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PROCESS FOR RECOVERING SILICA FROM LITHOMARG CLAY: VALUE ADDITION OF UNEXPLOITEDMINING REJECT

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ABSTRACT

Physico-chemical treatment was adopted for processing alumino-siliceous lithomarg clay known as saprolite. The study explained the potential of utilizing saprolite clay as fast resource for recovering silica mineral phases for value added utilization of unused mining reject. The conversion of saprolite to silica enriched low iron precursor was achieved by chemical activation with 1:1 v/v aqueous hydrochloric acid. Recovery of nano-silicate was achieved from the low iron precursor by dissolution in aqueous sodium hydroxide followed by precipitation in acid medium and centrifugation. Physical characterization of silicate nano particle was accomplished by scanning electron microscopy (SEM) and the range of impurities was determined by inductively coupled plasma (ICP) analysis.

Keywords: mining rejects, saprolite, silica, beneficiation, nanosilica, characterization.

INTRODUCTION

Recycling of secondary resources has numerous advantages over the primary production, such as environmental benefits, energy conservation, ore conservation and economic benefits [1]. Regarding the environmental aspect, recycling of mining rejects releases fewer amounts of greenhouse gas and process byproducts. In general, these materials are refined form of resource for recovering useful mineral values therein. Therefore, the process byproducts containing various minerals can be conserved as processed resource for future uses. Additionally, huge amounts of energy also can be saved by recycling and reprocessing secondary resources. Hydrometallurgical processes are generally preferred over pyrometallurgical process to handle low grade and complex material due to their selective leaching characteristics and flexibility in the application of suitable solvents at a moderate temperature to obtain the desired chemical reactions. At large, unit operations of hydrometallurgical processes can be simplified as leaching of the desired metal into solution, concentration and purification of the pregnant solution and recovery of the mineral components [2]. Leaching is a process related to the dissolution of mineral from the raw materials or concentrates by a suitable aqueous solution having acidic or basic pH by agitation or percolation depend on the complexity of raw material. A combination of thermal treatment in the acid/alkali environment helps in the selective dissolution of some mineral phases [3].

The mining sites of non-ferrous metals such as aluminium, manganese, gold, zinc, lead, coper, etc. are prominent source for the generation of unprocessed solid rejects of high silica, alumina, iron bearing minerals for fast processing and recovery of the mineral values therein. Over a period of time these resources are investigated for recovering alumina and iron values for metallurgical and non-metallurgical uses. Still recovery option of silica from these resources were not in consideration probably due to the complexity in the material matrix and convenience of analogous resources caused storage of mining rejects in landfills.

Growing awareness of energy efficiency, low cost process implementation and sustainable utilization of mineral resources boosted exploitation of relevant secondary resources as raw materials for varieties of value-added products. Silica nanoparticles (SiO_2NP) due to their high surface-volume ratio become tremendously reactive and possess extraordinary thermal, pozzolanic, physical properties. In any material, the particle size of metal oxides determines its structure, size and other properties. [4, 5]. The SiO_2NP has become of demanding among the fields including drug delivery systems, catalysis, biomedicals, biological imaging, chromatography, sensors, liquid armors and as filler in composite materials, etc. SiO_2 nanoparticles are far superior to other materials as modifiers of polyester on account of their high transparency, low density, low cost, and easy availability [6 - 8].

A method of synthesis of SiO_2NP by the hydrolysis of tetraethyl orthosilicate (TEOS) as a precursor in alkaline medium was first proposed in 1968 [9] and possess the distinct advantages of systematic variation of reaction parameters [10] to control particle size, distribution and morphology. Reaction parameters such as reaction time, temperature gives the information about the spherical-shaped and non-agglomerated silica nanoparticles. In addition to TEOS, sodium solution (SSS) is another cost-effective precursor which has widely used for the synthesis of silica nanoparticles [11]. Accordingly, it was thought the choice of utilizing silica bearing mineral phases in processed and unprocessed rejects materials are the right option of precursor materials for replacing commercial sodium silicate. The mining industry rejects of nonferrous metals are ample and easily available. Therefor the present study exploring the possibility of utilizing alumino siliceous mining rejects of bauxite mines [12 - 14] as source materials for selectively recovering silicate mineral values for making value added nano-silicates useful for many industrial applications. The emphasis of this paper is to use saprolite mainly as the raw material for the preparation of silica nanoparticles. Alumina along with the other components such ferric oxide and titania is associated with the silica in the matrix which restrict its direct utilization for synthesis process. A range of acid leaching method is employed to remove the other metallic oxides from the mineral matrices. The high silica residue (HSR) obtained after the acid treatment is the precursor material for future silica nanoparticles preparation. The HSR further undergoes thermal treatment with sodium hydroxide at elevated temperature to form sodium silicate solution. The SSS obtained was subjected for chemical precipitation followed by centrifuge to obtain silica nanoparticles. The technical aspects of the material processing, recovery of enriched silicate followed by nano-conversion and characterization of SiO_2NP are summarized in the respective sections.

EXPERIMNTAL

Chemicals and Reagents

Chemical reagents used in the process are sodium hydroxide, (AR Grade, Qualigens, India), hydrochloric acid (Fischer, India), sulphuric acid, Whatman No 41 and No 42 grade quantitative filter paper were used for filtration. All other chemicals used were of analytical grade. Double distilled water was used for preparation of analytical reagents, experimental samples and chemical precipitation of SiO_2 nanoparticles.

Apparatus

Sample preparation trials, gravimetric and titrimetric trials were carried out at the chemical laboratory equipped with all standard analytical tools. Mettler Toledo (Switzerland) pH meter was used for pH measurements. The photometric measurements were carried out on Dual Wavelength UV Visible spectrophotometer (Thermo Scientific Evolution 201 Model 840-210800). Trace analysis was carried out by inductively couple plasma spectrometer (IRIS Intrepid II XDL, Thermo).

Raw materials

Unprocessed saprolite was selected for the study. The representative samples of saprolite (SL) were collected from the mining sites of western ghat deposit of Maharashtra, India. The bauxite mineral deposits are originated from Deccan Trap Basalt. The sample was dried at room temperature to remove excess moisture and then crushed using jaw crusher and ball milled to homogenize and sieved. The samples were passed through different meshes and different fractions of 100, 150 and 200 were collected for the study. The representative sample passed chemical and mineralogical analysis for chemical constituents as well as the mineral phases.The samples were crushed to - 25 mm size by Jaw crusher/manually (as the sample is soft in nature). For the characterization study - 200 mesh size samples have been prepared by universal mill/bond mill and thoroughly mixed using homogenizer. The representative sample was drawn by conning and quartering procedure. It is observed that at places saprolite zone consists of reddish material enrichment as band may be due to leaching/water action.

Fig. 1. Crushed natural saprolite.

Material characterization

Natural saprolite appears in white color as shown in Fig. 1. The whiteness changes with respect to the concentration of iron oxide and moisture contents. The chemical and mineralogical analysis of saprolite samples has been done by wet chemical method and XRD with XDB software, respectively. Chemical characterization of the major elements present in raw material was determined by standard wet analysis procedures [15, 16]. Saprolite is characterized by high silica SiO_2 (25 - 50 %), low iron oxide Fe_2O_3 (1.5 - 2.5 %), quite low alumina Al_2O_3 (34 - 36 %) and titania TiO_2 (3 - 4 %) content. Mineralogical analysis by XRD shows that presence of kaolinite minerals in saprolite is the characteristic feature. About 80 % alumina and silica present in the form of kaolinite. The iron oxide as alumo-goethite and titania as anatase present. Haematite, sodalite, diaspore, alumo-goethite, quarts, rutile anatase, ilmenite, gibbsite are the major mineral phases identified by XRD. The diffractograms of saprolite test sample prepared from the raw sample indicating presence of the major mineral phases of alumina, silica iron oxide and titania are shown in Fig. 2. The surface morphology of raw saprolite assessed by scanning electron microscope (SEM) specified the kaolinitic texture of the major mineral phases as shown in Fig. 3. It is noticed that crystal

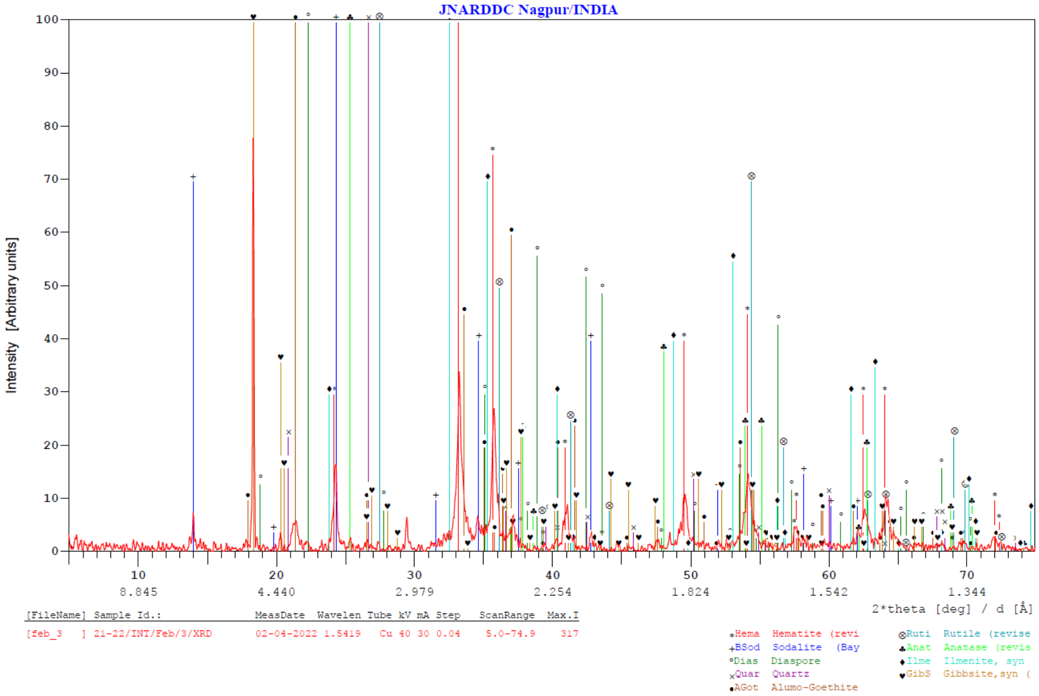

Fig. 2. XRD Diffractogram of raw saprolite.

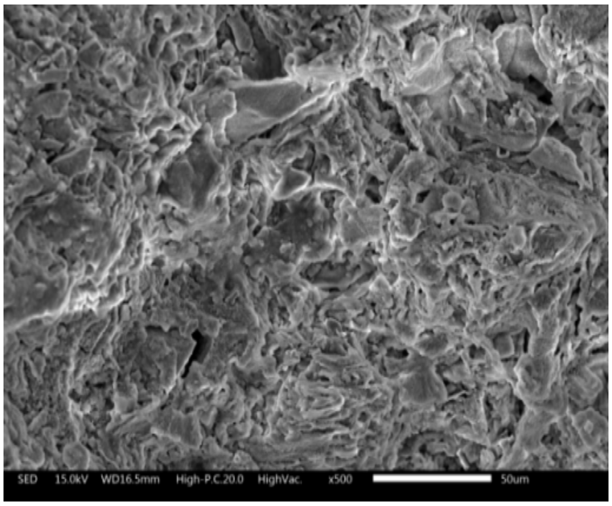

Fig. 3. SEM Micrograph of saprolite showing kaolinitic cluster.

shape and habit of minerals phases is not prominent in the raw material. Gibbsitic alumina (Al_2O_3) and quarts (SiO_2) crystalline phases were not identified in the SEM micrograph probably due the overlay of prominent non-crystalline kaolinitic phase.

Preparation of high silica residue

The finely ground saprolite sample was subjected for preliminary acid treatment and during this process an appreciable decrement in the overall amount of alumina (Al_2O_3) was observed in the silica rich precursor material, that is 1.02 %, while the silica (SiO_2) in the matrix enriches up to 64.18 % as shown in Table 2. The chemical precipitation step was then initiated involving the dissolution of calculated quantity of high silica residue (HSR) (Table 3) in alkaline medium. Subsequently the acid (Aqueous HCl) neutralization step followed by decanting excess solution and centrifugation of the gelatinous nano silicate was executed. The residue was taken out and washed several times with double distilled water and dried to constant weight for characterization by SEM and ICP. Afterward we have used the silica enriched saprolite residue (HSR) as precursor for preparation of SiO_2NP by chemical precipitation method which enabled formation of gelatinous silica nanoparticles. The centrifuged gel was washed and dried at 100 ± 2°C for surface morphology assessment by SEM to check the size of individual particle size as shown in Fig. 4. The annealed (400 ± 2°C) SiNP was used for BET surface area measurement and particle size studies. The qualitative spot analysis by EDAX confirmed Si as major constituent of the prepared nanoparticles.

Considering better purity of SiO_2NP (Table 3) compared to raw saprolite and HSR, the overall outcome to achieve value added products from the reject is found satisfactory. The ICP analysis of SiO_2NP indicated the need of further studies and systematic trails for reducing aluminium and sodium for achieving better purity for selective industrial applications of nano-silicate prepared from saprolite reject.

Chemical precipitation of SiO_2 nanoparticles

100 g of raw saprolite sample (representative sample of known chemical and mineralogical composition) was used for the study. The sample was mixed with 500 mL of 6 M aqueous H_2SO_4 solution maintaining the solid:liquid ratio 1:5 w/v and left for stirring at 90°C - 100°C on electrically controlled hot oven for 1 h. Subsequently, the wet slurry was filtered with washing to remove the acid traces from the silica rich saprolite. Afterward, 10 g of oven dried (at 100 ± 5°C) High Silica Residue (HSR) obtained was then taken in a clean dry teflon beaker and mixed with 100 mL of 5N aqueous NaOH. The reaction mixture was subjected to continuous stirring with uniform heating at 100°C for 2 h and filtered to remove the undissolved components.

Whatman No.41 filter paper was used in all filtration steps and the residue was washed several times with hot water for washing out the traces of soluble silica. The filtrate of sodium silicate (SS) solution was neutralized with dropwise addition of dilute aqueous HCl. The viscous white gelatinous precipitate of silicate was centrifuged at ambient conditions to separate water and the solid gel of SiO_2 nano-particle was washed with distilled water for removing soluble impurities. The experimental conditions for the preparation of SiO_2 nanoparticles from raw saprolite are summarized in Tables 1 - 3 and the methodology involving process steps in the preparation of high silica saprolite residue and precipitation of nanosilicate gel is summarized in Fig. 4.

Characterization of silica nanoparticles

Characterization of nano-silicate prepared from saprolite was carried out by scanning electron microscopy (SEM) at Mechanical Testing Laboratory. Morphology of the sample was assessed by standard procedure.

Table 1. Conditions used for acid leaching of raw saprolite.

Sample	Sample weight (g)	Acid & Conc. (M)	Volume (mL)	Time (m)	Temperature (^{0}C)	Solid: Liquid (w/v)	Condition
SL*	100	H_2SO_4 6	500	60	90	1:5	Stirring and heating

**SL: Saprolite*

Table 2. Characterization of high HSR**.**

Composition %				
Al_2O_3	Fe_2O_3	SiO_2	LOI	TiO_2
1.02	1.43	64.18	ND*	2.64

**ND: Not Detected*

Table 3. Conditions used for alkali treatment of HSR.

Sample weight (g)	Alkali Conc. (M)	Volume (ml)	Time (m)	Temp (^{0}C)	Solid : Liquid (w/v)	Conditions
10	5	100	120	100	1:5	Heating

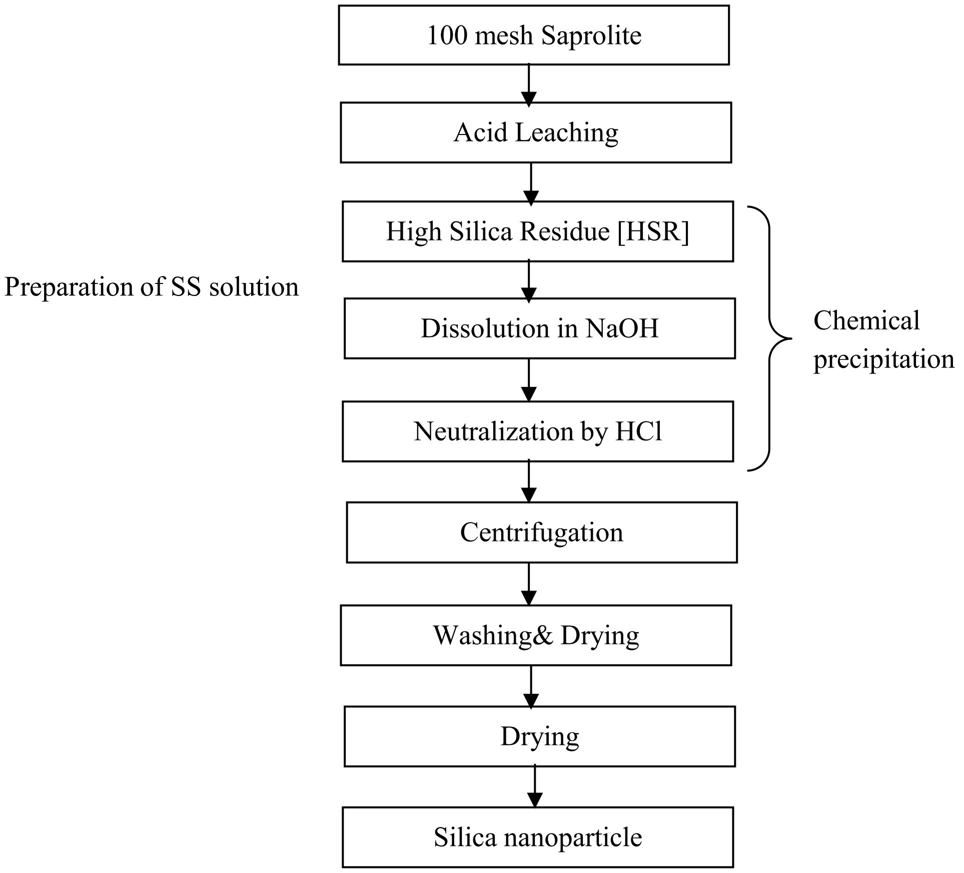

Fig. 4. Process stepwise in preparation of nanosilicate (SiO_2NP).

The SEM micrographs shown spherical well defined and agglomerated particles of nanosilicates (Fig. 5). Whereas, EDAX confirmed silicon (Si) as major constituent with oxygen in the spot analysis (Fig. 6).

Purity analysis of SiO_2NP was carried out by inductively couple plasma spectrometer (IRIS Intrepid II XDL, Thermo). The ICP analysis reported traces of impurities such as Al, Fe, Ti, Na, Ca and Mg as shown in Table 4. Al and Na are the prominent inclusion detected in the prepared nanosilicate. The purity of SiO_2NP prepared from saprolite reject was considered the difference in percentage of total and impurity.

The BET (Brunauer-Emmett-Teller) surface area and particle size of SiO_2NP was determined using a

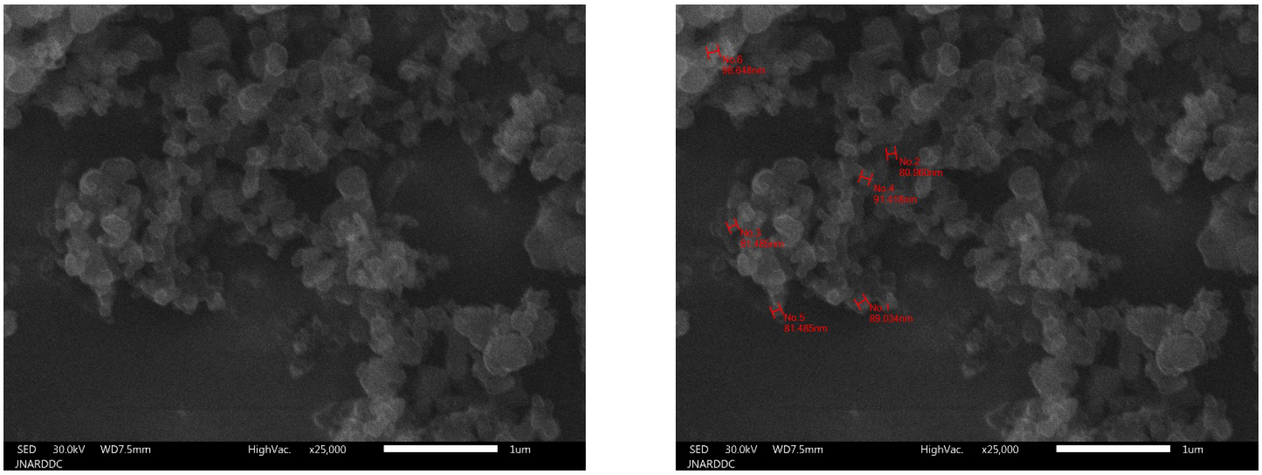

Fig. 5. SEM image of SiO_2NP prepared from SL.

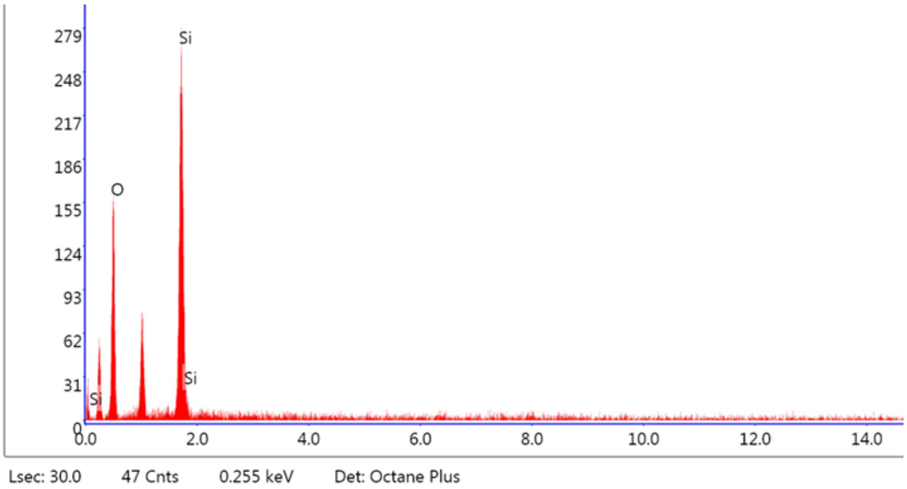

Fig. 6. EDAX analysis of SiO_2NP of SL showing Silicon (Si) and Oxygen (O).

Table 4. ICP analysis of nano-silicate prepared from saprolite.

	Constituents %					
SiO_2NP	Al	Na	Fe	Ti	Ca	Mg
	1.80	3.52	0.16	0.09	0.02	ND

** Average of three analysis; ND: Not detected; SiNP: Silica nano-particle* conventional BET multipoint N_2 physisorption apparatus to verify the large surface area to volume ratio. The analysis reported BET surface area of 72.0251 ± 0.2849 $m^2 g^{-1}$ for the SiNP (fired at 450^{o}C).

RESULTS AND DISCUSSION

The sol-gel process is widely applied to produce silica-based products like glass and ceramic materials at mild conditions. The process involves hydrolysis and condensation of metal alkoxides $[Si(OR)_4]$ or inorganic salts such as sodium silicate (Na_2SiO_3) in the presence of mineral acid or base as catalyst [3, 17]. Though the optimum reaction conditions for a particular system can be set in order to produce a desired particles size and morphology of silica particles, in the present study the effort was on the realization of converting the highly siliceous mining industry rejects into value added nanosilicate and the study was limited up to the conversion of available silica (SiO_2) in to nanosilica of particle size less than 100 nm. Characterization studies of SiO_2NP prepared from SS by scanning electron microscopy revealed the surface morphology and the SEM micrograph signposted well-defined sphere-shaped nano silicates, mostly in 80 - 93 nm as shown in Fig. 5.

The preparation process of SiO_2NP from SL involved semi-fluid silica gel to silicate transition leading to formation of solid material. Hither to it is an important step to make powdered silica nanoparticles [18]. Impact and union of the nanoparticles are the main factors that govern the extent of agglomeration in a nanoparticles powder system. Similarly, the intense ageing process that occurs during the drying of sol can lead to complex agglomeration behavior arising from polycondensation reactions [18, 19]. Since, drying of gel (in the presence of water) result in agglomeration of particles and a controlled drying process for SiO_2NP is very much in need for formation of well-dispersed silica particles. In the present study, we observed intense agglomeration of SiO_2NP as show in Fig. 4 and highlighted the need of careful efforts for achieving best result in the next stage of studies. According to the literature, the number of silanol groups per unit area of silica provides information regarding the distribution of silanol groups on the silica surface [20]. The concentration of silanol groups increases with the decrease in the particles size which is interrelated to the specific surface area. Further, it is stated that, the silanol number decrease with the decrease in the particle size suggests that these nanoparticles could be chemically reactive, therefore suitable for catalyst applications. The nanomaterial often exhibits unique physical and chemical properties compared to the bulk counterparts. The properties of nanomaterials are usually size dependent. Literatures describing the size-dependent properties of silica nanoparticles are not much available. The BET surface area analysis was carryout on fired (450^{o}C) SiO_2NP and the specific utilization of the nanoparticle prepared from SL needs more systematic studies which are beyond the scope of the preliminary investigations on converting the reject materials into value added precursor and products thereafter. Accordingly, the present study revealed the possibility of utilizing one of the major solid rejects generated at the bauxite mining areas of aluminium industry for making value added nanoparticles. The chemical and physical characteristic of the saprolite indicates 46.61 % SiO_2 which can be isolated from the matrix for different uses.

The concept of reaching zero waste has been attained in our study by utilizing the acid leached liquor obtained after the preliminary acid treatment step for enriching silica and reducing iron oxide. The leached solution consisting of all the aluminum sulphate in it has been utilized for alpha alumina preparation that has been discussed in our previous work [21].

CONCLUSIONS

The concept of applying physico-chemcial treatment for saprolite followed by chemical precipitation for value addition process developed at JNARDDC opened a new concept in the cost-effective utilization of mining industry rejects as low-cost precursor to value added processed materials. Selective chemical treatment of saprolite and other industrial rejects at selective conditions largely reduces the process cost of raw materials required for specific industrial applications involving utilization of nanosilicates. The present work identified a simple process route for preparation of Si nanoparticles from saprolite clay by thermo-chemical treatment techniques. It is expected that this work will promote the value addition and recovery of selective mineral values silicon in saprolite, laterite and similar reject materials which are plentiful for appropriate commercial exploitation.

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