

Synthesis of Calcium Sulphate from Limestone Waste Collected From Ewekoro and Ibeshe Mines

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ABSTRACT

Environmental pollution from limestone mine wastes can be detrimental by reducing both the soil and underground water quality which causes water shortage and poor plant growth. The high cost of purchasing calcium sulphate in the market for industrial purposes and the high cost of treating waste generated from this mine has been a source of concern to mine operators. The aim of this study is to use limestone waste to synthesize calcium sulphate. Precipitation method was employed in the synthesis of calcium sulphate from the waste material. The synthesized calcium sulphate was analysed using analytical techniques such as X-ray diffraction (XRD), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and Fourier transform infra-red spectroscopy (FTIR) in order to analyze the quality of the products. Gypsum mineral phase was identified as the only mineral phase (CaSO_4) for the synthesized calcium sulphate which shows a cylindrical rod like morphology typical to gypsum. The EDS spectra peak shows the presence of Ca, S, and O elements confirming the mineral identified in XRD analysis. The FTIR absorption peaks of the stretching and bending vibration were identified and linked to sulphate. The quality of the synthesized calcium sulphate shows similarity with the commercial reagent grade calcium sulphate. In conclusion, limestone waste could be a suitable material for making high quality calcium sulphate.

KEYWORDS: Limestone waste, calcium sulphate, synthesis, mines, quality

1. Introduction

Calcium sulphate (CS) is a useful natural occurring salt which exist in three different forms namely: calcium sulphate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, CSD), calcium sulphate hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, CSH) and calcium sulphate (CaSO_4) anhydrite. These salts can be distinguished base on the degree of hydration (Pan *et al.*, 2013b) and it is most abundant on surface of the earth majorly as anhydrite or gypsum. Naturally, calcium sulphate is mined from the ground in the form of gypsum mineral. On the other hand, calcium sulphate can be synthesized using different techniques such as sol-gel (Kuriakose *et al.*, 2004), precipitation (Arellano-Jiménez *et al.*, 2009; Liu *et al.*, 2001; Sinityna *et al.*, 2005), water-in-oil (w/o)

microemulsions (Kong *et al.*, 2012; Rees *et al.*, 1999), hydrothermal (Arellano-Jiménez *et al.*, 2009; Sinitsyna *et al.*, 2005; Yoon *et al.*, 2005). Apparently, calcium sulphate is very useful both in chemical industrial and clinical medicine. According to Park *et al.*, (2011) calcium sulphate hemihydrate also known as plaster of Paris, is a biocompatible material which is one of the simplest synthetic bone-like grafts with a long clinical history for more than 100 years (Gitelis *et al.*, 2001; Murashima *et al.*, 2002; Park *et al.*, 2011; Scarano *et al.*, 2010; Tay *et al.*, 1999; Woo *et al.*, 2009; Yang *et al.*, 2012). Also, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) has been used as a bone graft material in several animal and was found clinically to be an effective osteoconductive scaffold which improves bone regeneration (Park *et al.*, 2011; Sidqui *et al.*, 1995). In the construction industry, calcium sulphate is one of the oldest materials used for making cement, plasters, ceramics, retardants, indoor finishing, medical supplements or implants and renders (Arikan and Sobolev, 2002; Harris *et al.*, 2004; Melo *et al.*, 2005; Papageorgiou *et al.*, 2005; Peters *et al.*, 2006; Sievert *et al.*, 2005). The aim of this study was to use limestone wastes to synthesize calcium sulphate and compare it with commercial grade sample.

2.0 Materials and Methods

2.1 Chemicals

All the chemicals used were analytical grade reagents purchased from Merck chemical company: sulphuric acid (99.5%), hydrochloric acid (37%), nitric acid (55%), calcium sulphate (99%), and sodium carbonate (90%).

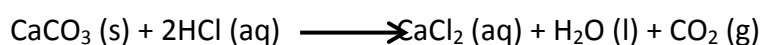
2.2 Sample collection and preparation

Limestone waste samples were randomly collected from two mines (Ibeshe and Ewekoro) in Ogun State, Nigeria. The samples were mixed and stored in different polyethylene bags to prevent the ingress of moisture.

Concentrated hydrochloric acid was diluted to 2 M HCl solution and used for decomposing the calcium carbonate in the limestone waste. 1 M concentrated sulphuric acid was diluted to 0.2 M H_2SO_4 solution and added to the acid digested limestone solution to synthesize calcium sulphate.

2.3 Synthesis of calcium sulphate

The limestone was treated with dilute hydrochloric acid to eliminate the carbon dioxide with the formation of calcium chloride solution which is the starting material for making calcium sulphate.



Different masses (2.0, 4.0, 6.0, 8.0, and 10.0 g) of limestone wastes were weighed separately into 250 mL beakers and 50 mL 2 M HCl solution was added to each sample to

generate soluble calcium ion solution which was stirred continuously for 30 minutes contact time. 30 mL of 0.2 M sulphuric acid solution was used to optimize the HCl treated limestone dosage solution by reacting H_2SO_4 with the calcium ion solution for a period of 30 minutes contact time. Different concentrations (0.2, 0.4, 0.6, 0.8, and 1.0 mol/L) of sulphuric acid solution were used to optimize the calcium ion solution using the optimized dosage for a period of 30 minutes contact time. Different contact times (4, 10, 15, 20, 35, and 30 minutes) of synthesizing calcium sulphate were optimized using the optimum dosage and concentration. The synthesis of calcium sulphate was conducted in triplicate. The precipitate formed was filtered, washed with 100 mL of de-ionized water twice before drying in a 60 °C regulated oven. The dried precipitate was weighed and returned to the oven, until a constant weight was obtained.



2.4 Characterization

After a constant weight was achieved, each of the synthesized and commercial calcium sulphate samples were analysed by using X-ray diffraction (XRD), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), and Fourier transform infrared (FTIR) analysis for phase purity, morphology and to identify related functional group. The X-ray diffraction (XRD) (XRD; D8 Advance, Bruker Inc., Germany) was conducted under $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) with operating current and voltage at 40 mA and 40 kV respectively. The samples were scanned at the rate of 0.02° (10 s per step) at diffraction angle 2θ range from 20 - 60° . FTIR analysis was conducted to identify the functional groups present in the synthesized and commercial calcium sulphate samples. The SEM and EDS techniques were used to provide available information on morphology and surface texture of individual particle as well as the chemical composition of the elements present in the calcium sulphate samples. In the preparation of sample for SEM measurement, a small quantity of sample was put on carbon coated sample holder grid or stub. A gentle blowing was applied to blow out the loosely bound particles and the remaining dust particles were stuck to the carbon coat on the sample holder enough to examine under the SEM measurement. The morphology of the synthesized and commercially purchased calcium sulphate was examined using High Resolution Scanning Electron Microscopy (HRSEM; Hitachi X 650, Japan) alongside the energy dispersive X-ray spectrometer (EDS) for surface elemental composition. The electron beam energy of 30 kV was used and the area of the sample analysed was captured at 10,000 X magnification. Each sample was mixed with KBr at different ratios to make it in pellets for the FTIR analysis. Perkin Elmer RX1 series FTIR spectrometer was used to record the IR spectra of the samples.

3.0 Results

3.1 Optimization condition for synthesizing calcium sulphate

The synthesis of calcium sulphate salt was conducted by optimizing the dosage of limestone waste, concentration of sulphuric acid and the contact time and the results are presented in Figures 1, 2 and 3.

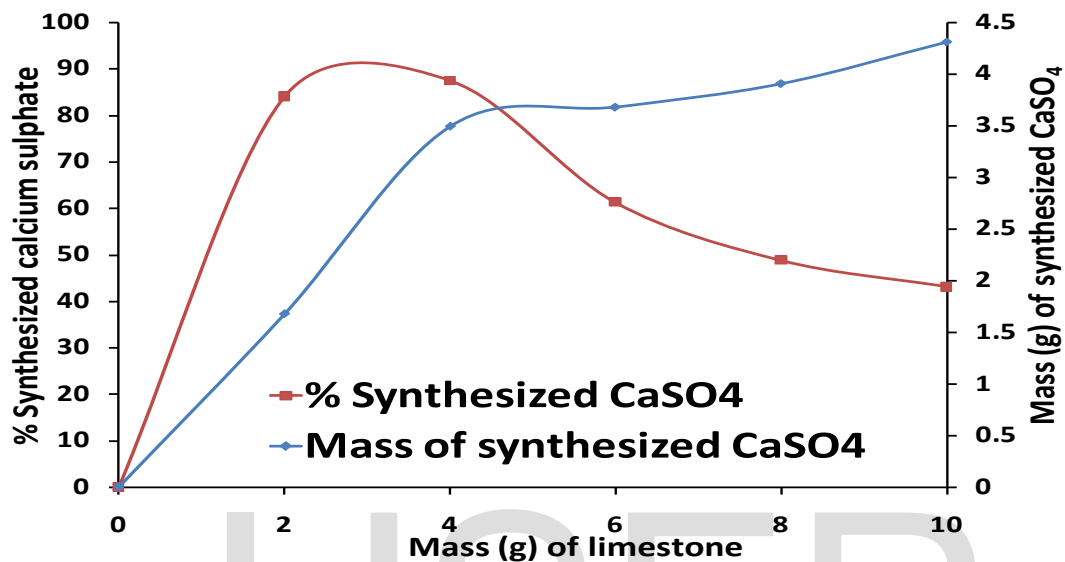


Figure 1: Dosage optimization of limestone

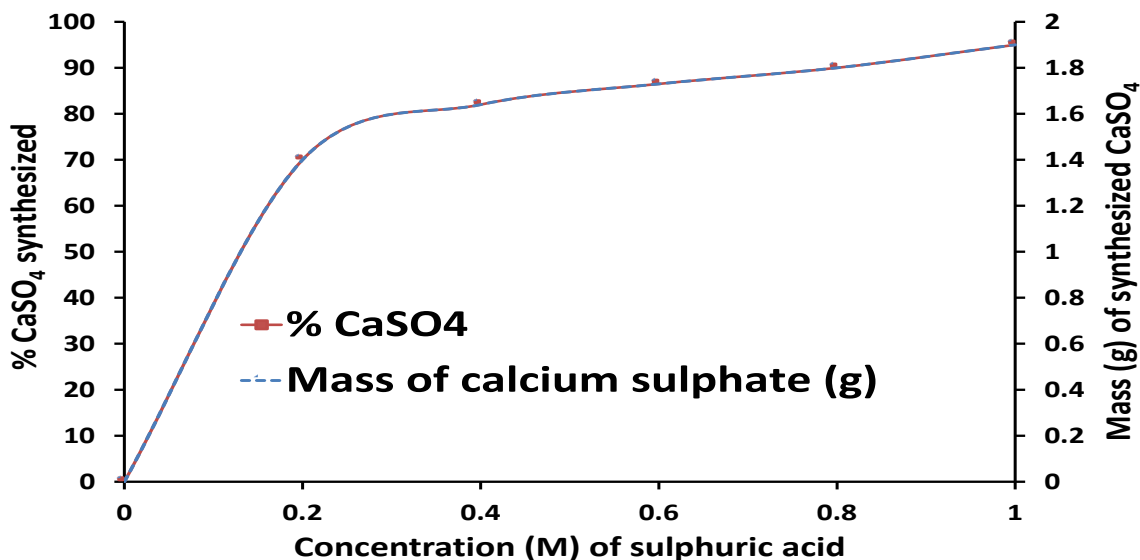


Figure 2: Concentration of sulphuric acid optimization

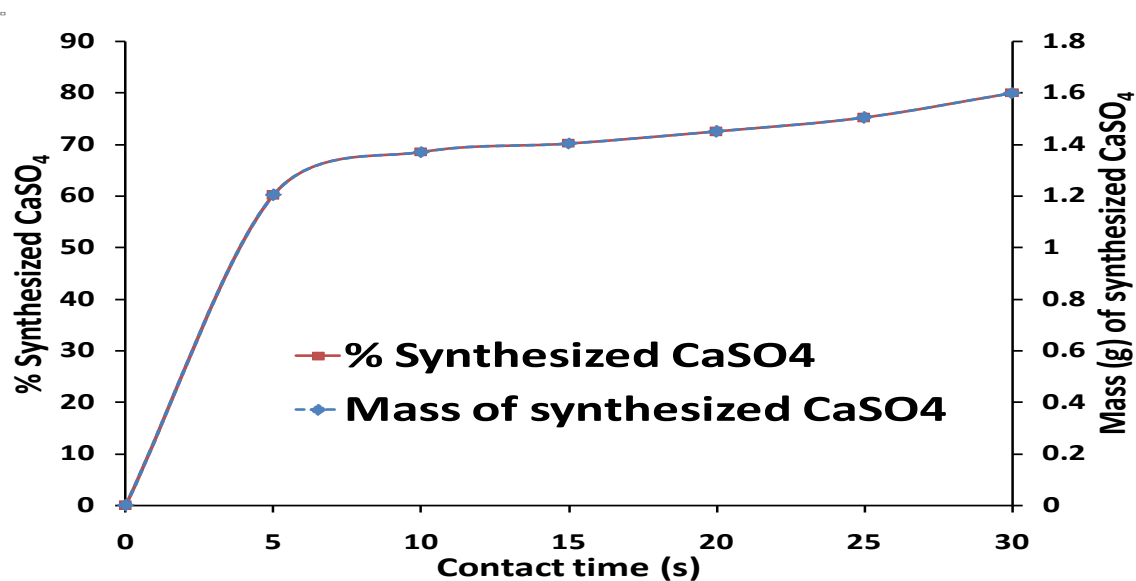


Figure 3: Contact time optimization

Figure 1 revealed that the optimum dosage of limestone waste required to synthesize calcium sulphate is 2.0 g while the concentration of sulphuric acid required was found to be 0.2 M as presented in Figure 2. In Figure 3, the optimum contact time for the synthesis of calcium sulphate was found to be 5 minutes.

The X-ray diffraction (XRD) analysis results of both the synthesized and the commercial calcium sulphate is presented in Figure 4.

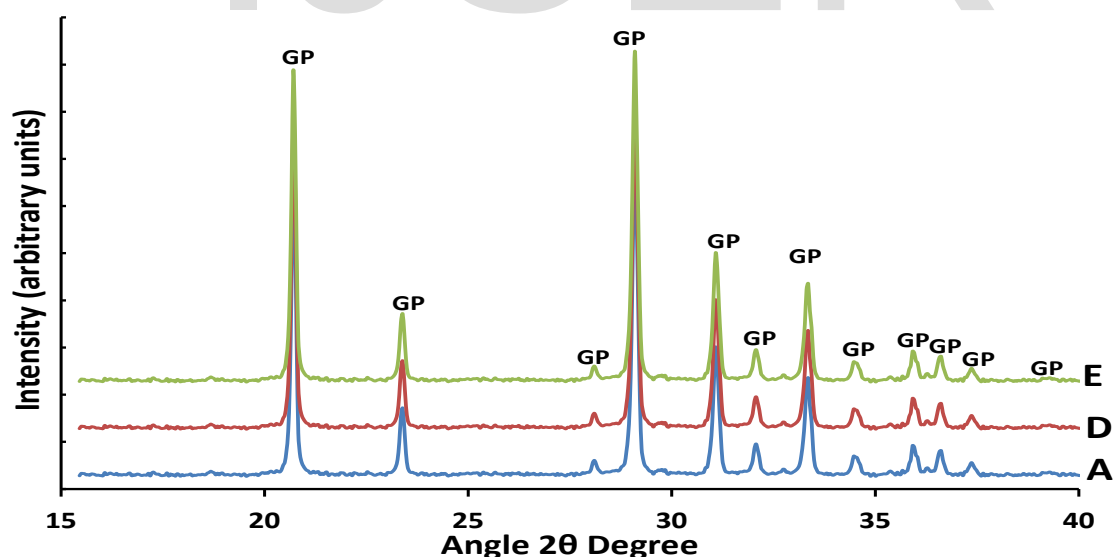


Figure 4: Mineral phases of synthesized (A and D) and commercial (E) calcium sulphate

The XRD pattern of the synthesized (A and D) and commercial (E) samples as presented in Figure 4 shows that gypsum (CaSO₄) is the only mineral phase identified. The diffraction patterns of the crystallites showed spectral peaks of the calcium sulphate at reflection angle 2θ indexed at 20.7°, 23.4°, 28.1°, 29.1°, 31.1°, 32°, 32.1°, 33.3°, 34.5°, 35.4°, 35.9°, and 36.6°

which corresponds to (021), (040), (111), |(041), (221), (112), (131), (220), (151), (060), (202), and (022) lattice plane of based centered monoclinic crystalline gypsum. The JCPDF file 33-0311 was used to identify the angles which are characteristic of the gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) mineral phase. This is in agreement with the results of previous studies reported in the literature (Li *et al.*, 2013a, 2013b; Ling and Demopoulos, 2005; Pan *et al.*, 2013a; Yang *et al.*, 2012).

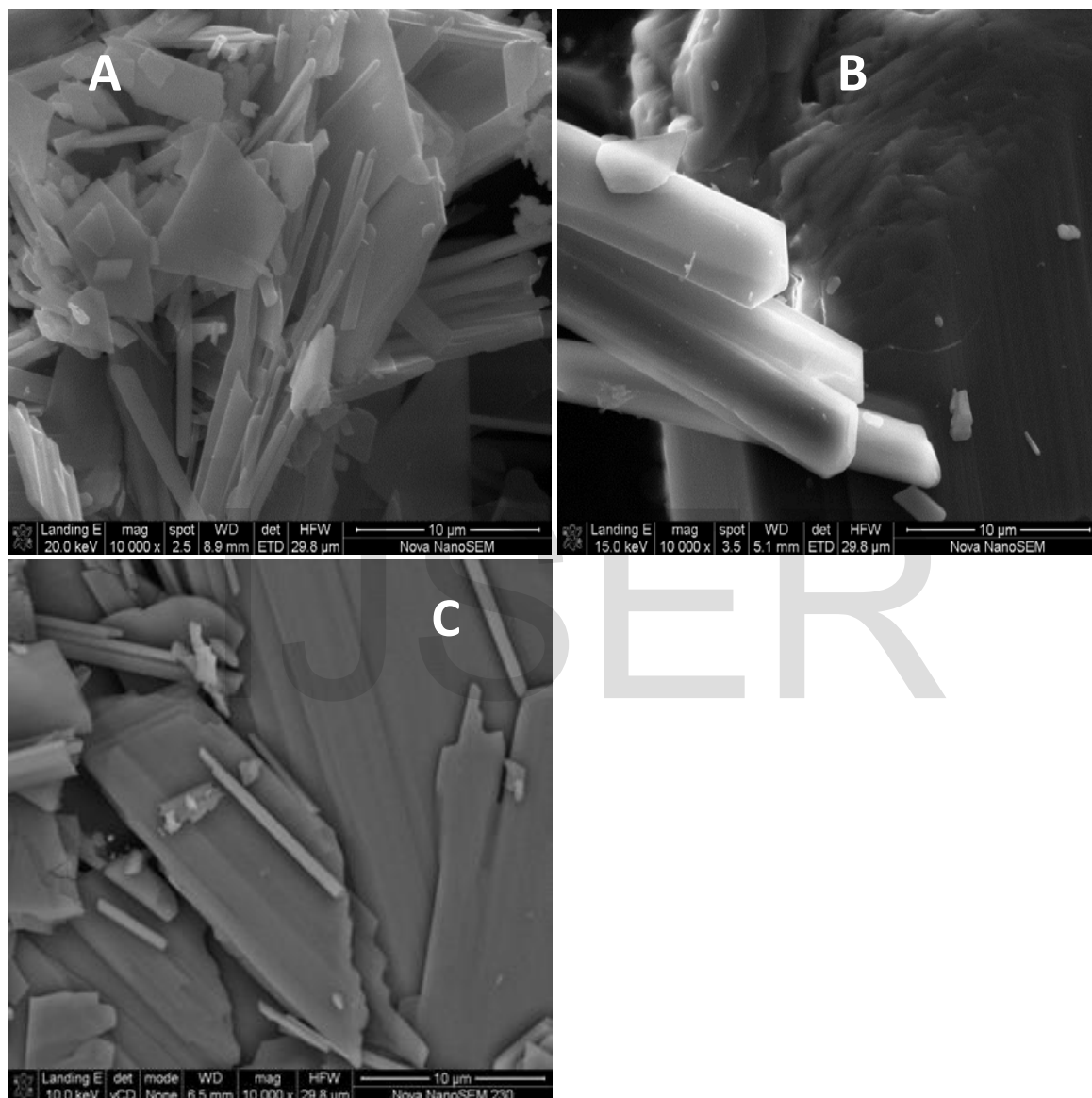


Figure 5: SEM images of synthesized calcium sulphate samples from Ibeshe (A) and Ewekoro (D) lime stones and commercial CaSO_4 (E)

Figure 5 presents the SEM images of synthesized (A and D) and commercial (E) calcium sulphate respectively. The SEM revealed that both the synthesized and commercial crystals have fine and uniform morphology which appear as rod-like structures. This morphology was observed by Singh *et al.*, (2005), as a piece of broken sticks. The EDS spectra were taken from different spot of the homogeneous regions (selected visually by SEM) of the SEM

images of the specimen sample to get reliable information as regards the presence of elements in the specimens along with their relative abundance (Fig. 4).

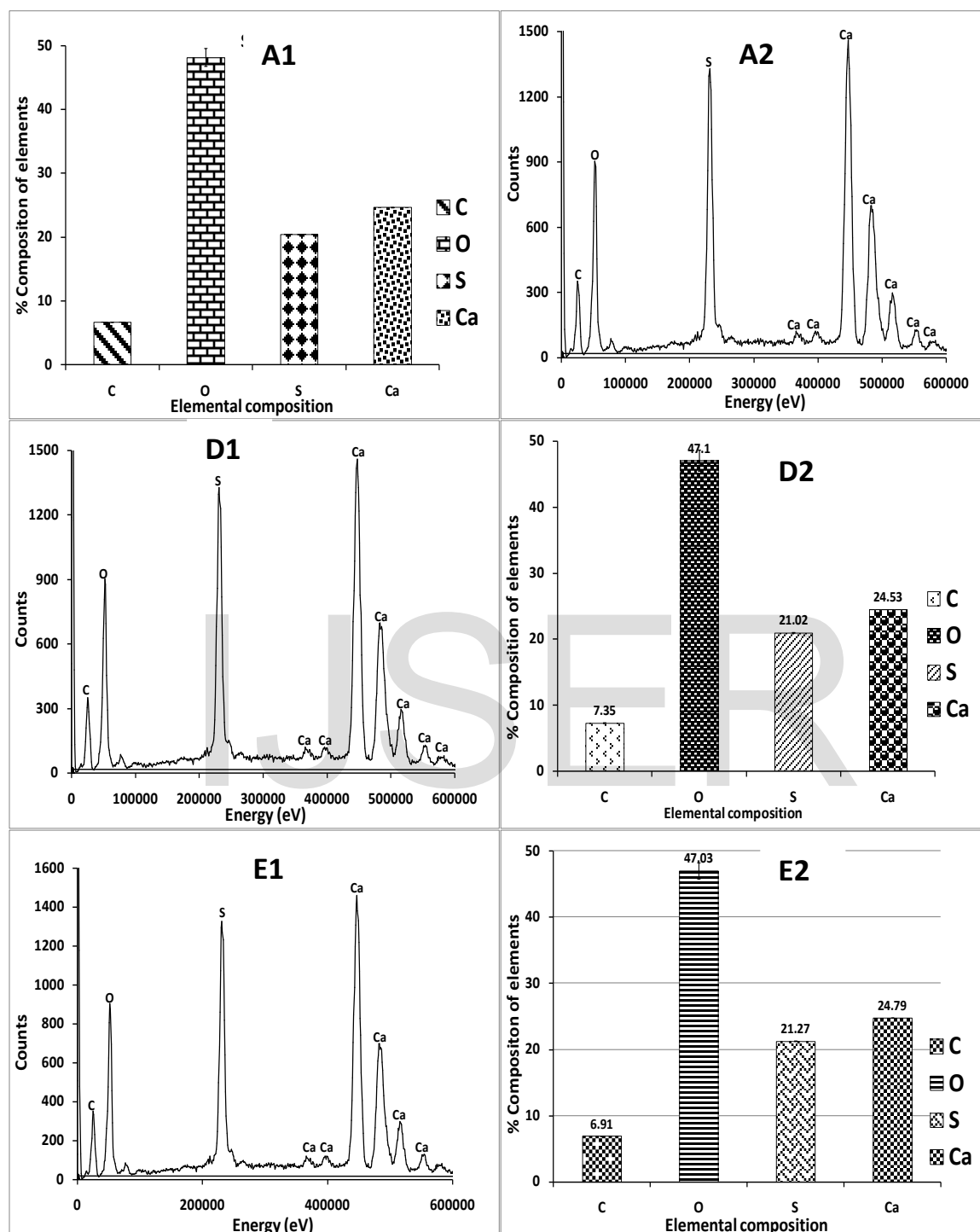


Figure 6: Spectral analysis (1) and elemental composition (2) of synthesized calcium sulphate from Ibeshe and Ewekoro limestone and commercial calcium sulphate

The spectral analysis (1) and elemental composition (2) of the synthesized (A and D) and the commercial calcium sulphate (E) samples are presented in Figures 6. The EDS was used to determine the surface elemental composition of the samples. In Figure 6, the EDS identify

these elements C, O, S, and Ca in all samples. Carbon is an impurity which comes from the carbon coat used to create the stub or platform on which the substrate (calcium sulphate) is placed on the sample holder. The percentage elemental composition of C, O, S, and Ca present in all of the samples shows similar trend of elemental quantification (see Figure 6). According to Liang *et al.*, (2004) and Park *et al.*, (2011), the spectral analysis and the elemental composition found in gypsum (CaSO_4) mineral phase identified contained were O, S and Ca which is similar to the element present in the synthesized and commercial calcium sulphate.

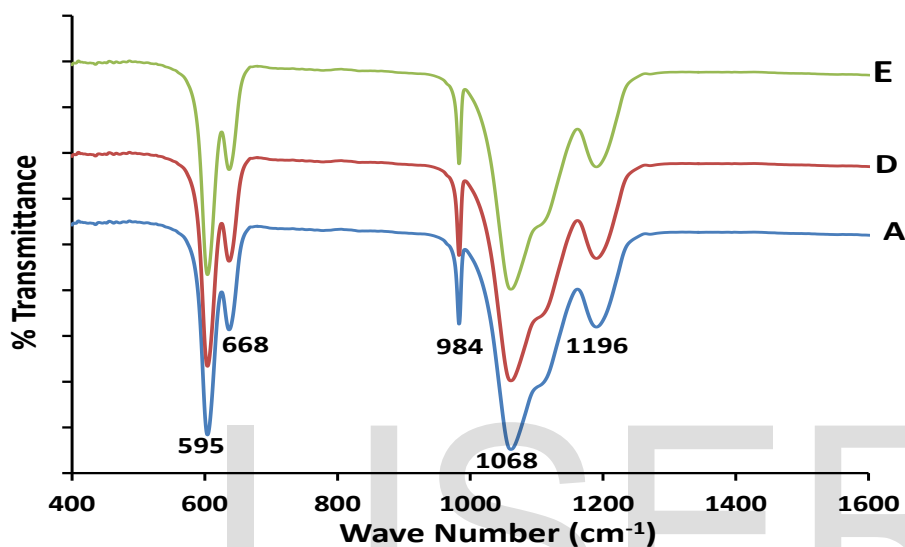


Figure 7: Absorption spectrum of the synthesized (A and D) and commercial (E) calcium sulphate samples

The absorption spectra obtained for the synthesized (A and D) and commercial (E) calcium sulphate samples is presented in Figure 7. The FTIR spectra of the synthesized and commercial samples showed absorption peaks at 595, 668, 1114, and 1618 cm^{-1} (Zhang *et al.*, (2011)). The absorption bands between the ranges of 1068-1196 cm^{-1} is assigned to S-O stretching of inorganic sulphate while the peak at 984 cm^{-1} is associated with the symmetrical vibration of sulphate. The absorption peaks at 606-634 cm^{-1} are assigned to bending vibrations of inorganic sulphate (Sun *et al.*, 2014). Zhang *et al.*, (2011), reported that the absorption peaks at 1173, 1110, 982, 633 and 610 are assigned to stretching characteristic of CaSO_4 . According to Yuhua *et al.*, (2007) the band centred at 1073-1192 cm^{-1} and the shoulder at 982 cm^{-1} were the symmetrical vibration of sulphate (SO_4^{2-}) and the peaks at 610 and 638 cm^{-1} corresponds to the out-of-plane bending vibration of SO_4^{2-} .

Conclusion

This present study has shown that limestone wastes collected from the mine can be used to synthesize calcium sulphate salt. The quality of the synthesized calcium sulphate was compared with the commercial based sample using techniques such as XRD, SEM-EDS and

FTIR. Gypsum was the only mineral phase identified with a cylindrical or rod/stick shaped structure of a typical calcium sulphate. Interestingly, the quantitative elemental composition showed only the presence of Ca, S and O elements with bond formation of sulphate group. Thus, we can reduce the volume of the wastes we discharge into our environment by reusing or converting the waste to a valuable material (as gypsum). The different characterizations revealed that both the synthesized and the commercial samples have almost the same quality.

Acknowledgement

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