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Synthesis and characterization of organic zinc chelates through FT-IR

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Abstract

Zinc is an important micronutrient which is required for better plant growth and alleviate its deficiencies in various crops through its involvement in many metabolic functions. Generally zinc use efficiency hardly exceeds 2% hence to improve the use efficiency zinc has been chelated with various organic acids. The zinc chelates synthesized with various chelating agents like citric acid, glycine, lysine, maleate, tartrate, and oxalate were analysed with the extent of chelation with Fourier Transform Infrared spectroscopy (FT-IR). Out of the six zinc chelates produced, zinc glycine sulphate and zinc citrate sulphate were processing better chelation properties and characteristics.

Keywords: Zinc, chelate, FT-IR, Amino acid, synthesis and characterization

Introduction

Zinc (Zn), a fundamental plant micronutrient, essential for many physiological processes such as photosynthesis, respiration and protein synthesis, nucleic acids, and plant hormones such as IAA. It is currently considered as the fourth most vital supplement in agricultural crops which restricts yield significantly. The common sources of zinc used are inorganic Zn fertilizers, synthetic and natural organic chelates in order to increase its availability and to maintain desirable concentrations in soils (Cakmak *et al*, 1999b) [1]. Inorganic Zn fertilizer sources in soils have relatively low efficiency due to their precipitation as insoluble salts and high impurities (Khoshgoftar manesh *et al*, 2010) [6]. Synthetic chelates are effective not only in correcting Zn deficiency, but also in inhibiting Zn precipitation in soil (Vadas *et al*, 2007) [16]. As a result, synthetic organic chelates are more efficient zinc supplements than other sources. Chelating agents are organic molecules capable of trapping or encapsulating metal ions such as Ca, Mg, Fe, Co, Cu, Zn and Mn and slowly releasing these metal ions to become available for plant uptake. Since the metals bound in chelate rings have lost their cationic characteristics in essence, during chemical reactions they are less prone to precipitation which makes these compounds useful as a effective plant nutrient supplement (Sekhon, 2003) [14].

As they are rapidly absorbed, translocated and metabolized by plants, natural amino acids are used to chelate the micronutrients. In addition, they are very small molecules and are absorbed and translocated as other small molecules within the plant. Metals fully chelated with amino acids are neutral in charge hence are not attracted to or repelled by leaf surfaces which are negatively charged. Organic-chelated zinc sources were generally reported to be superior than inorganic sources of zinc. Chelates of amino acids are gaining momentum to deliver selected micronutrients with maximum bioavailability, low cost and safety (Murali *et al*, 2018) [7].

Fourier Transform Infrared Spectroscopy (FTIR) is widely used in assessing chelates, properties. Free organic acids and their respective metal chelates exhibit significantly different FT-IR absorption spectra, and the possibility of utilizing these infrared spectral differences quantitatively determine the extent of chelation in Zn- citrate sulphate, Zn- glycinate sulphate, Zn- lysine sulphate, Zn- maleate sulphate, Zn-oxalate sulphate and Zn-tartrate sulphate in solid state was studied in this investigation (Painter *et al*, 198; Miller *et al*, 2015) [10, 7]. These metals and organic acid combinations and represent a significant market share among the mineral chelates currently sold as fertilizer and nutritional supplements.

Hence the present study was taken up with a hypothesis of developing Zn-amino and organic acid chelates as alternate new Zn fertilizer sources which can be more effective than Zinc sulphate in improving zinc use efficiency. Six amino and organic acid based chelates were synthesized and characterized with FT-IR spectroscopy and discussed.

Materials and Methods

Synthesis of Zn - organic acid chelates

Six zinc organic acid chelates are prepared using citric acid, glycine, lysine, maleic acid, oxalic

acid and tartaric acid using the protocol outlined by Trusovs (2003) [17]. About 0.1 mole of Zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), 0.1 mole of Amino acid or any one specified organic acid and 100 ml ethanol were placed into a beaker provided with a reflux condenser. The mixture was stirred and

boiled for 5 – 10 hours which differs with chelates produced. The mixture was then cooled and thereafter filtered which yields Zinc chelates in the form of a fine powder. The details of the protocol used in the study was outlined in figure 1.

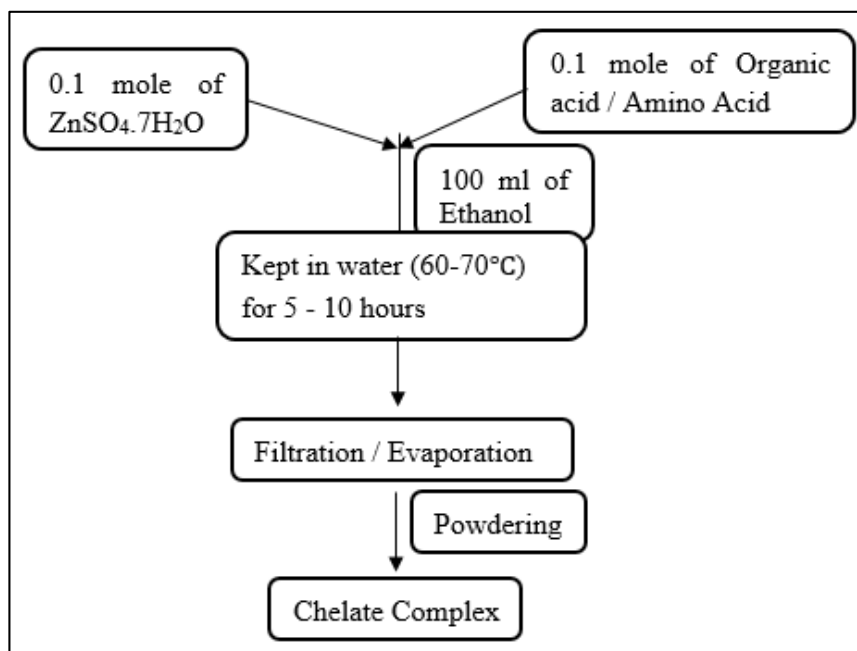


Fig 1: Protocol for synthesizing zinc chelate

Characterization of zinc chelates through FT-IR

The functional group present in the Zn chelates were confirmed in the finely ground Zn chelated samples by directly fed into FT-IR (Model -6800 Jasco, Japan) equipped with ATR PRO ONE accessory and TGS detector. Registration was carried out in the region of $400 - 4000 \text{ cm}^{-1}$ (resolution 4 cm^{-1} with a number of scans 40). The report was then processed using origin @ 8.0 software and interpreted.

Results

The synthesized chelates along with zinc sulphate and the pure chelating agents were subjected to FT-IR spectroscopic analysis and the results were given in table 1.

FT-IR spectral characteristics

A. Zinc citrate sulphate

The FT-IR spectral of standard citric acid results revealed the presence of sharp peak at 500.43 cm^{-1} . This peak was absent in zinc citrate sulphate. Apart from this sharp peaks with centroids at 1719.23 cm^{-1} and 1682.59 cm^{-1} were observed in citric acid. In zinc citrate sulphate, the peaks were shifted to 1712.48 cm^{-1} and 1641.13 cm^{-1} respectively. The peaks at 3321.78 cm^{-1} , 3221.5 cm^{-1} and 3011.3 cm^{-1} were also observed in citric acid.

In zinc sulphate heptahydrate, the peak corresponding to the sulphate bond at 1056.8 cm^{-1} was obtained. However in the new chelate viz, of zinc citrate sulphate, FT-IR analysis pointed out sharp peaks at 1641.13 cm^{-1} , 3742.19 cm^{-1} , 3828.97 cm^{-1} and 3844.4 cm^{-1} . A weak broad band with a width of 2700 cm^{-1} to 3400 cm^{-1} with a centroid at 3281.29 cm^{-1} (table 1) was noticed.

B. Zinc glycine sulphate

Infrared spectroscopy of pure glycine revealed several peaks which ranged from 2500 cm^{-1} to 3200 cm^{-1} where 2520.51 cm^{-1} ,

2603.43 cm^{-1} , 2703.71 cm^{-1} , 3001.66 cm^{-1} and 3149.17 cm^{-1} observed sharp peaks. A peak at 1056.8 cm^{-1} characteristics of sulphate was observed in zinc sulphate heptahydrate. The FT-IR spectral investigations of synthesized chelate indicated peaks at 1065.48 cm^{-1} , 1393.33 cm^{-1} , 3782.69 cm^{-1} and 3169.44 cm^{-1} . A broad band from 2700 cm^{-1} to 3300 cm^{-1} with a centroid at 3169.44 cm^{-1} was also observed (table 1).

C. Zinc lysine sulphate

The standard lysine was investigated with FT-IR spectroscopy and noticed a broad band ranging from 2500 cm^{-1} to 3200 cm^{-1} with a centroid at 2879.20 cm^{-1} . Other peaks were observed at 472.47 cm^{-1} and 1414 cm^{-1} . In zinc sulphate heptahydrate, the peaks was observed at 1056.8 cm^{-1} . The spectroscopic image of synthesized chelate indicated peaks at 1079.94 cm^{-1} , 3963.01 cm^{-1} and 3782.26 cm^{-1} . A broad band with a width of 2700 cm^{-1} to 3400 cm^{-1} and a centroid at 2921.41 cm^{-1} was also noticed in zinc lysine sulphate (table 1).

D. Zinc maleate sulphate

The FT-IR spectroscopic imaging of standard maleic acid revealed peaks at 1703.8 cm^{-1} , 1426.2 cm^{-1} and 73.42 cm^{-1} . The characteristic peak at 1056.8 cm^{-1} was observed in zinc sulphate. The bonding pattern of the synthesized zinc maleate sulphate indicated peaks at 1084.76 cm^{-1} , 1716.34 cm^{-1} , 1410.67 cm^{-1} , 3782.69 cm^{-1} , 3693.01 cm^{-1} and 2873.42 cm^{-1} (table 1).

E. Zinc oxalate sulphate

From the FT-IR spectrum of oxalate the IR bonds at 3411.48 cm^{-1} , 2952.48 cm^{-1} , 1592.91 cm^{-1} , 1344.14 cm^{-1} and 1417.42 cm^{-1} was recorded. While the spectrum observed in the synthesized zinc oxalate sulphate with broad range from 3000 cm^{-1} to 3500 cm^{-1} with a centroid at 3366.14 cm^{-1} and 3104.83 cm^{-1} with to strong and band stretching. The IR peaks at 1612.2 cm^{-1} , 1432.85 cm^{-1} and 1357.64 cm^{-1} (table 1).

F. Zinc tartrate sulphate

A peak at 1056.8 cm^{-1} was obtained for the standard zinc sulphate. While for the pure tartaric acid, the sharp peaks were obtained at 1440.56 cm^{-1} , 485.97 cm^{-1} , 2962.13 cm^{-1} , 3395.07 cm^{-1} and 3323.64 cm^{-1} . The characteristic peak formed in zinc sulphate at 1056.8 cm^{-1} was shifted to 1097.3 cm^{-1} in the newly synthesized zinc tartrate sulphate. In case of zinc tartrate sulphate, sharp peak was obtained at 1581.34 cm^{-1} and 3782.69 cm^{-1} . Some of the characteristic peaks found in tartaric acid were absent in the newly synthesized zinc tartrate sulphate (table 1).

Discussion

The newly synthesized zinc chelates and their standards showed characteristics peaks, frequency and strength.

Zinc citrate sulphate

The peak of 500.43 cm^{-1} observed in citric acid indicated the presence of carboxyl group where the absorption of infra-red occurs. But, when it bound to Zn, the peak get diminishes and no such peak is absorbed in Zn-citrate sulphate. In zinc sulphate heptahydrate, the sulphate peak has been observed with a centroid 1056.8 cm^{-1} and similar peak was observed in synthesized zinc citrate sulphate chelate also with a centroid 1056.69 cm^{-1} whereas such SO_4^{2-} peaks were not observed in free citric acid. By these above points it is evident that the sulphate has been bonded with zinc citrate (Saha and Podder, 2011) [4]. Kanagadurai *et al.*, (2009) [13] and Zhang, 2018 [19] reported that stretching vibrations of the water molecule are expected in the region of $3000\text{--}3600\text{ cm}^{-1}$ in pure zinc sulphate heptahydrate. The sharp peaks in synthesized zinc citrate sulphate at 3742.19 cm^{-1} , 3828.97 cm^{-1} and 3844.4 cm^{-1} indicated the evidence of multicoordinated $\nu(\text{OH})$ group respectively. The single sharp peak at 1641.13 cm^{-1} indicated the presence of ring formation in synthesized chelated compound.

On comparing FT-IR spectrum of citric acid and zinc citrate sulphate, the former one gets peak at 1719.23 cm^{-1} and 1682.59 cm^{-1} which is assigned to the very sharp stretching of C=O group. In the latter one, these peaks are shifted at 1712.48 cm^{-1} and 1641.13 cm^{-1} . Above points confirms the presence of C=O groups in the structure of Zn^{2+} . FTIR spectrum of citric acid at wavelength 3321.78 cm^{-1} , 3221.5 cm^{-1} and 3011.3 cm^{-1} is due to broad stretching of carboxyl groups (COO^-). The peaks at 2667.07 cm^{-1} and 2553.29 cm^{-1} is assigned to weak stretching of OH groups (Murali, 2016) [15]. It can be observed that the spectrum of Zn^{2+} citrate contains only one weak broad band of high intensity in the range of 2700 cm^{-1} to 3400 cm^{-1} with centroid at 3281.29 cm^{-1} , which can be attributed to valance vibrations of OH stretching. The peaks characteristics to zinc citrate sulphate are mentioned in Figure 2.

Zinc glycine sulphate

Similar peak of zinc sulphate heptahydrate was observed in synthesized zinc glycinate sulphate chelate also with a centroid 1065.48 cm^{-1} whereas such SO_4^{2-} peaks were not observed in free glycine indicated that the sulphate has been bonded with zinc citrate (Saha and Podder, 2011) [4].

The symmetric structure of COO^- in glycine was noticed with a sharp peak at 1402 cm^{-1} . On co-ordination, the vibration peak shifts to the position of 1393.32 cm^{-1} in Zn-glycine sulphate complex (Chinonye *et al.*, 2017; Reddy (2005); Lin *et al.*, 2015) [2, 14, 2]. By these similar peaks in free amino acid and

in synthesized chelated compounds, it was clearly confirmed the formation of carboxylate bonding to zinc.

In amino acid, the peak at 498.50 cm^{-1} indicated the carboxyl group where the absorption of infra-red occurs. But, when it bound to Zn, the peak get diminishes and no such peak is absorbed in synthesized chelate. The peak at 3782.69 cm^{-1} in zinc glycine sulphate indicates the presence of $\nu(\text{OH})$ groups (Rahmouni *et al.*, 2019; Zhang *et al.*, 2018) [9, 19]. In Glycine, several peaks have been observed in the range 2500 cm^{-1} to 3200 cm^{-1} and the peaks at 2520.51 cm^{-1} , 2603.43 cm^{-1} , 2703.71 cm^{-1} was due to twisting vibrations of CH_2 . The peaks at 3001.66 cm^{-1} , 3149.19 cm^{-1} is due to NH_2 groups present in the amino acid glycine (Murali, 2016) [15]. Upon chelation, the peaks obtained for alkene groups get disappeared and the peaks for amine group is get shifted to 3169.44 cm^{-1} . One of the significant difference obtained in IR spectrums of zinc glycinate sulphate is the presence of broadened band vibrations of high intensity obtained in the spectra range of 2700 to 3300 cm^{-1} with centroid at 3169.44 cm^{-1} (Feng *et al.*, 2015) [1]. Disappearing and shifting of these peaks in the synthesized chelates indicated that new coordinate bond is formed through the terminal amine groups and alkene groups with metal zinc. The peaks characteristics to zinc glycine sulphate was shown in Figure 2.

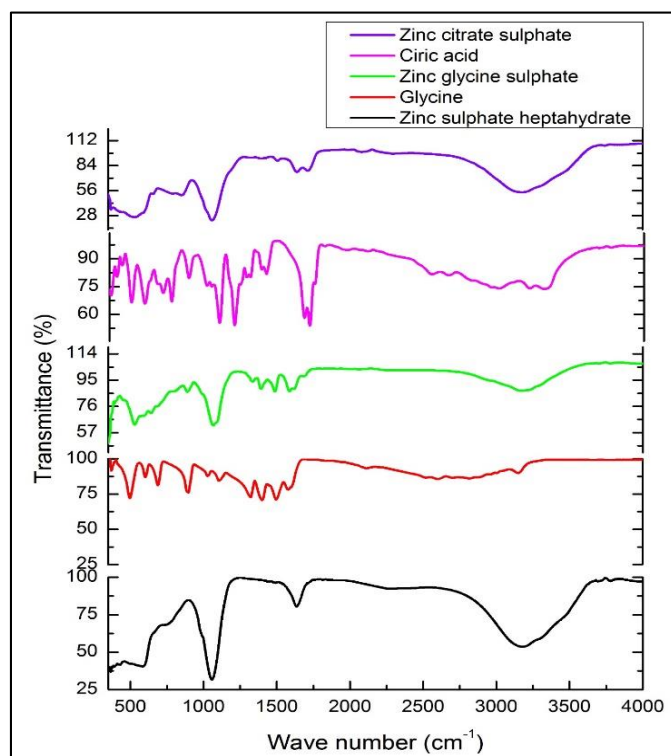


Fig 2: Comparative FT-IR peaks of zinc sulphate heptahydrate, Glycine, Zinc glycine sulphate, Citric acid, Zinc citrate sulphate

Zinc lysine sulphate

A broadband has been absorbed in standard Lysine with the peak from $2500\text{--}3200\text{ cm}^{-1}$ with the centroid at 2879.2 cm^{-1} which indicated the presence of NH_2 group in the standard. whereas, in the chelate Zn-Lysine sulphate, the NH_2 group band shifts from 2700 cm^{-1} to 3400 cm^{-1} with the centroid 2927.41 cm^{-1} . This vibrational shift in the Zn-Lysine sulphate indicates the presence of NH_2 group. In Amino Acid Lysine, the peak at 472.47 cm^{-1} indicates the carboxyl group where the absorption of infra-red occurs. But, when it bound to Zn, the peak get diminishes and no such peak is absorbed in Zn-Lysine sulphate.

The SO_4^{2-} peak in Zinc sulphate heptahydrate was observed at 1056.8 cm^{-1} with broad band. But the same band in Zinc lysine sulphate chelate has been shifted to 1079.94 cm^{-1} which confirms the presence of SO_4^{2-} in synthesized chelate compound (Saha and Podder, 2011) [4]. The symmetric structure of COO^- in lysine is with sharp peak at 1414 cm^{-1} . On co-ordination, the vibration peak shifts it to the position of 1409 cm^{-1} in Zn-Lysine complex (Chinonye *et al.*, 2017) [2]. The peak at 1718.26 cm^{-1} in zinc lysine complex indicates the presence of ring formation. Similarly the peaks at 3963.01 cm^{-1} and 3782.26 cm^{-1} in the chelated compound represents the multi-coordinated $\nu(\text{OH})$ group as mentioned in Figure 3.

Zinc Maleate Sulphate

The SO_4^{2-} peak in Zinc sulphate heptahydrate was observed 1056.8 cm^{-1} with broad band. But the same band in Zinc maleate sulphate chelate has been shifted to 1084.76 cm^{-1} which confirms the presence of SO_4^{2-} in synthesized chelate compound (Saha and Podder, 2011) [4]. In order to evaluate, the sulphate peak is not present in maleic acid standard which indicates that sulphate compound in zinc sulphate has been bonded to maleic acid as zinc maleate sulphate. The peak at

1716.34 cm^{-1} in chelated zinc maleate is due to sharp stretching of $\text{C}=\text{O}$ and similar peak was observed in maleic acid at 1703.8 cm^{-1} with slight vibrational shift.

The symmetric structure of COO^- in maleic acid is with sharp peak at 1426.2 cm^{-1} . On co-ordination, the vibration peak shifts it to the position of 1410.67 cm^{-1} in Zn-maleate complex (Reddy 2005[14]; Lin *et al.*, 2015; Chinonye *et al.*, 2017) [14, 5, 2].

Similarly the peaks at 3782.69 cm^{-1} and 3693.01 cm^{-1} in the chelated compound represent the multi-coordinated $\nu(\text{OH})$ group. On comparing free maleic acid and chelated zinc maleate from the FT-IR reports, the former one shows a vibration peak at 2873.42 cm^{-1} which was due to twisting vibration of CH_2 groups. Upon chelate formation, the vibration peak at 2873.42 cm^{-1} gets disappears, which indicates a new coordinate bond formation occurred through the carboxylic acid. As well as, the asymmetric carboxylic group gets peak at 3052.76 cm^{-1} which is get disappeared. A new broad peak is formed in zinc maleate sulphate from $2700\text{ cm}^{-1} - 3500\text{ cm}^{-1}$ with a centroid at 2937.06 cm^{-1} indicating the formation of co-ordinate complexation of zinc with CH_2 and COO^- groups (Persson *et al.*, 2005) [11] Figure 3.

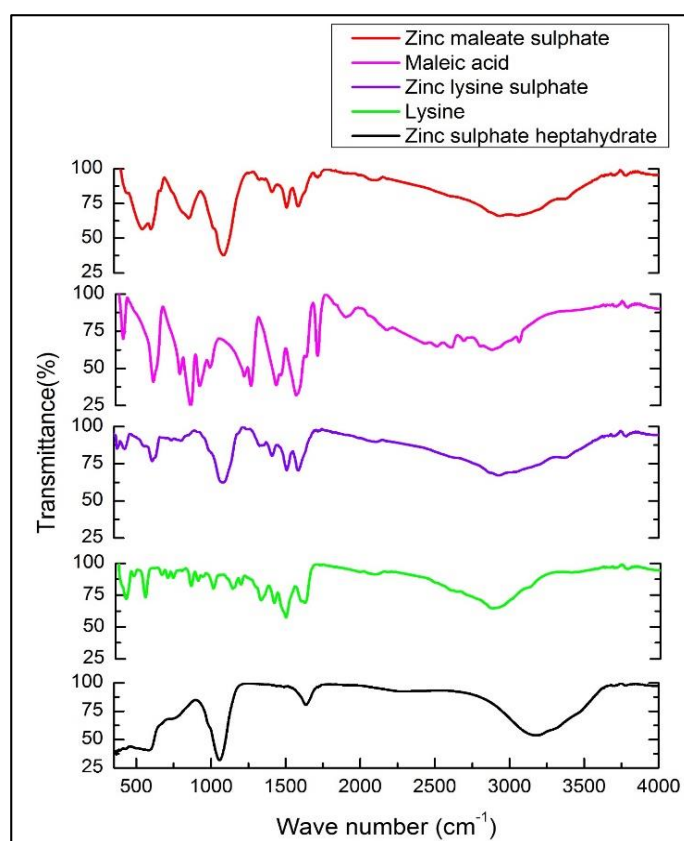


Fig 3: Comparative FT-IR peaks of zinc sulphate heptahydrate, Lysine, Zinc Lysine sulphate, Maleic acid, Zinc maleate sulphate

Zinc oxalate sulphate

From the FT-IR spectrum of Oxalate the IR bonds at 3413.39 cm^{-1} and 2644.69 cm^{-1} is due to strong and broad stretching of OH group. It indicates that presence of alcohol and weak stretching of carboxyl groups. The peaks in FT-IR at 1644.98 cm^{-1} and 1112.73 cm^{-1} assigned to the carboxylate aromatic ring made due to $\text{C}=\text{O}$ strength and broad stretching of alcohol (C-O).

By comparing the spectra of Zn^{2+} - oxalate sulphate and oxalic acid. It can be observed that the spectrum of zinc oxalate sulphate contains broad high intensity in the range from 3000 cm^{-1} to 3500 cm^{-1} with at centroid 3366.14 cm^{-1} due

to strong and band stretching of OH group, which further indicates presence of alcohols (Murali S, 2016) [15].

The wavelength at 1652.4 cm^{-1} , 1442.4 cm^{-1} in synthesized chelate are assigned to indicate presence of carboxylate aromatic ring made due to $\text{C}=\text{O}$ strength and broad stretching of alcohol (C-O) which are shifted from 1644.98 cm^{-1} and 1112.73 cm^{-1} present in standard oxalic acid. As compared to the positions of those bonds in the spectrum of oxalic acid which confirm the presence of primary and secondary carboxyl groups in the structure of zinc oxalate. As compared to the positions in the spectrum of zinc oxalate sulphate, these bonds, exhibits in the oxalic acid spectra, this indicates

coordination of carboxyl group and Zn^{2+} ion. The peaks characteristics to zinc oxalate sulphate are mentioned in Fig 4.

Zinc tartarate Sulphate:

The broad peak in zinc sulphate at wavelength of 1056.8 cm^{-1} indicates the sulphate groups (SO_4^{2-}). The peak in Zinc tartarate sulphate at 1097.3 cm^{-1} with slight vibrational shift from the former clearly confirms that the sulphate compound has been bonded to the chelate from zinc sulphate heptahydrate (Saha and Podder 2011) [4].

The symmetric structure of COO^- in tartaric acid is with sharp peak at 1440.56 cm^{-1} . On co-ordination, the vibration peak shifts it to the position of 1411.64 cm^{-1} in Zn-maleate complex (M.U Chinonye *et al*, 2017; Reddy 2005; Lin *et al*, 2015) [2, 14, 5]. By these similar peaks in free organic acid and in synthesized chelated compound, it clearly confirms the formation of carboxylate bonded to zinc.

The stretching vibrations of the water molecule are expected in the region $3000\text{-}3600\text{ cm}^{-1}$ in the pure zinc sulphate heptahydrate (Kanagadurai *et al*. 2009; Zhang, 2018) [13, 19].

The single sharp peak in synthesized zinc maleate sulphate at 1581.34 cm^{-1} and 3782.69 cm^{-1} indicates the evidence of ring formation and multi-coordinated $\nu(OH)$ group respectively. In Tartaric acid, the peak at 485.97 cm^{-1} indicates the carboxyl group where the absorption of infra-red occurs. But, when it bound to Zn, the peak get diminishes and no such peak is absorbed in Zn-tartrate sulphate.

On comparing free tartaric acid and chelated zinc tartrate sulphate, the former one shows a vibration peak at 2962.13 cm^{-1} which is due to twisting vibration of CH_2 groups. Upon chelate formation the vibration peak at 2962.13 cm^{-1} gets disappears and shifted to 3098.08 cm^{-1} , which indicates a new coordinate bond formation has occurred through the carboxylic acid (Persson *et al*, 2004) [11]. Similarly the peaks observed in tartaric acid at the wavelengths of 3395.07 cm^{-1} and 3323.64 cm^{-1} due to asymmetric carboxylic group are disappeared in chelated zinc tartrate and a new broad peak is formed at 3098.08 cm^{-1} which is due to twisting vibrations of CH_2 and carboxylic acid. The peaks characteristics to zinc tartrate sulphate are as shown in Fig 4.

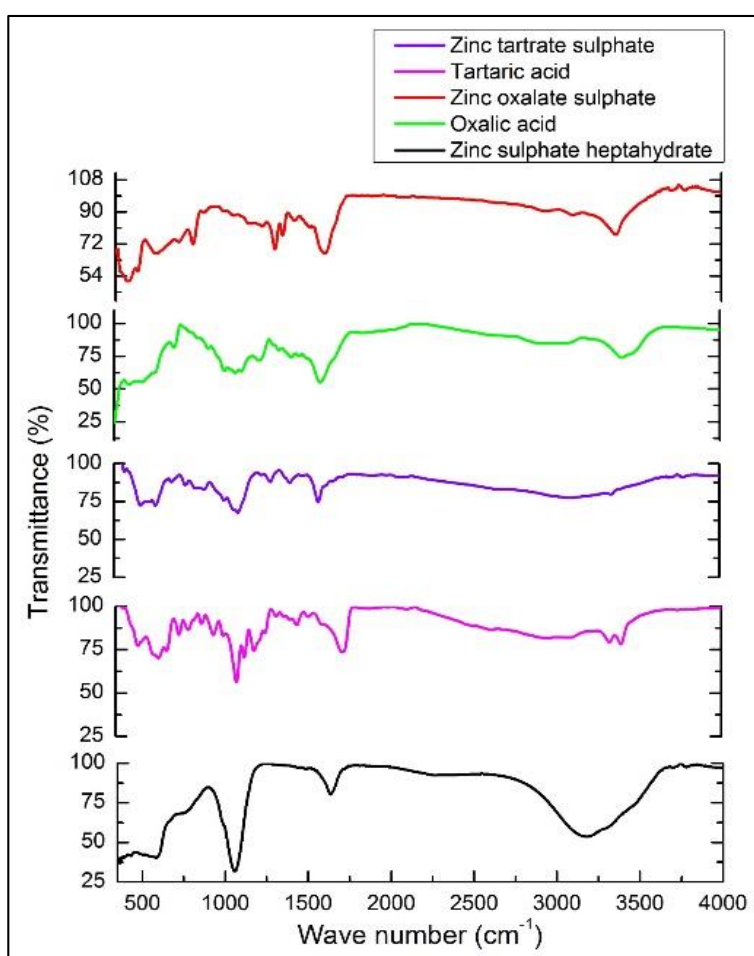


Fig 4: Comparative FT-IR peaks of zinc sulphate heptahydrate, Oxalic acid, Zinc oxalate sulphate, Tartaric acid, Zinc tartrate sulphate

Table 1: FT-IR characteristics of newly synthesized zinc chelates

| S. No | Chelate | SO_4^{2-} (cm^{-1}) | NH_2 broad peak (cm^{-1}) | $\nu(OH)$ (cm^{-1}) | C=O (cm^{-1}) | COO^- (sym) (cm^{-1}) | Complex of CH_2 and COO^- (asym) groups (cm^{-1}) |
|-------|------------------------|---------------------------|---------------------------------|-------------------------|-------------------|-----------------------------|---|
| 1. | Zn – Citrate sulphate | 1056.69 | - | 3000-3600 | 1712.48 | 1399.1 | 3176.44 |
| 2. | Zn – Glycine sulphate | 1065.48 | 3169.44 | 3000-3600 | - | 1393.32 | 3169.44 |
| 3. | Zn – lysine sulphate | 1079.94 | 2927.41 | 3000-3600 | 1718.26 | 1409 | 2927.41 |
| 4. | Zn – Maleate sulphate | 1084.76 | - | 3000-3600 | 1716.34 | 1410.67 | 2937.06 |
| 5. | Zn – Oxalate sulphate | - | - | 3000-3600 | 1652.4 | - | 3366.14 |
| 6. | Zn – Tartrate sulphate | 1097.3 | - | 3000-3600 | - | 1411.64 | 3098.08 |

Conclusion

Organic zinc chelates can be considered as a best source for alleviating zinc deficiency in the soils and crops of India. The characterization of newly synthesized zinc chelates using FT-IR revealed that chelation has resulted in the change of properties in zinc sulphate and chelating agents used for the production. FT-IR spectroscopy showed strong evidence for the concentration-dependent formation of bis and mono complexes of Zn (II). This allows for quantitative measurement of chelation in solid samples. It also proved that, the organic-zinc chelates are promising sources of zinc to overcome zinc deficiency in soils and crops.

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