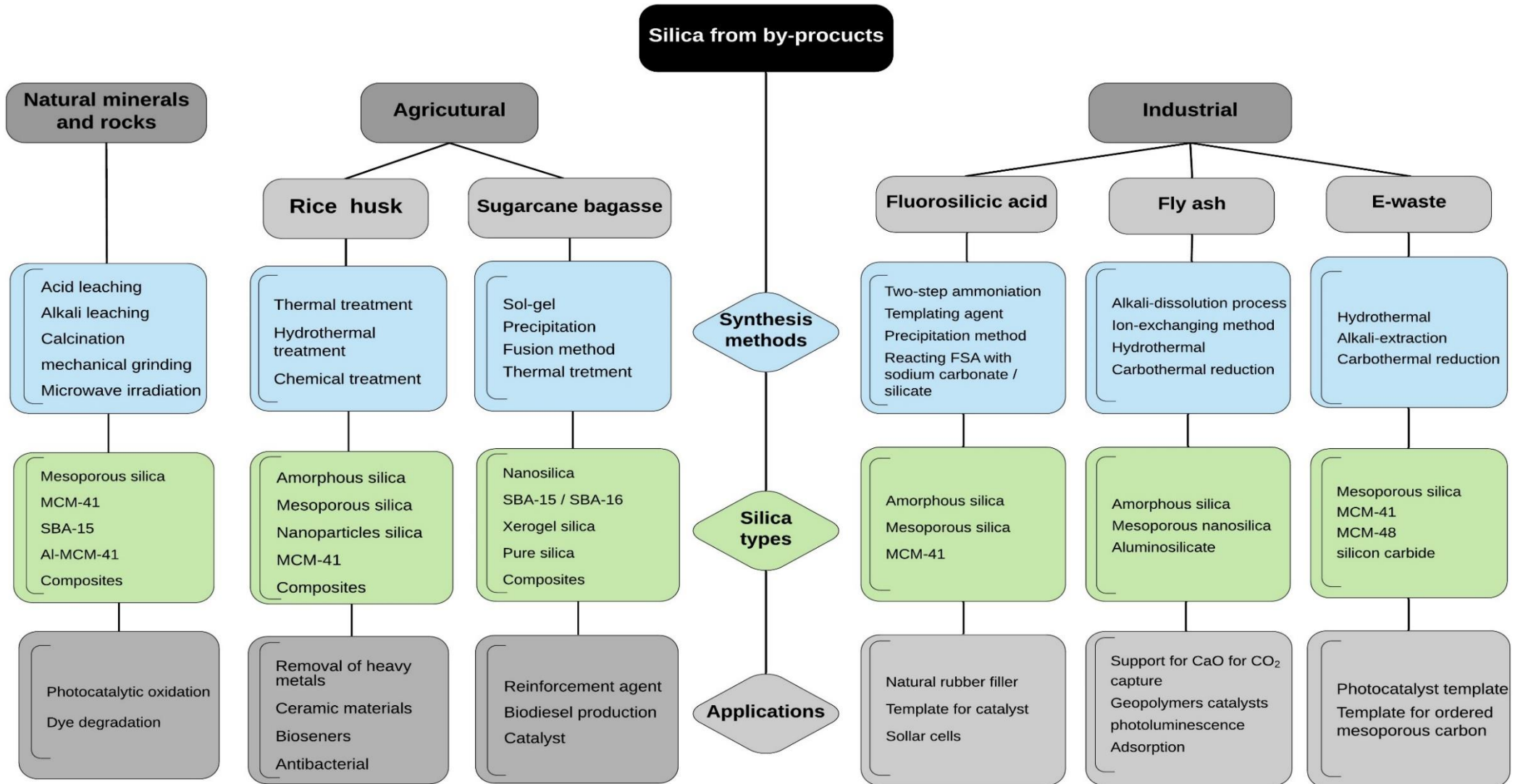


Fig. 48. Schematic illustration of the different silica wastes and their extraction methods with the different yielded silica types and applications.

6. Conclusion

Recycling by-products and wastes to produce porous structured and hybrid materials is becoming an increasingly and modern research area to insure sustainable economic systems. In this aspect, there is an emerging trend in utilizing mineral, agricultural, industrial and electronic wastes as promising silica sources. The potential valorization of these sources could be achieved using different extraction and synthesis methods. For example, while calcination, mechanical grinding, acid leaching and alkali treatment are used for the extraction of silica from natural minerals and agricultural waste. Carbothermal and alkali treatment are the used methods for this purpose in the case of industrial waste such fly ash and E-waste. As for fluorosilicic acid, less energy consuming methods are used such as two steps ammoniation, templating agent, and precipitation method. After the extraction of silica, comes the second step of processing different useful silica types with highly added value, mentioning nanostructured silica, mesoporous silica, SBA-15/SBA-16, MCM-41/MCM-48 and silica composites or porous silica hybrid materials which have been applied in different applications , such as catalyse area for the synthesis of useful chemicals and adsorption technology for the removal of pollutants in aqueous solution as well as fillers for membrane technology and thermal insulation purposes,

The selected extraction and synthetic methods shown to affect the particle size, the textural and structural properties of different silica nanoparticles and their hybrid composites and thus their application in different technological areas of catalysis and adsorption.

It was also demonstrated that the source of silica strongly affects the purity, structure and properties of silica materials which are associated to the rate of silica in waste products and also other existing residues.

It was also shown that the chosen temperature, the presence of additives or surfactants, and the used chemical treatments influence also the quality and the type of silica particles and their hybrids which can range from amorphous to different porous or crystalline materials.

However, the production of these materials is still in its early stages. Therefore, to reach an industrial level, more comprehensive cost and life cycle analysis should be done in view of all features of technical application, economic feasibility, waste management, and carbon credits.

Acknowledgements

This research was supported by Chemical and Biochemical Sciences, Green Process Engineering (CBS-GPE) department and funded Mohammed VI Polytechnic University (UM6P).

Keywords

Waste valorization; nanoparticles; mesopores; templated synthesis; hybrid materials.

Conflict of Interest

The authors have no conflicts of interest to declare that are relevant to the content of this article.

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