Precipitation of Barium Sulphate from Sulphate-Rich Acid Mine Drainage

M.J.Alegbe[1, 2], B.A. Moronkola[1] and Omowonuola A.A[1]

[1]Department of Chemistry, Lagos State University, Ojo Lagos Badagry-Expressway, Nigeria

[2]Environmental Nanoscience Group, Department of Chemistry, University of The Western Cape, Private Bag X 17, 7535, Belle Ville, Cape Town, South Africa

ABSTRACT

Sulphate-rich acid mine drainage (AMD) generated by some mining industries is a serious issue to water treatment industry operators and the South African government. The aim of carrying this study is to reduce if not completely remove the high concentration of sulphate in the AMD by using reagent grade chemical barium chloride. Precipitation technique was used to synthesize barium sulphate from sulphate-rich acid mine water with the addition of barium chloride solution to form a white precipitate. The precipitate formed was characterized using analytical techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HTREM), Fourier transform infra-red (FTIR) spectroscopy and Brunauer-Emmett-Teller (BET). Synthesized barium sulphate was compared with reagent grade synthesized BaSO4 was characterize with XRD to identify the mineral phase, while SEM and HRTEM revealed similar morphology and the BET surface area for both synthesized and reagent grade barium sulphate crystals were determined to be 7.7 m^2/g and 68 m^2/g. The results from this study shows that sulphate in the acid mine water can be used to synthesize barium sulphate.

1.0 Introduction

Barium sulphate is an inorganic compound that is commonly known as barite is a white crystalline solid which is odourless and insoluble in water and it is inert in many chemical reactions. It is suitable for many diverse purposes because of its high specific gravity (4.5), opaqueness to X-rays, inertness and whiteness [1], [2]. Barium sulphate ($BaSO_4$) can be extensively used to investigate precipitation and crystallization processes [1], [3], [4]. It is mainly used as radio contrast agent, coating or filler in plastics, extender and pigments in paints, additive in pharmaceutical products and printing ink. Barium sulphate has some properties such as white or yellowish powder or crystals colour, odourless, melting point (1580°C), density (4.25 - 4.5 g cm^{-3}), also insoluble in water, dilute acids, and alcohol. It has industrial relevance due to some of its properties such as opacity to UV and X-rays radiation [2], [5];. $BaSO_4$ can be extensively used to investigate precipitation and crystallization processes [1], [3]. In this paper, we are trying to use sulphate in acid mine drainage (AMD) solution as a source of raw material or alternative to reagent grade sulphate chemical to synthesize barium sulphate crystals. Several methods of synthesizing barite nanoparticles have been reported in the literature some of which are micro-emulsion system [6], [7], precipitation [2], [8], [9][10], sol-gel [1], reactor [11] , membrane reactor , hydrothermal. $BaSO_4$ can be simply prepared by precipitation of Ba^{2+} with SO_4^{2-} in batch or semi-batch reactor tanks and sonochemical [12]. It can be used as enhancer in other industries such as cosmetics, pigment, offshore oil, and ceramics [13]. However, co-precipitation method is a low cost technique which is suitable for mass production than the other methods mentioned. Although, it is difficult to synthesize a uniform size $BaSO_4$ crystal by precipitation method due to the fact that it is difficult to mix reactants in the reactor.

2.0 Materials and method

2.1 Chemicals

Reagent grade barium chloride salt (AR) was purchased from Merck chemicals. Ultra-pure water produced by Milli RO-milli Q system was used throughout the synthesis process.

2.2 Sample and sampling technique

Two samples of AMD were collected randomly at different locations from West Rand Uranium mine situated in Gauteng Province in the Federal Republic of South Africa. The samples were stored in a plastic container and store in a refrigerator regulated at 4°C.

All chemicals used include absolute alcohol, barium chloride which are reagent grade merck chemicals and used without further treatment or purification.

2.3 Study Area

This is the map of the areas where the samples used to conduct this research study were collected. The acid mine samples were collected from two areas of West Rand Uranium mine: Rand Uranium (RUD) mine and Rand Uranium shaft 8 (RUS8) located in Gauteng Province, South Africa. The map of the sample location is presented in Figure 1.

2.4 Method

About 100 mL of acid mine drainage (AMD) was measured into a 500 mL beaker and agitated with a magnetic stirrer at 350 rpm speed. 30 mL of 1 M barium chloride

Tele:
E-mail address: alegbemj@gmail.com

solution was added to the AMD in a drop wise manner which results in the formation of white precipitates. The precipitate formed from the addition of barium chloride to the AMD was constantly agitated for a contact time of 30 minutes in order to achieve homogeneity. The precipitate mixture was filtered off, washed with 100 mL of ultra-pure water thrice and dried in a regulated oven at a temperature of 80°C for 3 hours. The dried precipitated was grounded gently by agate mortar before characterization.

$$BaCl_2 \text{ (aq)} + SO_4^{2-} \text{ (aq)} \longrightarrow BaSO_4 \text{ (s)} + 2Cl^- \text{ (aq)}$$

2.5 Characterization
2.5.1 X-ray diffraction

Dionex ion chromatography DX 4000i was used to determine the concentration of anions present in the AMD. The mineral phases present in the dried reagent grade and synthesized crystals of $BaSO_4$ was identified by X-ray diffraction (XRD) analysis which was conducted on an Bruker axis D8 Advance X-ray powder diffractometer under CuKα radiation (λ = 1.5418 Å). The operation voltage and current at 40 KV and 40 mA, and the 2θ range from 10 to 80° in steps of 0.04° with a count time of 2s. The average crystallite size of the precipitate was estimated automatically from corresponding XRD data (using X-ray broadening technique using the scherers formula). The morphology of the synthesized barium sulphate crystal was observed by scanning electron microscope (SEM) with accelerating voltage of 20 kV. Dried sample of $BaSO_4$ was placed on the coated carbon grid and allowed to dry at room temperature before the SEM analysis was conducted using a HITACHI S-4700 electron microscope. The elemental composition was identified using EDS spectrum that is recorded with the SEM instrument. The barium sulphate was prepared by the putting small amount of the particles in sample bottles containing 5ml absolute alcohol and sonicated for 10 minutes to obtain good particle dispersal on the copper grid and allowed to dry at room temperature. The morphology and particle size of the $BaSO_4$ was examined by Phillip Technei-F20 super-twain transmission electron microscopy (TEM) and the crystallinity of the crystals was conducted at an accelerating voltage of 200 kV. Fourier transform infrared (FTIR) analysis was conducted on the barium sulphate crystal to identify the functional groups present in the sample. The barium sulphate crystal was scanned within the range of 400 to 4000 cm^{-1}. The Perkin Elmer FTIR spectrometer was used for recording the IR spectra crystal sample. The instrument was calibrated the spectra of a standard polystyrene film at room temperature. The barium sulphate crystal was prepared in pellet form before subjecting it to FTIR analysis and the spectra was recorded. Surface areas (BET area) of the $BaSO_4$ precipitates obtained from AMD was measured at a temperature of 77.35K using nitrogen adsorption method with a Quantachrome NOVA 2000 surface analyzer. Before the surface area analysis, the samples were prepared by washing the particles with acetone and drying them at 120°C for 5-8 hours under the flow of nitrogen.

Table 1: Analysis of anions present in two AMD samples: RUD Rand Uranium Decant, RUS8 = Rand Uranium Shaft 8, n = 3

Sample	RUS8 (mg/L)	RUD (mg/L)
Cl^-	56.64 ± 0.18	67.84 ± 1.10
NO_3^-	20.08 ± 0.67	61.41 ± 1.08
SO_4^{2-}	2848 ± 48.5	4994.07 ± 68.50

3.0 Results and Discussion
3.1 Analysis of AMD

The AMD samples collected from two mining sites were analysed using IC for the anion composition presented in Table 1. The elemental analysis shows that the concentrations of Cl^-, NO_3^-, and SO_4^{2-}. However, the anion analysis of the 2 samples showed that the concentration of Cl^- was higher than that of NO_3^- but sulphate was predominant anionic species from both sources. RUD sample was the most suitable AMD used for synthesis of barium sulphate because of its high sulphate concentration (4994.07 ± 68.50 mg/L).

3.2 Characterization

Figure 2 presents the X-ray diffraction patterns of the reagent grade and synthesized barium sulphate precipitates obtained from the AMD. The X-ray diffraction patterns of the crystallite showed some spectral peaks of barite mineral phase with reflection angles of 2θ which corresponds to (020), (101), (111), (200), (021), (210), (121), (211), (002), (221), (022), (230), (122), (311), (212), (041), (132), (330), (312), (113), (142), (123), (250), and (332) lattice plane of pure orthorhombic crystalline barium sulphate. The spectrum of the barite crystals contained all the major peaks referring to JCPDS file No. 24-1035 which is in good agreement with the results reported in the literature (Zhao et al, 2007; Romero-Ibarra et al. 2010; Sun et al. 2013; Wang et al. 2005; Wu et al, 2013). The mineral phase of the crystal precipitate was barite.

SEM images of reagent grade (A) and synthesized (B) barium sulphate ($BaSO_4.2H_2O$) are presented in Figure 3. $BaSO_4$ was observed under SEM, revealed a star-like image with lamellar arrangement like flower petals. The SEM images were taken at a magnification of 60, 000 kv and the crystal size distribution of the barite in Figure 3 gave an average particle size diameter of 0.03 μm. Figure 4 presents the EDS elemental composition (a) and crystal size distribution (b) of the precipitated obtained from the AMD using barium chloride. The analysis showed that the precipitate was composed of C (10%), O (28%), S (9%) and Ba (54%). The presence of carbon in the precipitate can be attributed to the carbon coat used to hold the sample on the grid. The Energy-dispersive X-ray spectroscopy (EDS) spectral analysis of the barium sulphate crystal in Figure 5 revealed the spectra of elements such as Ba, S and O. Figure 6 presents the shape of the single-crystal of HRTEM image (a) and SAED (b) pattern of barium sulphate crystal precipitated from AMD using barium chloride. The shape of the $BaSO_4$ crystal is a 10 petal-like lamella structure with some snow-flakes and agglomeration at the top of the image [13]. The particle size of the barium sulphate crystal was measured to obtain an average size diameter of 14 nm using image J software. The selected area electron diffraction (SAED) pattern of the barium sulphate crystal was recorded by focusing the electron beam at the brim of the sphere. The result shows the crystals to be polycrystalline in nature because of the scattered white particle spots around the diffraction ring.

The FTIR absorption spectra analysis of barium sulphate crystal precipitate is presented in Figure 7 and the crystal was scanned between 400 and 1600 cm^{-1}. The observed FTIR absorption spectra of the barite crystal in Figure 6.4 showed absorption peaks at 606, 634, 982, 1060 and 1191 cm^{-1}. The absorption bands at 1060-1191 cm^{-1} are assigned to S-O stretching of inorganic sulphate while the peak at 984 cm^{-1} was assigned to the symmetrical vibration of sulphate. The

absorption peaks at 606-634 cm^{-1} are assigned to bending vibrations of inorganic sulphate [9], [14], [15]. The nitrogen adsorption-desorption isotherms of barium sulphate precipitated from AMD using barium chloride is presented in Figure 8. The BET surface area of the crystals obtained in this study was 46.73 m^2/g and 7.7 m^2/g for A and B respectively. They exhibited poor porosity properties. The absorption isotherm of the barite sample is classified to be Type II which is characteristic of mesoporous materials based on IUPAC classifications and the absorption-adsorption hysteresis loop is classified as H3[16]. The BET surface area of barium sulphate crystals obtained in this study were higher than some reported in the literature [17] such as 2.3 m^2/g and 6.7 m^2/g for lamellar and agglomerated tubular barium sulphate respectively [5], [18] and higher than some found in the literature.

Conclusion

In summary, barium sulphate nanoparticle can be synthesized from acid mine drainage (AMD) by precipitation using barium. The use of barium ions have been reported to be very effective for the removal of sulphate ions in acid mine water and waste chemical solutions. The XRD analysis of reagent grade and synthesized precipitates were identified as barite which is a mineral phase of pure barium sulphate. The diffraction analysis revealed that the particles of the precipitate are orthorhombic structure of barium sulphate. The morphology of the precipitates from both sources was identified with SEM as a star-like petal structure with lamellar and the EDS spectral and elemental compositions confirmed that the presence of these elements: Ba, C, S and O on the surface of the precipitate. The HRTEM and SAED analysis of the precipitates (BaSO$_4$) revealed star-like petal lamellar structures with average particle size of 14 nm and 7.7 nm. The FTIR study revealed the presence of sulphate group in the synthesized nanoparticles. The BET surface area of the precipitate crystals A and B were 46.73 m^2/g and 7.7 m^2/g respectively. In conclusion, the use of sulphate-rich acid mine water as a substitute to the commercial reagent grade sulphate chemical salt was successful in the synthesis of barium sulphate nanoparticle. The quality of the reagent grade and synthesized barium sulphates were almost the same.

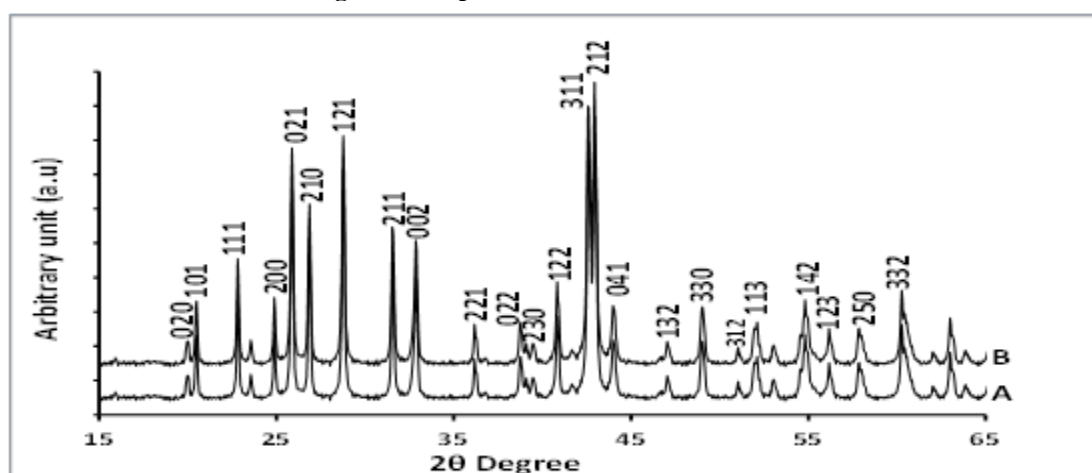**Figure 1. Map of West Rand Uranium mine**

Figure 2. Powdered XRD pattern of reagent grade (A) and synthesized (B) of barium sulphate crystals
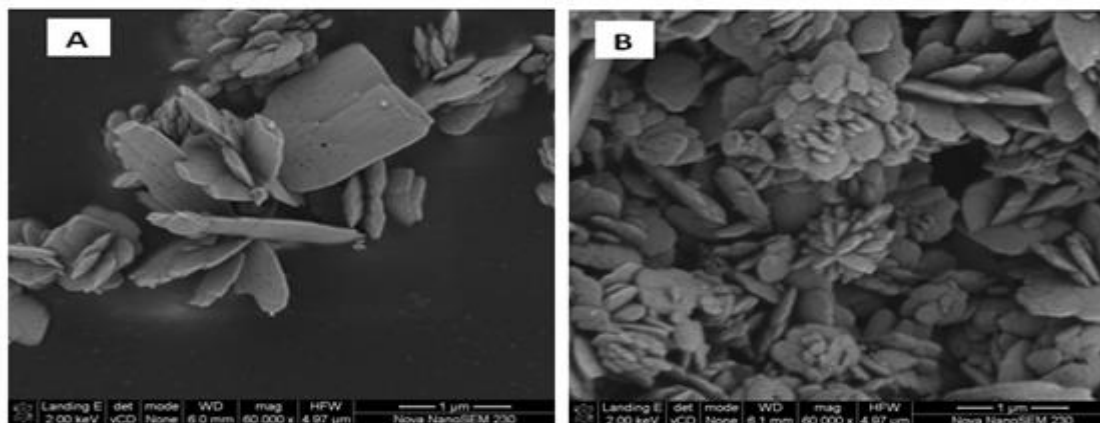
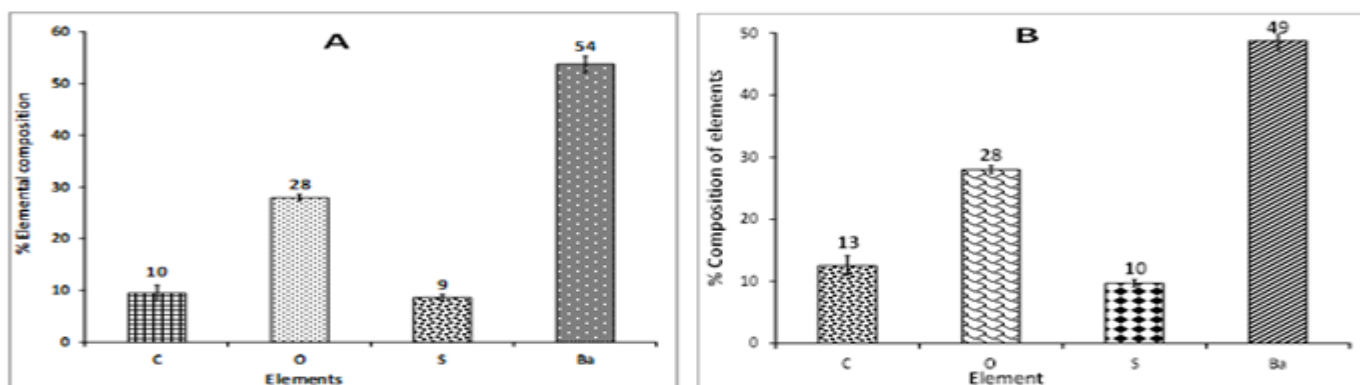**Figure 3. SEM microgram of reagent grade (A) and synthesized (B) BaSO₄ crystals**

Figure 4. EDS elemental composition of reagent grade (A) and synthesized (B) barium sulphate, n = 3.
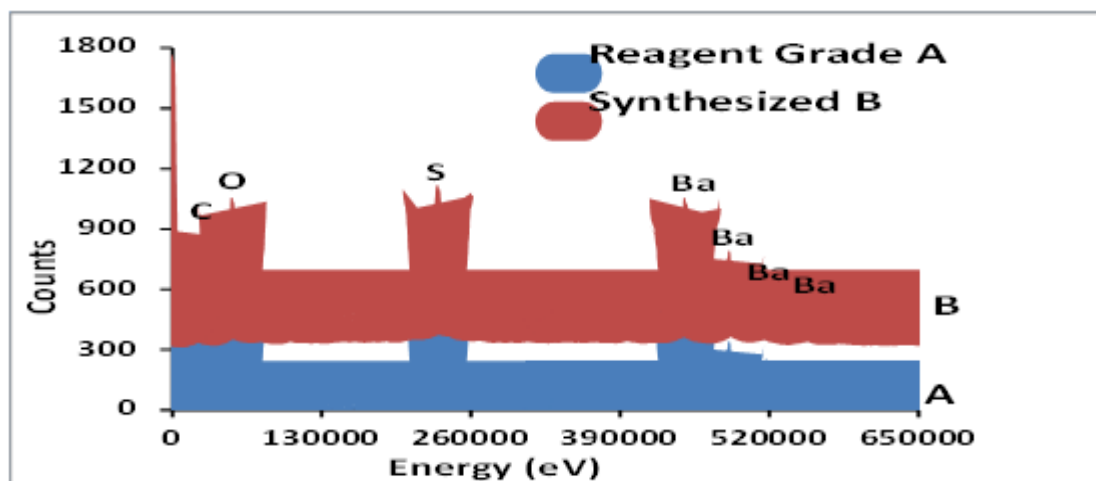

Figure 5. EDS elemental spectral analysis of reagent grade (A) and synthesized (B) barium sulphate
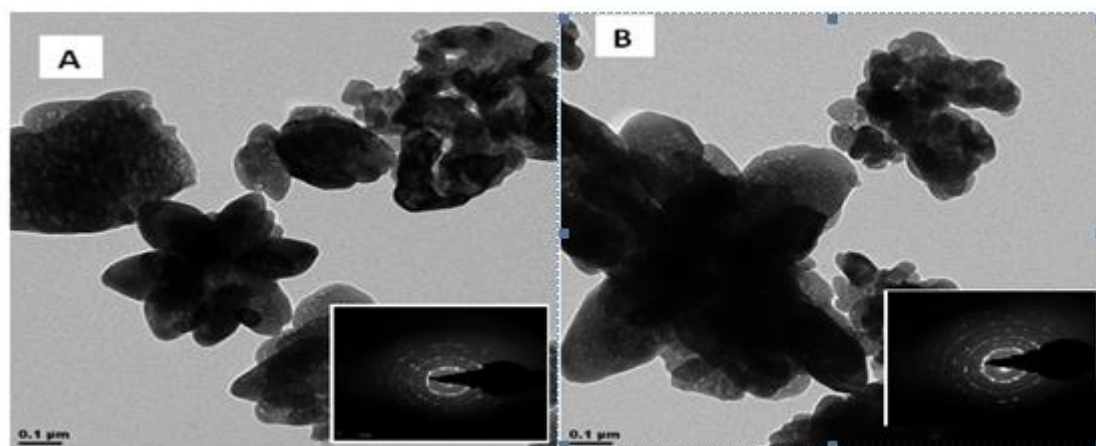

Figure 6. HRTEM images and SAED of reagent grade (A) and synthesized (B) barium sulphate
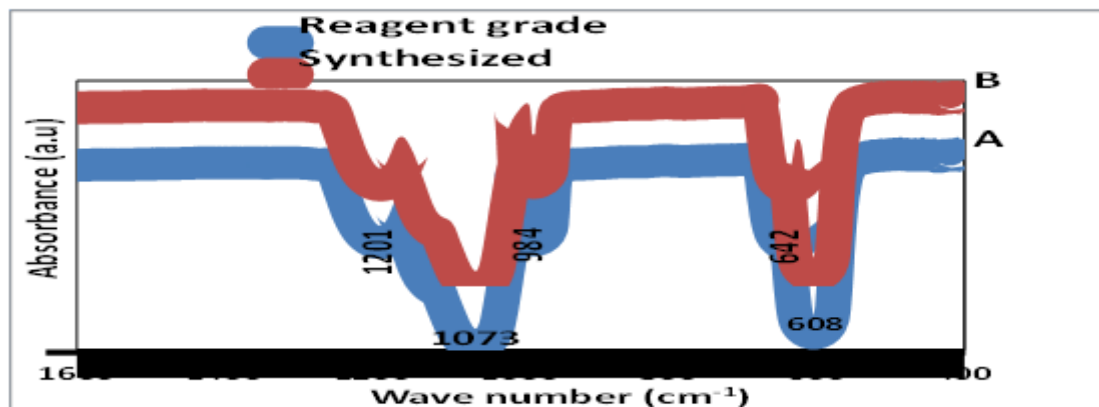
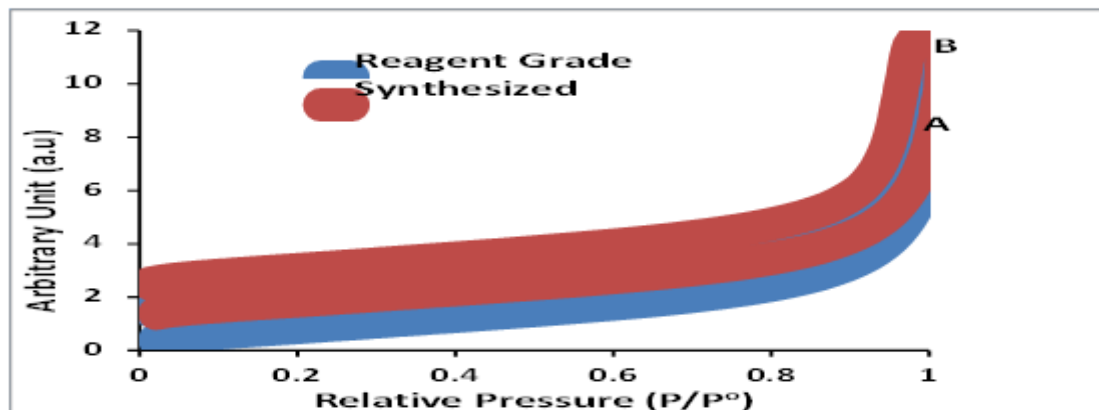**Figure 7. FTIR absorption bands of reagent grade (A) and synthesized barium sulphate precipitate**

Figure 8. Nitrogen adsorption isotherm of reagent grade (A) and synthesized (B) barium sulphate precipitate

References

[1]Ramaswamy .V, R. Vimalathithan , and Ponnusamy .V, (2010).'Synthesis and characterization of BaSO4 nano particles using micro emulsion technique.', Adv. Appl. Sci. Res, vol. 1, no. 3, p. 197–204.

[2]Romero-Ibarra, IC, Rodríguez-Gattorno, G, García-Sánchez, MF, A. Sánchez-Solís, and O. Manero, (2010). Hierarchically nanostructured barium sulfate fibers.', Langmuir, vol. 26, no. 10, p. 6954–6959.

[3]Kucher M, Babic, M, and Kind D, (2006). 'Precipitation of barium sulfate: experimental investigation about the influence of supersaturation and free lattice ion ratio on particle formation.', Chem. Eng. Process. Process Intensif., vol. 45, no. 10, pp. 900–907.

[4]Q.-A. Wang et al., (2009). 'Large-scale preparation of barium sulphate nanoparticles in a high-throughput tube-in-tube microchannel reactor.', Chem. Eng. Journal, vol. 149, no. 1, p. 473–478.

[5]Nagaraja B, Abimanyu H, Jung K, and Yoo KS., (2007). 'Preparation of mesostructured barium sulfate with high surface area by dispersion method and its characterization.', J. Colloid Interface Sci., vol. 316, no. 2, p. 645–65.

[6]Hopwood S, and Mann JD, (1997)'Synthesis of barium sulfate nanoparticles and nanofilaments in reverse micelles and microemulsions', Chem. Mater., vol. 9, no. 8, p. 1819–1828.

[7]Li M and Mann S, (2000). 'Emergence of morphological complexity in BaSO4 fibers synthesized in AOT microemulsions.', Langmuir, vol. 16, no. 17, p. 7088–7094..

[8]Wang F, Xu G, Zhang Z, and Xin X, '(2005). Morphology control of barium sulfate by PEO-PPO-PEO as crystal growth modifier.', Colloids Surfaces A Physicochem. Eng. Asp., vol. 259, no. 1, p. 151–154.

[9]Wu H, Wang C, Zeng C, and Zhang L, (2013). 'Preparation of Barium Sulfate Nanoparticles in an Interdigital Channel Configuration Micromixer SIMM-V2.', Ind. Eng. Chem. Res.

[10]S. A. Pillai et al., (2018).'In fl uence of urea on single and mixed micellar systems of Tetronics ®', J. Mol. Liq., vol. 252, pp. 9–17.

[11]Judat B, and Kind, M (2004). 'Morphology and internal structure of Barium sulfate-Derivation of a new growth mechanism', J. Colloid Interface Sci., vol. 269, no. 2, pp. 341–353.

[12]Shafi K, and Gedanken A, (1999). 'Sonochemical approach to the preparation of barium hexaferrite nan0particles', Nanostructured Mater., vol. 12, no. 1–4, pp. 29–34.

[13]Qi L, Colfen H, and Antonietti M, (2000). 'Crystal design of Barium Sulphate using Double-hydrophilic Block Copolymers', Ange. Chem. Int. Ed., vol. 39, no. 3, pp. 604–607.

[14]Akyol E, and Cedimagar M, (2016). 'Size and morphology controlled synthesis of barium sulfate', Cryst. Res. Technol., vol. 51, no. 6, pp. 393–399.

[15]Sun Y, Zhang F, Wu D, and Zhu H, (2014). 'Roles of polyacrylate dispersant in the synthesis of well-dispersed BaSO4 nanoparticles by simple precipitation.', Particuology., vol. 14, pp. 33–37.

[16]K. Sing et al., (1985). 'Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity.', Int. Union Pure Appl. Chem., p. 603–619.

[17]F. Li and G. Yuan, (2006). 'Preparation of mesostructured barium sulfate and its application in methane activation.', J. Catal., vol. 239, no. 2, p. 282–289.

[18]Chen Q, and Shen X, (2010). 'Formation of mesoporous BaSO4 microspheres with a larger pore size via Ostwald ripening at room temperature.', Cryst. Growth Des., vol. 10, no. 9, p. 3838–3842.