

**GREEN SYNTHESIS OF ZINC OXALATE AND OXIDE NANOPARTICLES” USING AVERRHOA BILIMBI L:- A RENEWABLE SOURCE OF OXALIC ACID**

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**ABSTRACT**

Metal carboxylates have been widely investigated and have been used as precursors in the production of metal oxide nanomaterials. Generally, these metal carboxylates are thermally decomposed at relatively low temperatures into the corresponding metal oxide nanomaterials. A facile and green approach for the synthesis of metal oxalates and their subsequent thermal decomposition to the oxide nanoparticles. This approach is based on mixing the metal ion solution and the fruit juice extract without the use of hazardous organic compounds or surfactants. The prepared complexes and their various thermal decomposition products have been characterized by FTIR, and SEM.

**INTRODUCTION**

The precursors are usually obtained when the metal salt reacts with the free acid or any of its labile carboxylates. The reactants are generally synthetic, but many of these carboxylates are readily available in our environment (mostly in plants) and need only to be harnessed. They include, amongst others, citric acid, tartaric acid, and oxalic acid. The latter is known to be one of the major acids in many plants (e.g., Rhubarb and Averrhoa bilimbi L.). Averrhoa bilimbi L, known as bilimbi, It is a small tree up to 15 meters high. Fruits are fairly cylindrical with five broad rounded longitudinal lobes, and produced in clusters During maturity stage occurs the maximum increase in fruits weight and dimensions, and their external green colour changes into light yellow The fruit juice has high levels of oxalic acid.

Ripe bilimbi fruits have thin skin, yellowish-green colour, soft texture and a peculiar smell, which resembles the one of carambola, a fruit of the same botanical family<sup>1-6</sup>. The oxalic acid level in bilimbi (ripe and half-ripe) harvested in rainy season was statistically different from ripe fruits harvested in dry season. Joseph & Mendonca (1989) also reported variations on levels of oxalic acid in bilimbi in Guyana, in two different seasons. Averrhoa bilimbi L is a very good source of oxalic acid the oxalic acid levels the oxalic acid levels in bilimbi ranged between 8.57 and 10.32 mg/g. These high levels of oxalic acid found in bilimbi are probably responsible for its extremely low pH value (0.9-1.5) Ripe bilimbi fruits have higher vitamin C content The levels of vitamin C in ripe and half-ripe bilimbi fruits varied from 20.82 to 60.95 mg/100g,<sup>[7-9]</sup>

Metal-oxides are emerging as technically important materials because of the wide variety of physical properties they possess, which make them attractive for applications such as photovoltaic devices, gas sensors, micro-electronics and corrosion protection devices. However, the production of high quality metal oxide films with a desired chemical composition has been costly and challenging. The synthesis of metal and metal oxide nanoparticles has attracted considerable attention in physical, chemical, biological, medical, optical, mechanical and engineering sciences where novel techniques are being developed to probe and manipulate single atoms and molecules,<sup>[10-13]</sup>

We here explore the feasibility of using this naturally available and sustainable resource (Averrhoa bilimbi L.) rather than the commercial sources for the synthesis of metal oxalates. The use of these natural renewable resources is of environmental significance and in the case of free oxalic acid rich fruits (e.g., Averrhoa bilimbi L.) Could result in a significant reduction in the level of the free acid, thus adding value to the elimination of toxic components through reaction with metal ions of biological and technological importance this could also open up the possibility of high value exploitation of spoiled fruits.

In order to render the synthesis cost effective and eco-friendly, the fruit juice can be used directly without initial purification steps or prior extraction of the acid. oxalic acid requires no initial alkaline deprotonation step to precipitate with the metal ions and the precipitation can therefore occur at the natural pH of the juice.

This paper gives a facile and green approach for the synthesis of metal oxalates and their subsequent thermal decomposition to the oxide nanoparticles. Our approach is based on

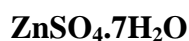
mixing the metal ion solution and the fruit juice extract without the use of hazardous organic compounds or surfactants. In this preliminary study, divalent 3d metal ion ( $\text{Zn}^{2+}$ , ) is used for the proof of concept. The as prepared complexes and their various thermal decomposition products have been characterized by FTIR, and SEM.

### Experimental Section

**Zinc Oxide is prepared by Hydrothermal Method in two stages.**

#### Stage 1: Preparation of the Precursor Zinc Oxalate

Equimolar proportions say 0.25g of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  dissolved in minimum volume of water and bilimbi, fruit extract of 20  $\text{cm}^3$  is and stirred for 15 minutes on a magnetic stirrer. A white colour precipitate for Zinc Oxalate is obtained at pH 6. The precipitate is washed with water and finally dried with acetone. The precipitate separated using micro centrifuge with 4000 rpm then dried at 104 °C for four hours.



**Bilimbi, Fruit Extract**

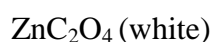


Added with Stirring for 30 minutes on a magnetic stirrer  $\text{ZnC}_2\text{O}_4$  Zinc oxalate

#### Stage 2: Preparation of Zinc Oxide Nanoparticles

The prepared metal oxalate precursors are mixed with polyvinyl alcohol in the weight ratio 1:5, powdered in a mortar, mixed in a crucible and ignited in an electric furnace. The temperature should not exceed 300 °C

The ZnO dried samples were separated and powdered



Polyvinyl alcohol (weight ratio is 1: 5)



Powdered in a Mortar, ignited in an electric furnace not more than 300°C White ZnO

## RESULTS AND DISCUSSION

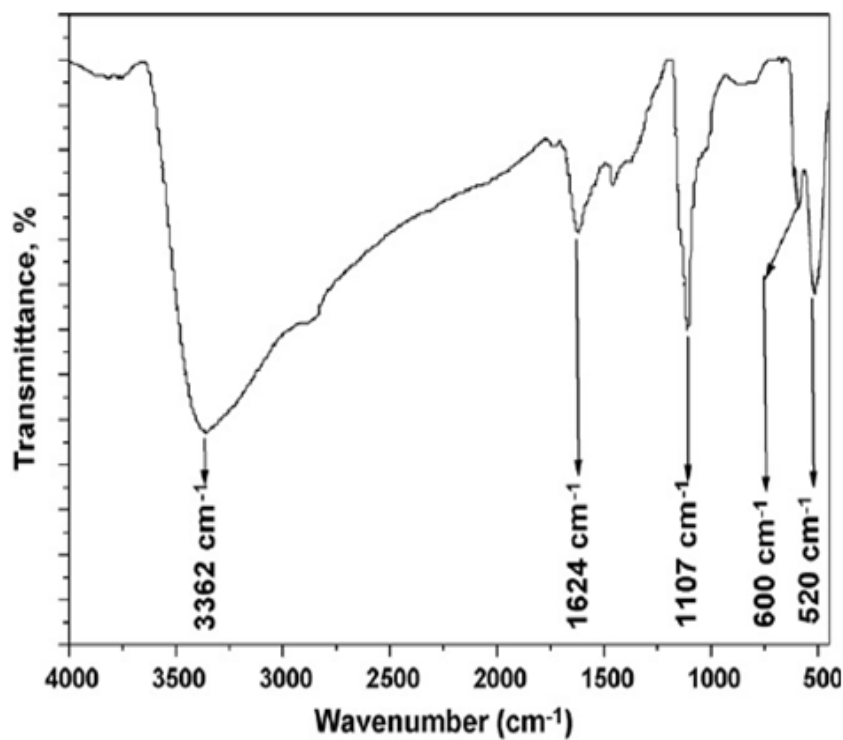


Fig. 1:-a) FTIR spectrum of ZnO nanoparticle.

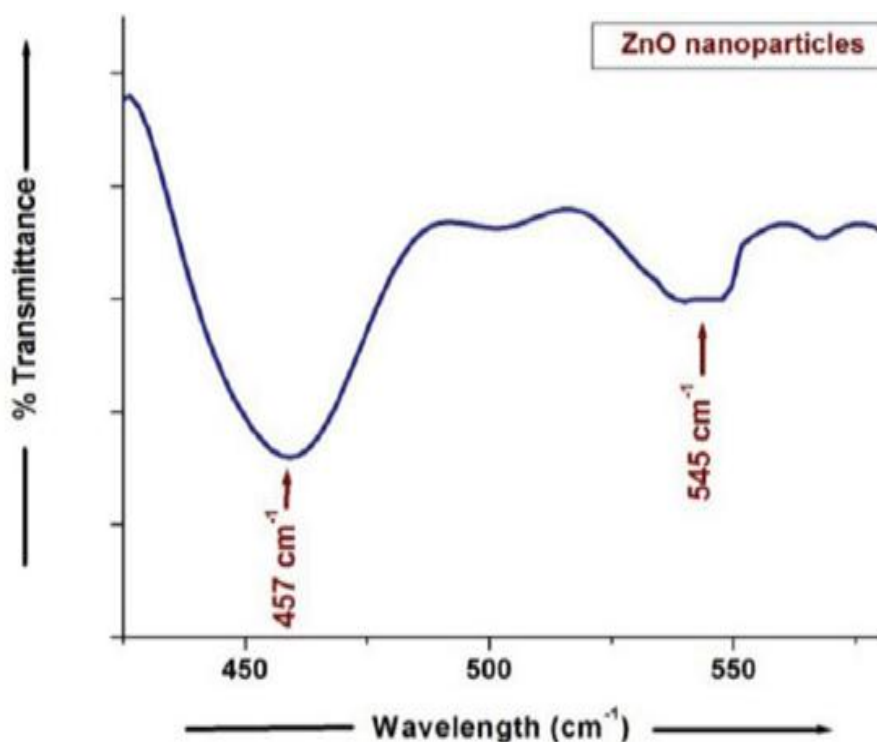


Fig. 1:-b) FTIR spectrum of ZnO nanoparticle.

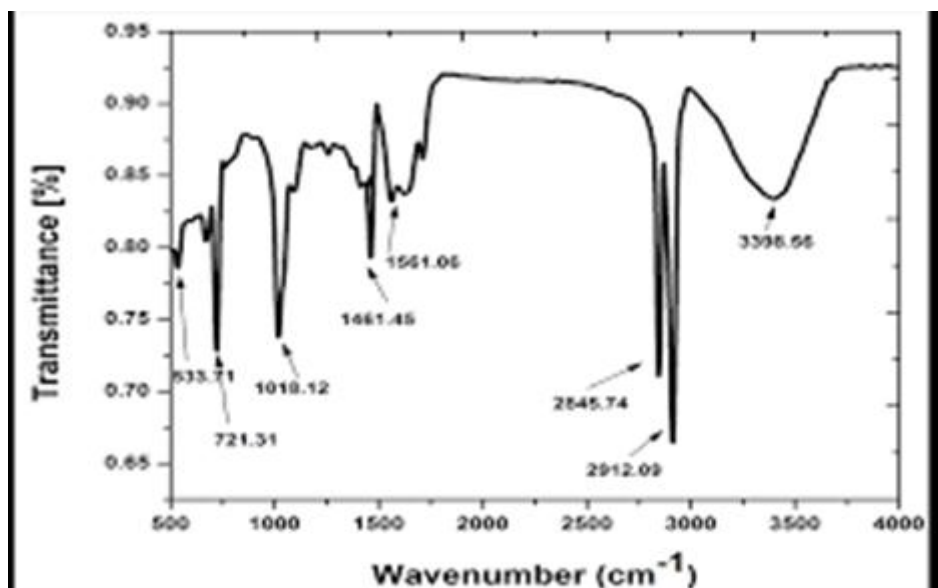


Fig. 1:-c) FTIR spectrum of ZnO nanoparticle.

### The FT-IR spectra analysis

Fig.1a,b,c shows FT-IR spectra of Zinc oxalate and zinc oxide nanoparticles. The supplement of bilimbi, fruit extracts solution to the copper sulphate and Zinc sulphate solution cause to the precipitation of a white zinc oxalate. The broad band at 3362.26  $\text{cm}^{-1}$  was allocated to both the  $\text{s}(\text{O}-\text{H})$  and  $\text{as}(\text{O}-\text{H})$  of hydration water. The extreme band at 1624.51  $\text{cm}^{-1}$  was allocated to asymmetric and water tensional tremble ( $\text{H}-\text{O}-\text{H}$ ). The shoulder Two peaks at 520  $\text{cm}^{-1}$  and 600  $\text{cm}^{-1}$  reported for  $\text{CuO}/\text{ZnO}$  NPs due to stretching of  $\text{M}-\text{O}$  which are in close agreement with that of literature values.

### The SEM images analysis

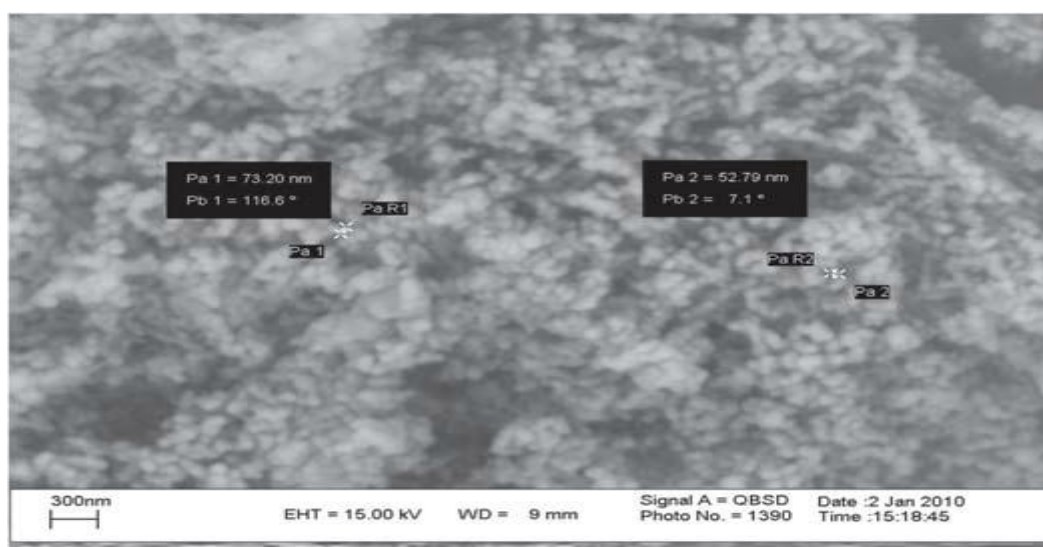


Fig. 2: SEM images of ZnO.

Fig.2 shows the SEM images of Zinc Oxide of Nanoparticles. The SEM image shows morphology of the synthesised Zinc Oxide nanoparticles and is found to be of spherical shaped. The size of ZnO Nanoparticles are noted, ZnO of 92nm as seen. Other particles joined as group and form bigger particles. SEM images of nanoparticles were showed that Zinc oxide metal nano particles were exactly in the shape of spherical and clustered. Also SEM images were confirmed that all of nanoparticles were exactly pure.

### Experimental Protocol

All chemical and solvents used were of A. R. grade. Further, remaining, pure reagents were purchased from S.D. chemicals.

I.R spectra of the synthesized nano particles were recorded on Shimadzu Fourier Transform Infra-Red Spectrophotometer (FTIR) 400-4000cm<sup>-1</sup> region in KBr disk.in chemo test laborotary at Sewree.

The SEM is carried out SAIF IIT Powai.

### CONCLUSION

- ❖ We have been able to use Averrhoa bilimbi L juice as source of oxalic acid for the synthesis of divalent metal oxalate.
- ❖ The synthesis required no special treatment of the juice as the product was obtained by directly mixing the metal ion solution and the juice.
- ❖ The products were all identified as the expected metal oxalates. Both the oxalates and their decomposition products oxides were found to be nanomaterials with their crystallite size ranging from 14 to 91 nm.
- ❖ It can be concluded that synthesis of these nano particles require no expensive ingredients and complicated equipments. This method is less time consuming and flexible.
- ❖ Development of synthesis of nanomaterials over a range of sizes, shapes and chemical composition is an important aspect of nano technology.
- ❖ The size-development and physical-chemical properties of nanoparticles have fascinated and inspired research activities.
- ❖ ZnO, synthesized characterization which and further studied maybe done for studying its applications.

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