# EFFECT OF NATURAL Ca SOURCE ON THE FORMATION OF CALCIUM OXALATE

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***Abstract***: Eggshell is a bio-waste which is a rich source of calcium. Scientists across the globe are exploring numerous ways to utilize this calcium source and currently it is a topic of research in many areas of science. In the present work, study has been done to utilize the calcium present in eggshell to convert it into calcium oxalate. The egg shells were powdered, calcined and chemically treated to obtain calcium nitrate. The calcium nitrate is then converted into calcium oxalate by wet chemical synthesis. The formed calcium oxalate was characterized by particle size analyser and FTIR.

***Keywords: Eggshell, Calcium Carbonate, Calcia, Calcium Oxalate.***

## 1. Introduction

Eggshells are major solid bio-waste across the globe with daily production of several tons from domestic and commercial sources. Besides used as fertilizers or animal feed ingredients, major portion of this is dumped as municipal wastes. The major constituent of an eggshell is calcium carbonate which is around 95-97% and hence can be transformed economically into some new values [1,2].

The calcium carbonate crystals present in the eggshell are stabilized by a protein matrix [3-5]. Recent techniques have allowed the separation of eggshell from the protein membrane. As both the calcium carbonate and the membrane protein can be used in numerous ways, complete separation of both the products is economical [6].

In literature, eggshells have been reported to be utilized in several ways. In biodiesel production it is reported to be used as a solid base catalyst which minimizes biodiesel pollutants and reduction in production cost along with environment friendly production process [7-9]. It has also been reported as an absorbent of heavy metals from wastewater. As a major source of calcium carbonate, it can be used as a raw material in lime or cement production. In agriculture, it is used as fertilizers for plants and also reported to be used as calcium supplements for animals and humans. Eggshells have further been reported to be used as calcium source in hydroxyapatite formation, a biomaterial used in repairing, regeneration and replacement of bone tissues [10-14].

In the present investigation, eggshells were used as source of calcium to obtain calcium oxalate by wet chemical synthesis. Calcium oxalate is a calcium salt of oxalate with chemical formula $CaC_2O_4.(H_2O)_x$, where x varies from 1 to 3. It is used in the production of ceramic glazes, oxalic acid and other organic oxalates. It is also reported to form a cohesive layer on marble surfaces for conservation of stone [15].

## 2. Material & Methods

The experimental work is divided into two parts: first part consists of conversion of eggshell into calcia (CaO) and formation of calcium nitrate from it. In the second part, calcium oxalate is formed using the calcium nitrate and ammonium oxalate. The raw materials used in experimental work are egg shells obtained from bakery, ammonium oxalate and nitric acid.

### 2.1 Conversion of eggshell into calcia (CaO) and formation of calcium nitrate

The egg shells were washed, cleaned and then sun dried for two days followed by oven drying at 110$^0$C for another 24 hrs. Dried and cleaned egg shells were then crushed and grounded with mortar pestle into egg shell powder. The powder was then calcined at 850$^0$C in muffle furnace during which the calcium carbonate is decomposed into calcium oxide and carbon dioxide:

$$CaCO_3 + Heat \rightarrow CaO + CO_2$$

The calcined powder (CaO) has low solubility in water, so was dissolved using minimum amount of nitric acid. The solution was filtered and precipitate was checked for presence of any calcium left. The following reaction takes place during the addition of nitric acid in the calcined powder:

$$CaO + 2HNO_3 \rightarrow 2Ca(NO_3)_2 + H_2O$$

The process of eggshell conversion to calcia, CaO and formation of calcium nitrate from it is given in figure 1 below.

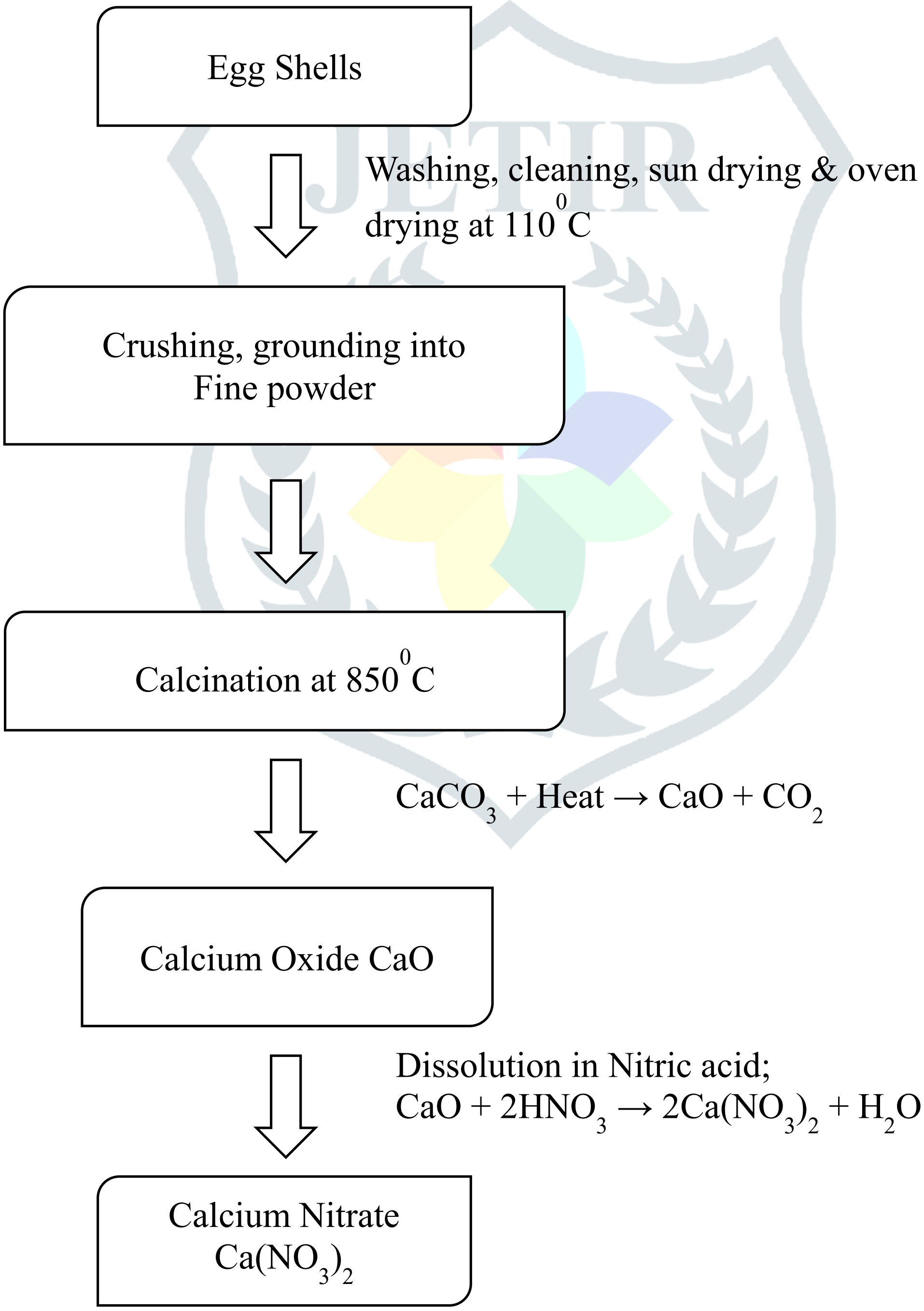


Figure 1: Conversion of eggshell into Calcia and formation of Calcium nitrate

### 2.2 Formation of calcium oxalate

In the second part of this work, calcium oxalate was synthesized using calcium nitrate as calcium source and ammonium oxalate as the oxalate source. The amount of calcium present in the calcium nitrate solution was determined and confirmed by both volumetric and gravimetric analysis.

For the formation of calcium oxalate, both the precursors were mixed in stoichiometric ratio and the precipitate formed is washed with water several times to remove the unreacted precursors and by-product. The following reaction takes place during the addition.

$$Ca(NO_3)_2 + (NH_4)_2C_2O_4 \rightarrow Ca(COO)_2 + 2NH_4NO_3$$

The precipitate formed were oven dried at 110$^0$C for 24 hrs and finally evaluated for its particle size and bonding pattern by FTIR spectrum.

### 2.3 Characterization

The raw materials and the formed products were characterized for their particle size and bonding nature with the help of a particle size analyser and FTIR spectroscopy respectively. The particle size distribution in the developed powder sample of calcium oxide and the product calcium oxalate is measured by dynamic light scattering (DLS) method in dilute condition with the help of a particle size analyser (Zetasizer zetameter, ZEN 3690, Malvern instruments, US make).

To identify the nature of bonding present in dried powder samples, Fourier transform infrared (FTIR) spectra of the powdered sample were taken by a FTIR spectrometer (Bruker Alpha, USA). For the measurement of FTIR spectra, very thin pellets were prepared by mixing about 2 mg of the dried gel powder with 20 mg of IR grade potassium bromide, KBr salt and pressing the mixture at a pressure of 3 ton for 1 min. The wave number range used for absorption spectra measurement was 4000 cm$^{-1}$ to 500 cm$^{-1}$.

## 3. Result and Discussion

The raw materials and the product formed were characterized for their particle size and bonding nature. The particle size distribution (PSD) curve of the synthesized Calcium Oxide and Calcium Oxalate is given in figure 2(a) and 2(b). The PSD plot for Calcium Oxide shows that all the particles are within the size range of 250-600 nm with a peak around 390 nm. For Calcium Oxalate, particles are within the size range of 300-700 nm with a peak around 460 nm (Table 1). It should be noted that the samples were heat treated at higher temperatures before particle size analysis. The high temperature treatment during formation results in agglomeration of finer particles as well as increase in grain growth. The DLS methods of particle size analysis consider the agglomerates as a single particle. Thus this method doesn't reveal the actual particle size which is always less than the measured value.

Table 1: Particle Size Analysis

| | **Calcium Oxide** | **Calcium Oxalate** |
|---|---|---|
| **Particle Size Range** | 250-600 nm | 300-700 nm |
| **Particle Size (d.nm)** | 390 nm | 460 nm |

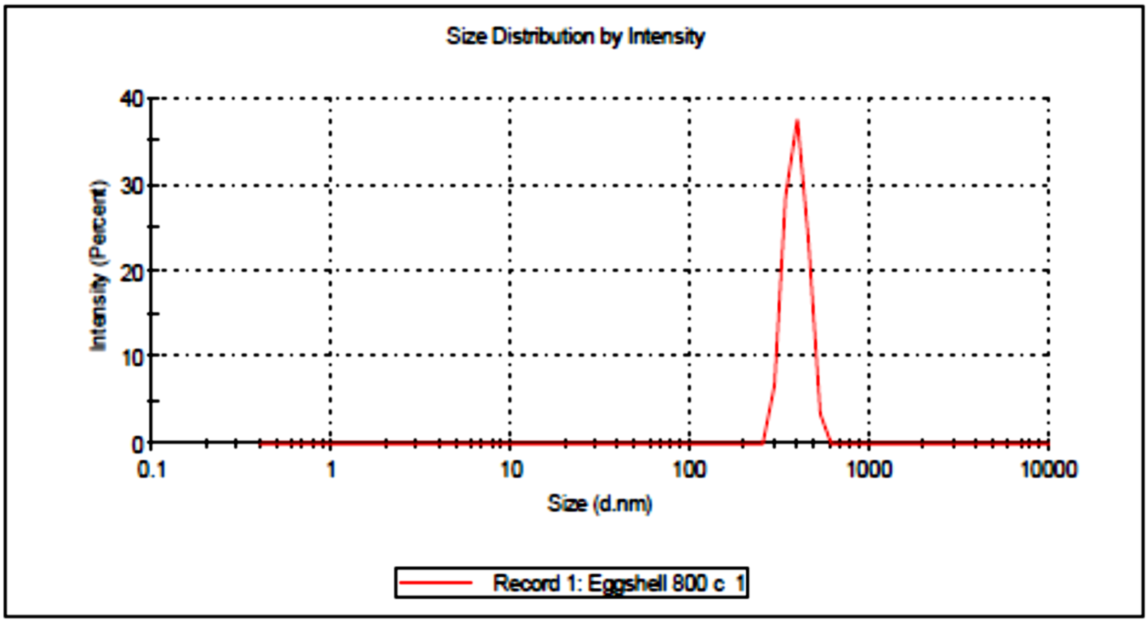


Figure 2(a): Particle size analysis of Calcium Oxide

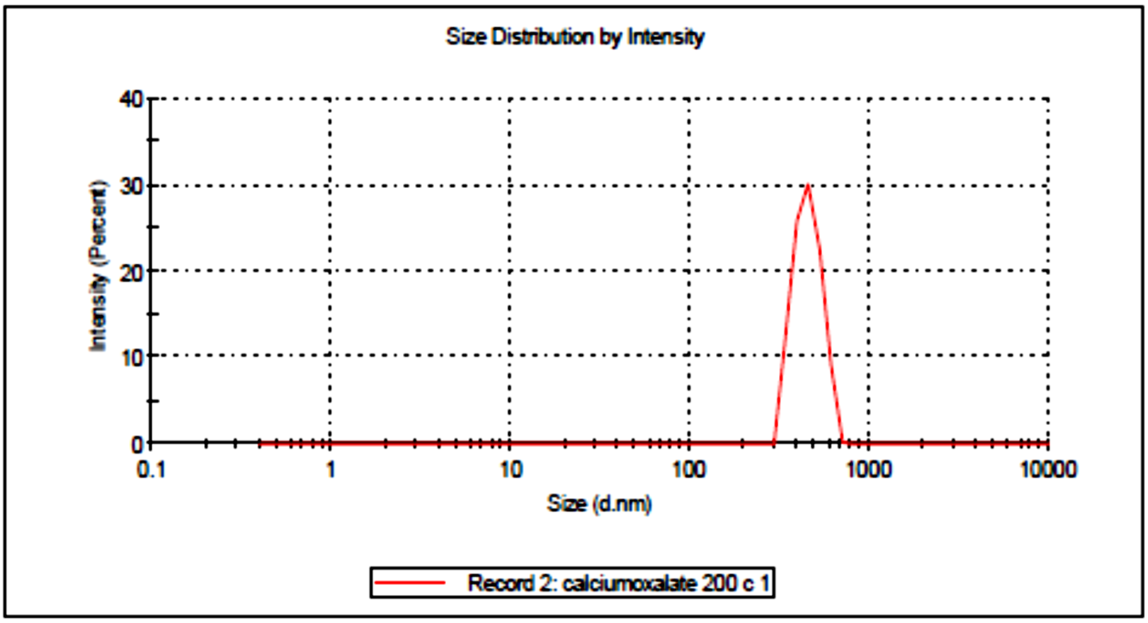


Figure 2(b): Particle size analysis of Calcium Oxalate

The FTIR spectra of the heat treated eggshell powder and calcium oxalate are given in figure 3 and 4 below. The different peak positions in the spectra are in accordance with the values given in previous literatures. In the CaO FTIR spectrum (Figure 3), the peak at 711.18 $cm^{-1}$ was due to Ca–O bonding. The absorption peaks at 1413.07 $cm^{-1}$,874.41 $cm^{-1}$ and 3435.3 $cm^{-1}$ corresponded to C–O and O–H Stretching bonds. The weak absorption peaks at 2873.16 $cm^{-1}$ and 2981.22 $cm^{-1}$ were assigned to C–O vibrations bond. The peak at 2512.85 $cm^{-1}$ was due to O-H Stretching bonds. The peak at 1799.26 $cm^{-1}$ was due to C=O Stretching bonds. [16-18]

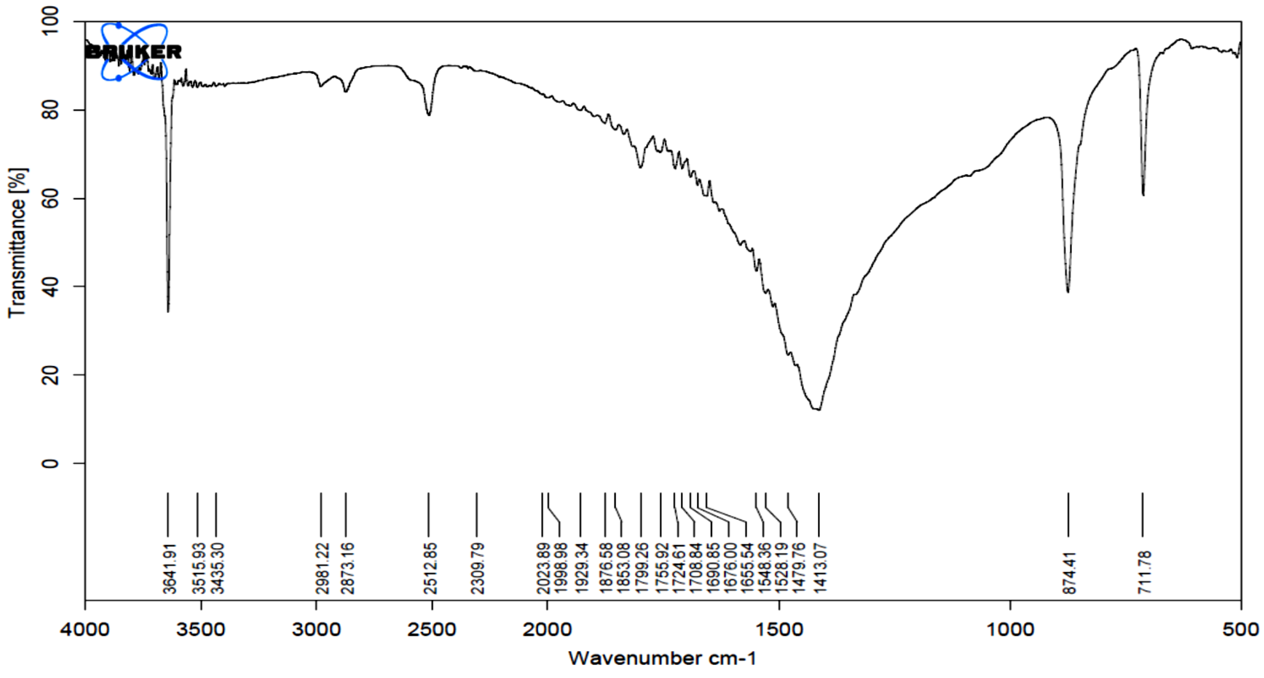


Figure 3: FTIR of Calcium Oxide

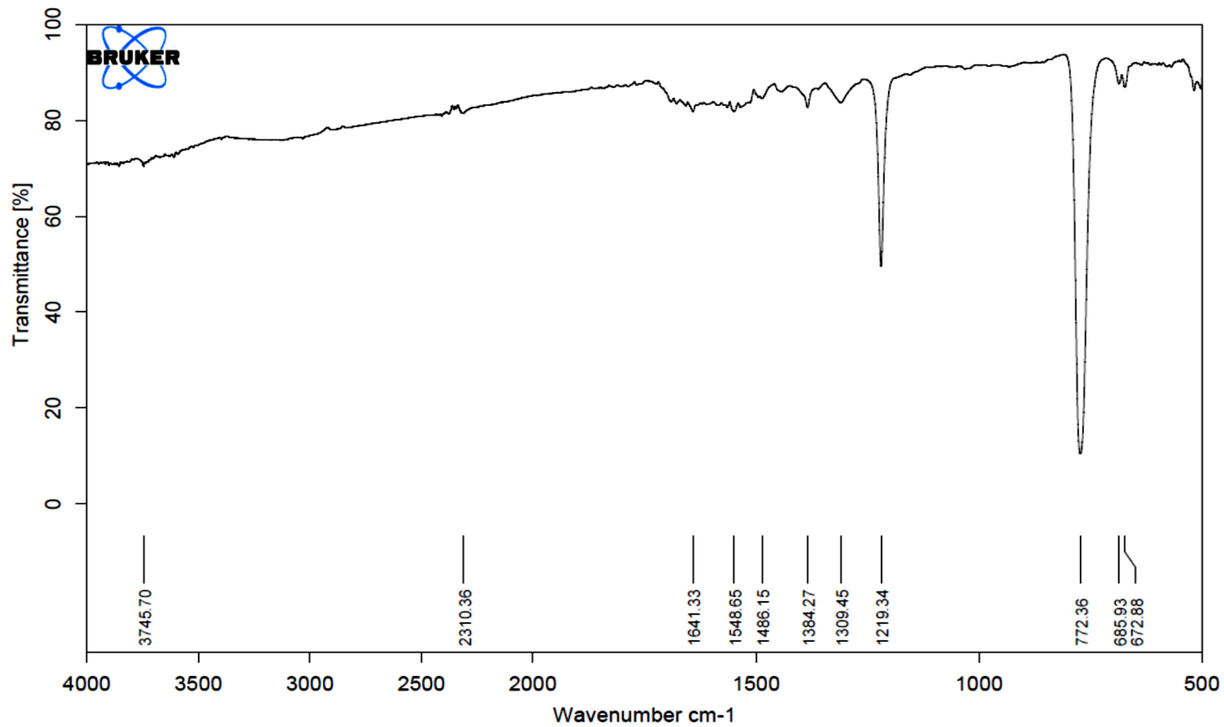


Figure 4: FTIR of Calcium oxalate

The FTIR spectrum of calcium oxalate in figure 4 shows major peak positions at 1641cm$^{-1}$, 1548 cm$^{-1}$, 1486 cm$^{-1}$, 1384 cm$^{-1}$, 1309 cm$^{-1}$, 1219 cm$^{-1}$, 772 cm$^{-1}$, 685 cm$^{-1}$and 672 cm$^{-1}$. The peaks present at 1641 and 1309 cm$^{-1}$ corresponds to asymmetric and symmetric C=O stretching vibrations respectively specific for the calcium oxalate monohydrate. The peak at 1486 cm$^{-1}$ may be due to C-O stretching vibrations. The peak at 1384 may be related to C-C stretching vibrations. The peak at 772 cm$^{-1}$ corresponds to O-C=O Stretching vibrations. The bands at 685 & 672 cm$^{-1}$ may arise due to O-H bending. The experimental peak positions for calcium oxalate are similar to values given in literature for calcium oxalate. [18,19]

## 4. Conclusion

Eggshell is a common bio-waste which is mainly composed of $CaCO_3$. Due to its high calcium content, many applications have been reported in literature. In the present work, eggshells were successfully utilized for generation of Calcium oxalate. At first, the eggshells were converted into calcium oxide by heat treatment, which is then converted into calcium nitrate using nitric acid. For the formation of calcium oxalate, ammonium oxalate was treated with calcium nitrate in stoichiometric ratio. Both the products were characterized for its particle size and bonding pattern by analysing its IR spectrum.

## 5. References

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