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Synthesis and characterization of silica nanoparticles from clay

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ABSTRACT

We report a method to synthesize silica nanoparticles from bentonite clay. A series of thermal and acid treatment processes was performed on bentonite clay to lower the alumina and increase the silica content. The obtained silica rich clay was treated in two different concentrations (10 wt% and 40 wt%) with sodium hydroxide solution to form sodium silicate solutions (SSS). One type of SSS was hydrolyzed with three different concentrations (5 M, 10 M and 15 M) of nitric acid in the presence of ethanol as cosolvent while the other SSS was hydrolyzed with nitric acid in the presence of three different quantities (10 ml, 20 ml and 30 ml) of ethanol as cosolvent. A range of silica particle sizes from nanometer to micrometer was obtained by varying the contents of silica rich clay, HNO_3, and ethanol. It was observed that the concentration of silica rich clay and HNO_3 had a direct effect on the particle size. The increase in the quantity of ethanol from 10 ml to 20 ml produced bimodal particles of nanometer and micrometer size, which maintained at 30 ml. Inductively coupled plasma optical emission spectroscopy, atomic absorption spectroscopy, X-ray fluorescence, scanning electron microscopy and X-ray diffraction were utilized to characterize the clay, SSS and nanoparticles.

1. Introduction

Silica nanoparticles have found applications in a variety of fields including drug delivery systems, catalysis, biomedics, biological imaging, chromatography, sensors, liquid armors and as filler in composite materials [1–4]. A method for the production of spherical and mono-dispersed silica nanoparticles by the hydrolysis of tetraethyl orthosilicate (TEOS) in basic conditions was first reported in 1968 [5]. Later, the effect of concentration of TEOS, water and alkali was also studied to find a correlation with the produced silica particle size [6]. The shape and size of silica particles can also be tailored by controlling the reaction parameters such as time, temperature and solvent concentration [7].

In addition to TEOS, sodium silicate solution (SSS) is another low cost precursor used for the synthesis of silica particles [8,9]. Rice husk, rice hull, bagasse ash and semi-burned rice straw ash are some of the waste materials used for the synthesis of SSS [10–13]. Silica particles are precipitated from SSS by using acids such as hydrochloric acid (HCl) [14] as precipitating agent; carbon dioxide is also used [15].

Bentonite clay is a potential source of silica, which contains smectite as a main clay mineral. As alumina component is present in clays along with silica, a range of acid and alkali hydrometallurgical methods are employed to isolate them from each other [16–19]. Usually acids are used for the processing of clay rather than alkalis [20] and HCl is preferred over other acids due to the easy separation of filtrate from the residue [21]. For effective removal of alumina from clays, calcination is a critical step; solubility of alumina increases after thermal treatment in the temperature range of 500–900 °C [22,23]. Previously, kaoline clay was studied for the production of aluminum sulfate and it was found that heating the clay to 700 °C for 1 h followed by acid leaching with sulfuric acid (H_2SO_4) were the optimum conditions to extract alumina [18]. In another work, removal of alumina component from kaoline to produce pure alumina was studied and the recommended process involved the calcination of clay at 600 °C for 1 h followed by leaching with HCl. However, the synthesis of silica particles from bentonite clay has not been studied previously and demands investigation in this field.

In the present study, silica particles were synthesized from bentonite clay in nanometer and micrometer size range. Alumina content in bentonite clay was lowered by a series of thermal and acid treatments. SSS was derived from the clay and the solution was hydrolyzed with HNO_3 in the presence of ethanol. The effect of concentrations of clay, acid and ethanol on the particle size and morphology of silica was studied.

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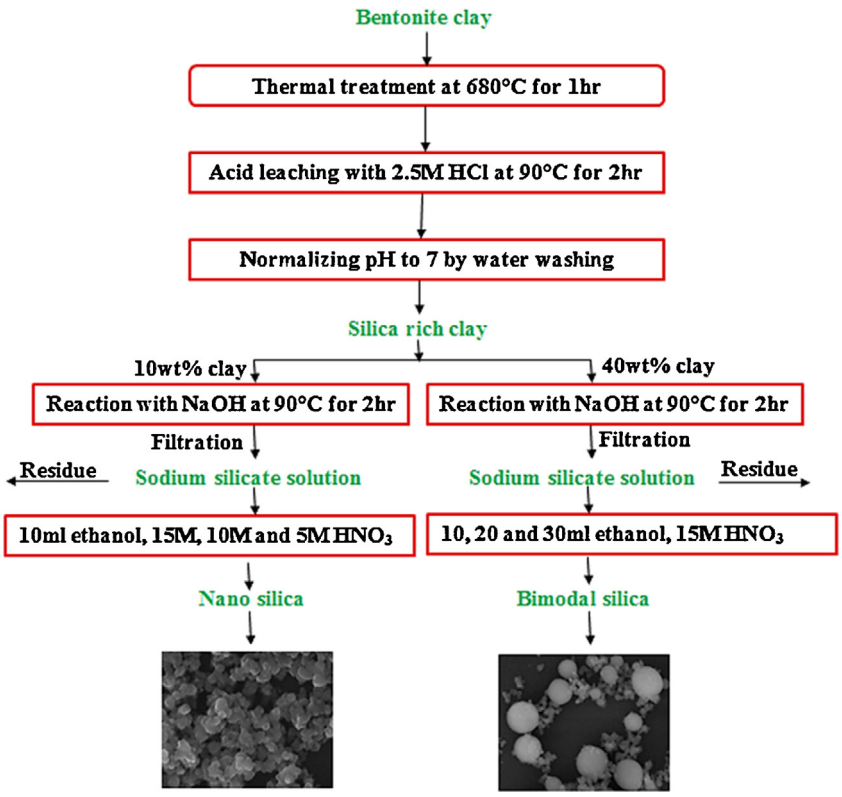

Fig. 1. Flow chart representing the process to produce silica particles from bentonite clay.

2. Materials and methods

2.1. Materials

Bentonite clay of foundry grade was provided by a local foundry. Ethanol (C_2H_6O) was acquired from Lab-Scan and 37% hydrochloric acid (HCl) was purchased from Fisher Scientific. 65% nitric acid (HNO_3) was provided by EMSURE®. Commercially available sodium hydroxide (NaOH) was purchased from local market while locally available distilled water was used during the entire process.

2.2. Methods

Bentonite clay was sieved through a mesh size of 100 μm. It was then heated at a temperature of 680 °C for 1 h in a muffle furnace. Later 100 g of clay was added in 1000 ml 2.5 M HCl solution and left for stirring at 90 °C for 2 h and filtered to separate the silica rich bentonite clay. It was then washed and filtered repeatedly until the pH was neutralized. Two different SSS were prepared by dissolving two different loadings (10 wt% and 40 wt%) of clay in 2 M NaOH solution at 90 °C for 2 h. The solution was filtered to separate residue and unwanted impurities. The obtained SSS was neutralized with HNO_3 at 50 °C in the presence of ethanol as a cosolvent. The SSS prepared by dissolving 10 wt% clay was treated with three different concentrations of HNO_3 (15 M, 10 M and 5 M) while keeping the amount of cosolvent constant. The SSS prepared by dissolving 40 wt% clay was treated with three different amounts of ethanol (10 ml, 20 ml and 30 ml) while keeping the acid concentration constant; the details are given in Table 1. The neutralized solutions were centrifuged and the obtained silica particles were washed repeatedly to remove the impurities including sodium. A graphical abstract of the process of synthesizing silica particles from bentonite clay is given in graphical abstract and the flow diagram of the process is represented in Fig. 1.

Table 1
Details of experiments including clay concentration and experimental conditions for the synthesis of silica particles.

Clay (wt%)	Sodium silicate solution (ml)	Nitric acid concentration (M)	Ethanol (ml)	Particle size
10	50	15	10	98 ± 20 nm
10	50	10	10	86 ± 11 nm
10	50	5	10	69 ± 8 nm
40	50	15	10	223 ± 68 nm
40	50	15	20	169 ± 53 nm 1.3 ± 0.2 μm
40	50	15	30	99 ± 23 nm 1.4 ± 0.3 μm

2.3. Characterization

Compositional analysis of as-received bentonite clay and silica rich clay was performed by X-ray fluorescence (XRF) (WD XRD PANalytical). Elemental analysis of SSS obtained from silica rich clay was performed by inductively coupled plasma optical emission spectroscopy (ICP-OES) (IRIS ICP-OES, Thermo Jarrel Ash). Quantification of the sodium present in the SSS was performed by using atomic absorption spectroscopy (AAS). X-ray diffraction (XRD) of bentonite clay (before and after thermal treatment) and silica nanoparticles was performed for the phase analysis (Broker D8 Advance, CuKα, λ = 1.54184, Step size = 0.02045 and scan speed is 190 steps per minute). Before XRD analysis, the samples of silica particles were washed with 8 M HCl solution to remove the sodium and other impurities. Morphological examination and size measurement of silica particles was performed by using field emission gun scanning electron microscope (FEG-SEM) (Mira 3 TESCAN). For SEM, silica was dispersed in ethanol and then dropped on glass slide followed by carbon coating. For the average particle size and