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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF IRON (III) PLANT-BASED OXALATO COMPLEX FROM *SPINACIA OLERACEA* (SPINACH)

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ABSTRACT

Soluble oxalates were extracted from *Spinacia Oleracea* **(**spinach) using deionized water. About 61% of the soluble oxalate leached into the boiling water at 100°C within 2 minutes. The extracted oxalate was precipitated as calcium oxalate and converted to oxalic acid through sulphuric acid liberation. The oxalic acid was crystallized, characterized using FTIR and the oxalato anion used as a ligand to synthesize a potassium ferric-oxalate complex with standard oxalic acids as control. Percentage yields of 89.7% and 95% were obtained for the extracted and standard oxalato ligands respectively. FTIR result showed peaks at 1666.55 cm^{-1} (C=O stretching), 3437.27 cm^{-1} (O-H stretching) and 1095.60 cm^{-1} (C-O stretching) for the extracted oxalate, similar to that of the standard. The melting point of the crystals was 190-196 °C and 189-190 °C for extracted and standard oxalic acids respectively. This result showed that oxalate, $C_2O_4^{2-}$ can be sourced from non-toxic natural sources like vegetables and used for the same purpose as industrially manufactured ones thereby saving cost.

KEYWORDS: Characterization, Oxalate, plant-based, spectroscopy, spinach.

INTRODUCTION

Oxalate (ethane dioate) is a group of salts derived from oxalic acid. They contain the dianion, $C_2O_4^{2-}$ which can also be written as $(COO)_2^{2-}$.A diet high in soluble oxalates increases the risk of developing kidney stones which predominantly contain calcium oxalate [1]. The consumption of foods containing high level of soluble oxalate may have a considerable effect on the amount of calcium, iron and magnesium absorbed. This is because the soluble calcium, magnesium and iron combine with the soluble oxalate in the intestine to precipitate the insoluble salts of the metals. This can be deleterious especially to pregnant women as it affects the development of the foetus as severe iron deficiency increases babies risk of being given birth prematurely [2-3].

About 20-40% of the oxalates in our bloodstream come from preformed oxalates in our foods [4]. While oxalates are found in both plant and animal foods, plant foods have long been the research focus, since some plants have especially high concentrations. Some of the major plant foods containing appreciable amount of oxalates (fresh weight basis) are: spinach, 0.3-1.2%; rhubarb, 0.2-1.3%; beet leaves, 0.3-0.9%; tea, 0.3-2.0% and cocoa, 0.5-0.9%. Other plants with low amounts of oxalates are potatoes, lettuce, carrots, cabbage, peas and beans [5-7].

The anion, $C_2O_4^{2-}$, a bidentate ligand easily formed complexes with both main groups (K, Na, Caetc) and some transition metals like iron and nickel. The industrial manufacturing processes of oxalic acid from which oxalato anion, $C_2O_4^{2-}$is gotten like direct acidification of sodium oxalate, acidification of sodium formate, oxidation of propylene with nitric acid etcare complex and involved toxic chemicals. With the difficulty of achieving success with these industrial processes and the dwindling economy of most sub-Saharan countries, the need to look for alternative and cost effective means of sourcing chemicals for laboratory uses and minimization of pollution is necessary. In this research, *Spinacia Oleracea* **(**spinach), a common vegetable grown globally and rich in soluble oxalate is being harnessed and used as a cheap source for the synthesis of an oxalato complex of iron.

MATERIALS AND METHODS

Sampling and Preparation

Spinach was randomly sampled from Maza market in Jos, North Central, Nigeria, washed with distilled-deionized water and stored for use. All the chemicals and reagents used for this work were of laboratory standards and prepared according to standard analytical procedures.

Preparation of ligand (oxalic acid) from *Spinacia Oleracea*

A modified Liu *et al* [8] method was used. The spinach was cut into small pieces. Exactly100 g were weighed and boiled with deionized water for 30min. The boiled spinach was homogenized using a food Blender, centrifuged and the liquid separated by decantation. Calcium chloride solution (0.5M) was added drop wise with stirring until full precipitation occurred. This was filtered and washed with cold water severally and 10% H_2SO_4 added.

Excess $H_2SO_{4\ (aq)}$ was removed by heating the solution in a gas fume cupboard at about 100 °C for 10 min. The solution was kept in a refrigerator at about 0° C for 2 days for crystallization of oxalic acid (as confirmed). The crystals were washed with ice-cold water and dried. The process and postulated equations are shown below;

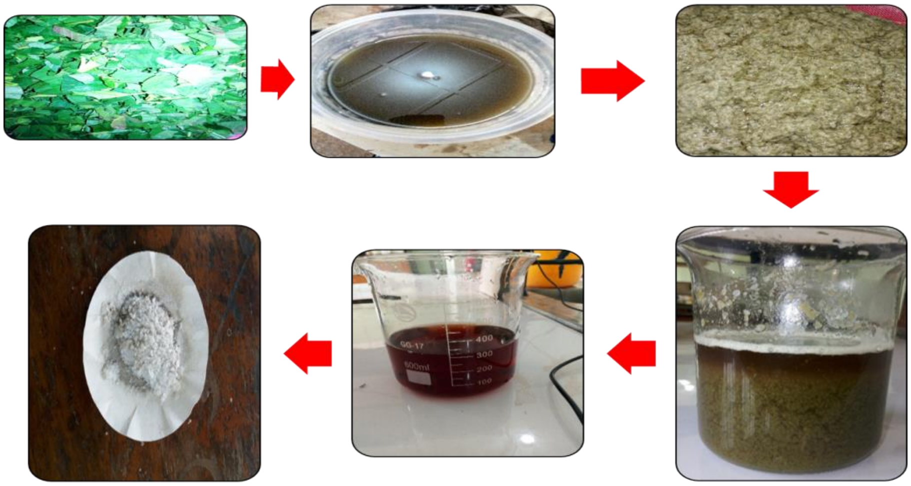


Figure 1: Extraction of soluble oxalates from *Spinacia Oleracea* and conversion to oxalic acid

$$K_2C_2O_{4(aq)} + CaCl_{2(aq)} \longrightarrow CaC_2O_{4(s)} + 2KCl_{(aq)} \quad - - - - - - -(1)$$

$$CaC_2O_{4(s)} + H_2SO_{4(aq)} \longrightarrow CaSO_{4(s)} + H_2C_2O_{4(aq)} \quad - - - - - - (2)$$

Synthesis of Potassium Ferric Oxalate $K_3[Fe(C_2O_4)_3].xH_2O$

All chemicals and reagents used are of analytical grades and prepared according to standard laboratory procedures. Byjus method [9] was slightly modified and used for the synthesis. In a 200 ml beaker, exactly 5g of $Fe(NH_4)_2(SO_4)_2.6H_2O$ was dissolved in 15 ml of deionized water in a 200 ml beaker to which 5 drops of 3 M H_2SO_4 have been added. To this solution, 25 ml of 1 M $H_2C_2O_4$ solution was added and the mixture heated to boiling with continuous stirring to a yellow precipitate. This was filtered and washed deionized water and decanted. Exactly 10 ml of saturated $K_2C_2O_4$ solution was added to the solid and the solution slowly heated to about 40° C. A further 20 ml of a 3% H_2O_2 was added drop-wise with continuous stirring at constant temperature until boiling. To the boiling solution, 8 ml of 1 M $H_2C_2O_4$ was added slowly until a green solution is formed. The hot green solution was filtered and then allowed to cool to room temperature. Exactly 10 ml ethyl alcohol was added to the precipitate and wrapped with aluminium foil. This was kept at room temperature in a cupboard for 3 days to grow crystals before separating through filtration using a Buchner funnel. The crystals removed were dried and characterized using a Shimadzu 8400S FT-IR (Japan).

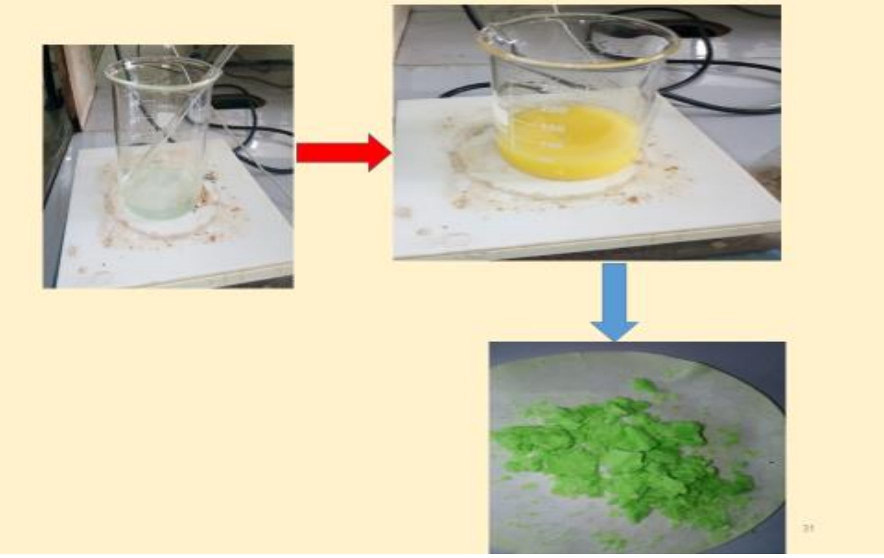


Figure 2: Synthesis of potassium ferric oxalate

The equations of the reactions involved are shown below;

$$Fe(NH_4)_2(SO_4)_2.6H_2O_{(aq)} + H_2C_2O_{4(aq)} \longrightarrow FeC_2O_4.2H_2O_{(s)} + (NH_4)_2SO_{4(aq)} \text{-} \quad - 3$$

$$FeC_2O_4.2H_2O_{(s)} + H_2C_2O_{4(aq)} + H_2O_{2(aq)} + 3K_2C_2O_{4(aq)} \longrightarrow 2K_3[Fe(C_2O_4)_3].H_2O_{(s)} \text{ - } 4$$

Determinations melting point, pKa and FT-IR

The melting point of the oxalic acid crystals were determined using the Thiele tube method where a capillary tube containing the crystals was immersed in a heated paraffin oil bath and the temperature at which the crystals began to melt was recorded and the temperature at which the crystals completely melted was recorded. The pKa value of the crystals was determined using the Irving-Rossotti method [10-12]. A Shimadzu FT-IR 8400S spectrophotometer was used to obtain the spectra of the extracted oxalic acid crystal and the synthesized complexes according standard methods.

RESULTS AND DISCUSSION

The results for the extracted oxalate from *Spinacea Oleracea* of 10 samples in 2 minutes boiling water (A) and that of the total soluble oxalates (B) are shown in Table 1. About 61.40% of the soluble oxalate in spinach was extracted using the boiling water. This shows that boiling can be an effective way of removing a good amount of soluble oxalate from vegetables before consumption. Boiling vegetables may be an effective strategy for decreasing oxalates in individuals predisposed to development of kidney stones.

Table 1: Amount of Oxalic Acid (in mg) extracted per 100 g of *Spinacea Oleracea*.

SNo.	A/100g	B/100g
1	170.2	286.7
2	178.5	289.9
3	167.3	262.7
4	156.3	263.9
5	171.8	252.3
6	148.9	290.1
7	189.6	304.5
8	176.2	296.4
9	180.5	286.5
10	188.3	280.4

A= Oxalic acid from soluble oxalates extracted by boiling water.
B= Oxalic acid from total soluble oxalates

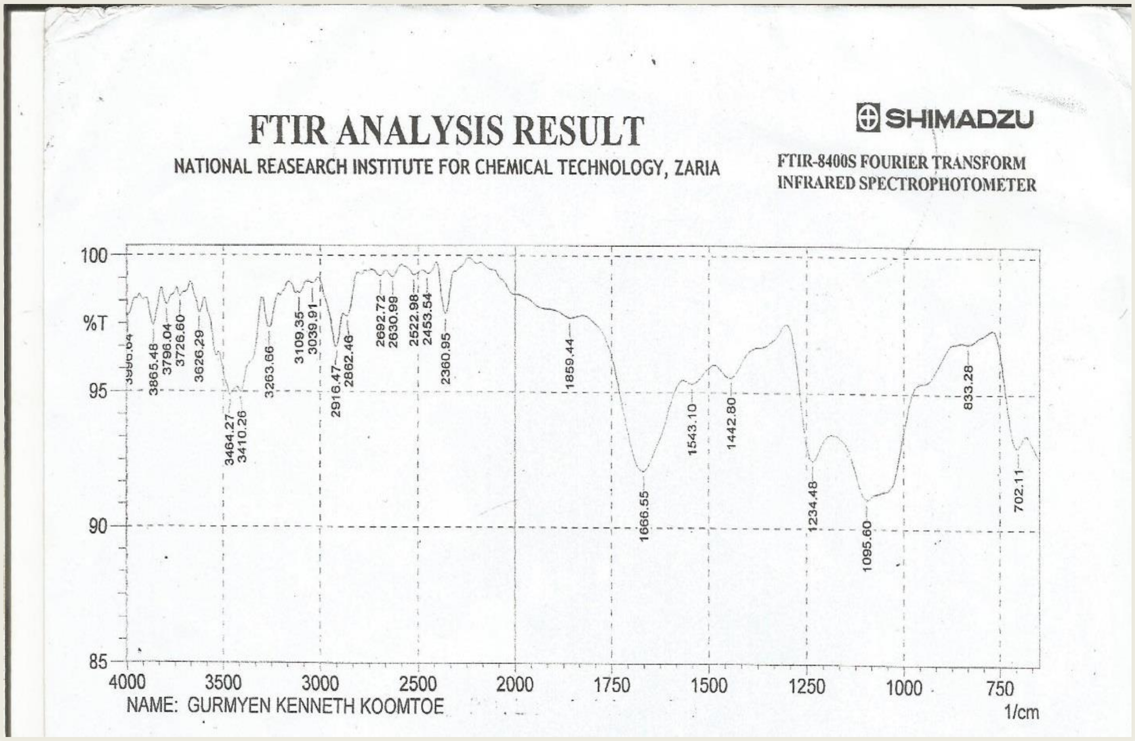
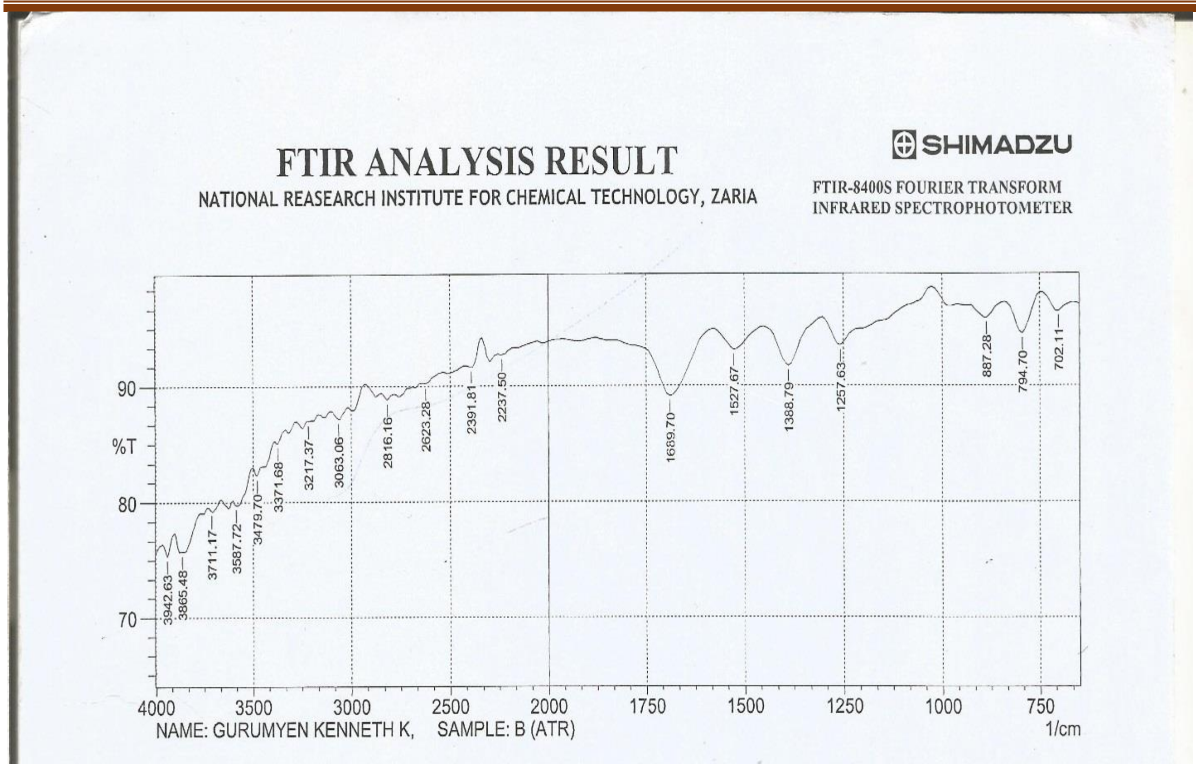


Figure 3: FTIR Spectrum extracted oxalic acid crystals

The FT-IR band of the oxalic acid (OA) crystals is shown in Figure 3. The result shows peaks at 3437.27 cm^{-1}, 1666.55 cm^{-1} and 1095.60 cm^{-1}. These peaks are suspected to be hydroxyl group (-OH), carbonyl group (C=O) and C-O groups respectively. All peaks are similar to peaks from a carboxylic compound. The melting point of the plant based crystals was found to range between 190– 196 ^{o}C. These values are very close to the melting point of standard oxalic acid which is 189-191 ^{o}C. The +5^{o}C difference can possibly be due to some dissolved $CaSO_4$ $_{(s)}$ in the oxalic acid and impurities (dust) during drying.



FTIR ANALYSIS RESULT

NATIONAL REASEARCH INSTITUTE FOR CHEMICAL TECHNOLOGY, ZARIA

SHIMADZU

FTIR-8400S FOURIER TRANSFORM
INFRARED SPECTROPHOTOMETER

NAME: GURUMYEN KENNETH K, SAMPLE: B (ATR)

Figure 4: FTIR Spectrum for $K_3[Fe(C_2O_4)_3].xH_2O$ Synthesized using Plant-based Oxalic Acid

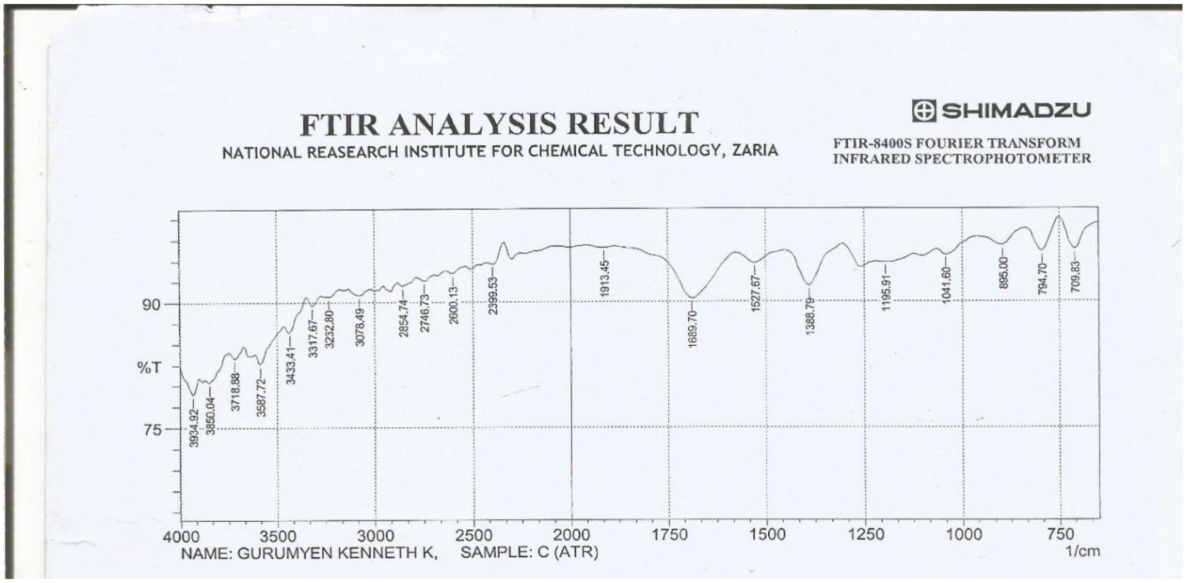


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Figure 5: FTIR Spectrum of $K_3[Fe(C_2O_4)_3].xH_2O$ using Standard Oxalic Acid

The FT-IR spectrum of the plant-based oxalate complex, OAC, (Figure 4) and that of the complex synthesized using standard oxalic acid, SOAC, (Figure 5) are similar. The spectrum show the absence/disappearance of the peak suspected to be hydroxyl group of a carboxylic acid after synthesis, a possibility of coordination. This is confirmed by the fact that in potassium Ferric Oxalate, there are no free hydroxyl groups as bonding has taken place at the –OH groups. The disappearance of the peaks shows that complexation has actually taken place. The melting point of the plant-based complex was 230-232°C. This is close to the standard melting point of hydrated potassium ferric oxalate trihydrate which is 230 °C [9].

CONCLUSION

Spinach is one of the most consumed vegetables in Nigeria. It has high oxalate content which affects the availability of iron, calcium and Magnesium in the body. Deficiency in those metals has caused serious health problem to man. High oxalate in food is the major causes of kidney stone when absorbed into the body due to formation of calcium oxalate. If considerable amount of soluble oxalates can be removed before consumption, it will not only help in avoiding the above mentioned problems, but can be utilized as ligand in synthesizing oxalato complexes which is cost effective. Results obtained showed that there is no or little differences in melting points and FTIR spectra values of the plant based crystals as compared to standard oxalic acid. The same similarity was obtained for the complexes synthesized. Boiling and leaching of oxalate can help in reducing the amount of soluble oxalates from vegetables. This soluble oxalate can be converted into oxalic acid which can be used in synthesis of compounds and can also be used in the industry when in large quantity. This study has not only revealed a cheap source of oxalic acid, but has also created an awareness to the fact that people susceptible to oxalate-related kidney stones problems can use boiling as a means of reducing soluble oxalates from vegetables before consumption.

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