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SYNTHESIS AND CHARACTERIZATION OF NANOPARTICLES OF FERROUS SULFIDE BY TWO DIFFERENT STARTING MATERIALS IN THE PRESENCE OF IONIC LIQUID-CAPPING AGENT

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ABSTRACT: Room temperature ionic liquids (RTILs), a class of green and neoteric solvents, have attracted increasing interest over recent years as environmentally benign excellent alternatives to organic solvents in homogeneous and biphasic processes synthesis of several nanoparticles. A novel magnetically recoverable ionic liquid (1,1–Bis(3-Methylimidazolium-1-yl)methanechloride)-stabilized ferrous sulfide (FeS NPs) was fabricated by almost all the known a simple reduction method. Firm ferrous sulfide nanoparticles were prepared in good capitulate by reduction of ferric chloride using sodium borohydride by different reagents like thioacetamide (TAA) and sodium thiosulfate in the presence of ionic liquid such as 1,1-Bis(3-Methylimidazolium-1-yl) methane chloride. In the present investigation, FeS nanoparticles through different starting materials were synthesized and its characteristics were compared with each other. Structures were confirmed by elemental and spectral studies such as FT-IR spectroscopy, X-Ray Diffraction (XRD) analysis, Scanning Electron Microscope (SEM) analysis, Energy Dispersive X-ray spectroscopy (EDX), and Transmission Electron Microscopy (TEM) analysis.

INTRODUCTION: In recent years, metallic nanoparticles have received a lot of research due to their unique physical, chemical, and biological properties associated with their large surface-to-volume ratio and the quantum effects of inclusion [1]. In particular, the nanomaterial FeS was frequently used as a cathode for the power supply of lithium batteries [2], which are used in conjunction with copper sulfide for the production of photovoltaic solar modules with glass beams for the production of marcasite jewelry [3] *etc*. This is due to the fact that it has the property of inexpensive and non-toxic semiconductor material with a band gap of 0.95 eV.

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Iron sulfide nanoparticles and iron sulfide hydroxyl ethyl cellulose nanocomposites were synthesized from bis-(Dithiocarbamato) iron (II) single-source antecedents, with shapes differed from round to bar like with sizes in the range 23.90 – 38.89 nm for FeS_1, 4.50–10.50 nm for FeS_2, and 6.05–6.19 nm for FeS_3 [4]. Mackinawite type of FeS spherical grains [5-8], ellipsoid shaped FeS [9] and hexagon FeS nanoparticles [10] were synthesized with various methods such as spray pyrolysis method, chemical precipitation method and polyol mediated process.

Salem *et al.*, synthesized irregularly distributed spherical grains of iron sulfide nanoparticles from iron nitrate and sodium sulfide in the presence of *uncaria tomentosa* leaves aqueous extract at ambient temperature [11]. Ramasamy *et al.*, have dealt with the method to synthesize binary chalcogenides with variable stoichiometries such as iron sulfide, copper sulfide, tin sulfide, bismuth sulfide, cadmium sulfide, telluride sulfide, lead

sulfide, and nickel sulfide. Finally, routes to ternary materials, *e.g.,* copper indium sulfide, copper indium selenide, and the quaternary material copper zinc tin sulfide, were discussed [12].

Chromium is used in a variety of industries, including electroplating, leather tanning, metal processing, and dyeing. The chromium-containing wastewater discharge poses a high risk for the environment and public health due to its carcinogenicity, mutagenicity, and bioaccumulation. Chromium was mainly in the form of soluble and mobile Cr(VI) anions or precipitates of environmentally insoluble Cr(III) hydroxide, and the toxicity of the chromium in the form of solid is 100 times higher than that in the ion form. Therefore, many methodologies have been explored to the size-controlled biosynthesis of FeS NPs, and its application in Cr(VI) removal was investigated [13-21]. Furthermore, Arsenic (V) from the solution was removed by nanoscaled FeS coated with limestone synthesized biologically from iron-reducing bacteria (*Acidiphilium cryptum JF-5*) and sulfate-reducing bacterium (SRB) [22].

In this study, we present the structural studies of iron sulfide nanoparticles in different crystalline phases prepared from two different starting materials. Here ionic liquid is used as a solvent, as well as a capping agent. Among the distinctive ionic liquids, imidazolium-based room-temperature ionic liquids have pulled in impressive consideration because of their all-inclusive hydrogen bond organizes, exceptionally organized and the capacity of particles to shape traditional particle totals. Therefore, in the present work, an effort has been made to incorporate imidazolium ionic liquid (1, 1-Bis (3-methyl imidazolium-1-yl) methane chloride) as a catalyst.

MATERIALS AND METHODS: AR qualities of 1-methylimidazole, Dichloromethane, Sodium thiosulfate, Sodium borohydride, Iron chloride, Toluene, Thioacetamide were used in this study. They were purchased by Sigma Alrich. The reliability of the reagents was checked on TLC plates.

The IL- 1, 1 bis (3-methyl imidazolium -1-yl) methane chloride used in this study was synthesized according to the methods given in the literature [23].

Synthesis of Ferrous Sulfide Nanoparticles: FeS nanoparticles synthesized by a reduction method using TAA (Thioacetamide) and IL [1,1Bis (3-methylimidazodium -1-yl) methane chloride]. 0.008 mM of IL and 0.8 M of thioaceicdamide were dissolved in 100 ml of 0.8M sodium borohydride. The above reduction mixture was added to the vigorously stirring solution of 0.8 M ferric chloride ($FeCl_3$) in a 3:1 volume ratio and then the solution was stirred vigorously for uniform dissolution at room temperature for 3 h. The obtained FeS nanoparticles was separated with a magnet, washed with absolute ethanol for several times and dried in vacuum for 48 h for further characterization.

Synthesis of ferrous sulfide nanoparticles using sodium thiosulfate in the presence of 1,1Bis (3-methyl imidazodium-1-yl) methane chloride was carried out as per the procedure described above.

RESULTS AND DISCUSSION:

FT-IR Study: The assignments of the main peaks in the FT-IR spectra of FeS nanoparticles synthesized by different reagents are presented in **Table 1**. The spectral results show that starting materials play a vital role in product formation. Here FeS nanoparticles were prepared by different starting materials like thioacetamide (TAA) and sodium thiosulfate, which produce remarkable changes in the absorbed frequencies of the synthesized FeS nanoparticles.

TABLE 1: IR SPECTRAL COMPARISON STUDIES OF FeS NANOPARTICLES SYNTHESIZED BY DIFFERENT REAGENTS

Peak Assignment	Frequencies of absorption bands, cm^{-1} of FeS nanoparticle by TAA in the presence of IL	Frequencies of absorption bands, cm^{-1} of FeS nanoparticle by Sodium thiosulfate in the presence of IL
Fe-S stretching frequency	885.33	1020.34
Fe-O stretching frequency	1458.18	1419.61
-C=O stretching frequency	1730.15	1641.42
N-H stretching frequency	3433.29	3446.79

IL- 1,1-Bis(3-methyl imidazolium-1-yl)methane chloride

XRD Analysis: The XRD patterns of the FeS nanoparticle synthesized using TAA reagent in the presence of IL capping agent (1,1-Bis[3-methylimidazolium-1-yl]methane chloride) shows that the diffraction peaks at around 2θ = 15.4º, 21.0º, 23.5º, 36.5º, and 74.4º correspond to the (002), (101), (102), (104) and (306) planes, respectively for FeS nanoparticle, which attributes to the iron sulfide (FeS) [24].

The XRD models of FeS nanoparticles by sodium thiosulfate in the presence of IL have four marked peaks (2θ = 15.8, 22.2, 27.0, and 38.2 correspond to the Miller files (002), (102), (111) and (202) plans, individually. The four significant peaks in the samples are reliable with the values of the JCPDS standard values (ICDD 89-4076).

No sharp crystalline pinnacles were available in the diffractograms of the synthesized FeS nano-particles, showing that the synthesized FeS nano-particles had a low level of crystallinity. The size of the synthesized nanoparticles was determined from the Debye-Scherrer equation $D = K\lambda/\beta \cos\theta$. The average size of the iron sulfide nanoparticle was seen as 14.15 nm for nanoparticles synthesized from TAA and 10.32 nm for nanoparticles synthesized from sodium thiosulfate.

SEM Analysis: The constitution and morphology of the FeS nanoparticles synthesized from thio-acetamide in because of the IL are shown in Fig. 1a, which shows the agglomerated nanoparticles' flake shape. **Fig. 1b** shows the SEM image of FeS nanoparticles prepared by the combination of sodium thiosulfate, $FeCl_3$, and sodium borohydride in the presence of IL. It is clearly shown that the FeS nanoparticles are scales that have formed at a normal distance of approximately 20 nm. Paca and Ajibade [4] investigated the morphology of the orchestrated FeS nanoparticles that demonstrated leaf-like shapes. Additionally, Hurma *et al.*, [5] and Veloza *et al.*, [25] synthesized and detailed the round-shaped FeS nanoparticles.

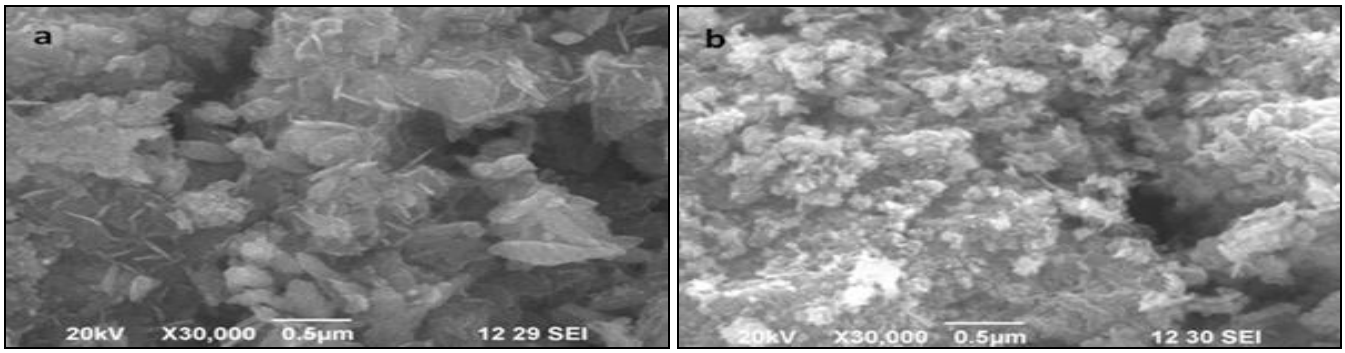

FIG. 1: SEM IMAGE OF SYNTHESIZED FeS NANOPARTICLE BY (A) TAA (B) SODIUM THIOSULFATE IN THE PRESENCE OF IONIC LIQUID

EDX Pattern: The virtue and organization of the FeS elements were investigated by Dispersive Energy X-ray spectroscopy (EDX). The results are shown in **Fig. 2a** & **b**. In the ethereal investigations of FeS, only signs of iron and sulfur were observed. From the result, it has been shown that the FeS nanoparticles produced were sufficiently pure.

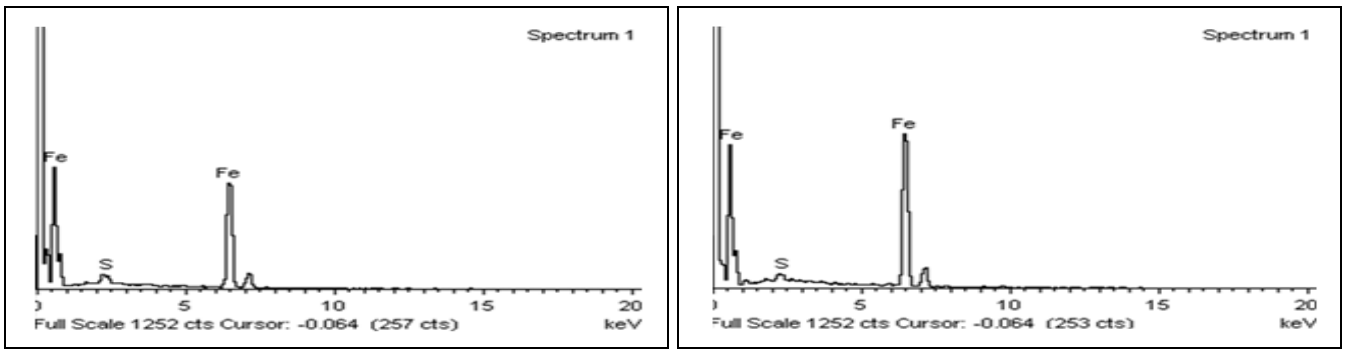

FIG. 2: EDX PATTERN OF SYNTHESIZED FeS NANOPARTICLE BY (A) TAA (B) SODIUM THIOSULFATE IN THE PRESENCE OF IONIC LIQUID

TEM Analysis:

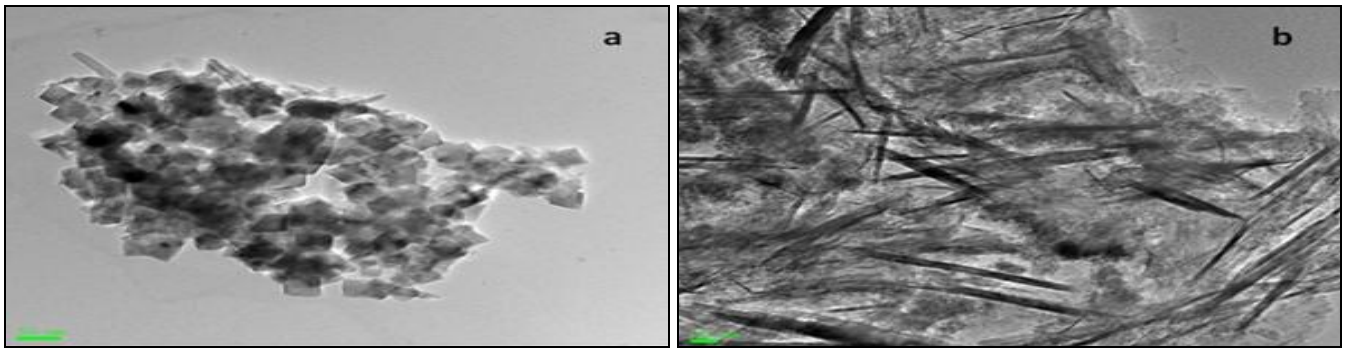

FIG. 3: TEM IMAGE OF SYNTHESIZED FeS NANOPARTICLE BY (A) TAA (B) SODIUM THIOSULFATE IN THE PRESENCE OF IONIC LIQUID

Fig. 3a and **3b** show the transmission electron microscope (TEM) image of the FeS nanoparticle synthesized by two different starting materials in the presence of IL. Examination of the micrograph of 3a shows that the morphology of the nanoparticles synthesized by TAA was cubic with smooth surfaces. The acquired nanoparticles were in the order of 20 to 25 nm. From 3b, it is obvious that the structures of the nanoparticles synthesized from sodium thiosulfate were nanorods.

Liu *et al.*, [9] had integrated 25 ± 10nm-sized accumulated flocs molded FeS nanoparticles, when preparation was made without utilizing CMC (Carboxymethyl Cellulose), and scattered circle or Ellipsoid FeS nanoparticles were formed when synthesis was carried out with CMC. Paca and Ajibade [4] integrated round to bar like shaped particles with sizes in the range 23.90–38.89 nm for FeS_1, 4.50–10.50 nm for FeS_2, and 6.05–6.19 nm for FeS_3 nanoparticles. Moreover, Salem et al. announced the TEM picture of FeS nanoparticles blended by *Uncaria tomentosa* leaves extract. They discovered the round form of FeS nanoparticles with breadth extending between 20 nm to 40 nm.

CONCLUSION: In summary, the FeS nanoparticles in cubic form and rod form were successfully synthesized by a simple reduction process using thioacetamide and sodium thiosulfate. An imidazolium-based mold-soluble ionic liquid was used as a catalyst to synthesize and stabilize the nanostructured FeS nanoparticles. The nanoparticles produced were shown in detail by field studies, such as IR, XRD, SEM, EDX, and TEM. The IR report shows that remarkable changes could be observed in the products with changes of starting materials used for the synthesis of nanoparticles. EDX investigations show that the synthesized FeS nanoparticles were not adulterated sufficiently. Moreover, the TEM results show that the size of the synthesized nanoparticles matched the XRD results. From the above distinctive examinations, it is noticed that starting materials assume a significant job in deciding the size and shape of the particles. While changing the starting materials, the size and shape of the as-formed FeS particles changed. When TAA was used, the size of the FeS nanoparticle was around 20nm and the shape was cubic fit. On the off chance that it was sodium thiosulfate the size was around 12nm, and the shape was observed to rod-like.

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CONFLICTS OF INTEREST: None

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