*IOSR Journal Of Environmental Science, Toxicology And Food Technology (IOSR-JESTFT)*
*e-ISSN: 2319-2402,p- ISSN: 2319-2399. Volume 6, Issue 2 (Sep. - Oct. 2013), PP 90-97*
*www.Iosrjournals.Org*

# Sythesis and Characterisation of Cerium (IV) Iodotungustate Copper Selective A Inorganic Cation Exchanger

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***Abstract:*** *Ten samples of a new inorganic ion exchanger cerium(IV) iodotungustate have been synthesized under varying conditions. The exchanger has been characterized by Ion excange capacity, Thermal Stability, Chemical Stability, Distribution Studies, FTIR, TGA and XRD studies. The maximum ion exchange capacity, for Sodium ions of the synthesized ion exchanger, has been found 1.0 meq/g. The state of the exchanger is found to be amorphous. The ion exchanger is found to be stable against some acidic and basic solutions of different concentration. Distribution studies were done and Kd values were calculated. The exchanger has the maximum Kd value for copper and minimum for lead ions.*

***Key words:*** *Cerium (IV) iodotungustate, Inorganic cation exchanger, Ion exchange capacity, Thermal stability, Chemical stability and Distribution studies.*

## I. Introduction:

Ion exchange is basically a process of nature occurring throughout the ages from even before the drawing of human civilization therefore the phenomenon of ion exchange is not of a recent origin. The earliest of the references were found in Holy Bible, which says 'Moses' succeeded in preparing drinking water from brackish water by an ion exchange method, which is extensively used in separation science. Ion exchange includes cation exchange and anion exchange. Ion exchangers basically can be divided into two main groups organic and inorganic exchangers. A new inorganic three component cation exchanger cerium(IV) iodotungustate has been synthesized.

The ion exchanger has a good ion exchange capacity. The ion exchange capacity of the material was determined by the column method. pH titration studies of cerium(IV) iodotungustate was performed by the added salt method. In thermal stability for each 100ºC rise in temperature, loss is weight & loss in ion exchange capacity for sodium ions as a function of temperature were determined for the exchanger. The ion exchanger is found to be stable against some acidic and basic solutions of different concentrations. Kd values were calculated. The exchanger can used for binary separations, ternary separation, water softening & decontamination of aqueious solutions. The role of ion exchangers is valibident from the literature. The application of various synthesized exchangers has been reported for different purposes. Significance of inorganic cation exchanger is in removal of the elements in trace amounts. The inorganic exchanger can be applied the exchanger have been applied successful even at higher temperatures. Better stability towards heat and radiations make inorganic exchanger important. The synthesized ion exchanger is also characterized by Infra Red analysis, X-ray differaction analysis and Thermogravimetric analysis is also obtained.

## II. Experimental:

### 1. Chemicals & Reagents:

During the entire research work all the chemicals and reagents used were of AR grade. The chemicals used were obtained from Qualigens/ CDH Private Ltd. India Products. The chemicals used for preparing the exchanger were ammonium cerium nitrate $(NH_4)_2Ce(NO_3)_6$, potassium iodate ($KIO_3$) and sodiumtungustate $Na_2WO_4.2H_2O$. In addition of the above the HCl, $HNO_3$ and pH paper were used to complete the synthesis.

In the characterization of the synthesized ion exchanger a number of chemicals/ reagents such as sodiumchloride, sodium hydroxide, sodium salt of EDTA, hexamine, hydroxylammoniumchloride, triethylamine and erichrome black-T were used. All the chemicals used were of analytical grade.

### 2. Instrumentation:

Electric Oven (NSWINDIA), electric Rotary shaker (TANCO), magnetic stirrer with hot plate, two pan balance, electronic balance (Samson Model 300D), Borosil Glasswares, muffle Furnace (SHIVAKI-T 701 TANCO), toshniwal research pH meter (Model 110) were used. Perkin Elmer (Pyris diamond) in alumina pan with a current of nitrogen for thermal gravimetric analysis (TGA), Philips analytical X-Ray B.V. Diffractometer for X-Ray, Thermonicolet, spectrophotometer for Infra Red (IR) were available at Indian Institute of Technology, New Delhi.

**3. Synthesis of Matrix:**

The ion exchanger was synthesized using different salt solutions of decimolar strength. The solutions were mixed in different volume ratios at room temperature with continuous stirring with the help of a magnetic stirrer. On mixing yellow precipitates were obtained in all the ten ratios. The pH was set to one. All the precipitates obtained were filtered. Two of the precipitates passed through the filter paper. Only eight precipitates were obtained. The precipitates were washed and dried in an oven at 40ºC (±5). Table -1

**4. Granulization :**

The dried precipitates were converted into granules by putting them in water. (Table2)

**5. Generation:**

The granules so obtained were charged by treating them with 0.1 M $HNO_3$ solutions for 24 hours. The precipitates got charged and became ready to perform ion exchange.

**6. Characterization :**

**i) Ion-exchange capacity determination:**

The column method was used for the determination of the ion exchange capacity of each sample. 0.5 gm of dry ion exchanger in $H^+$ form of the eight exchanger samples were loaded into different columns having a glass wool support for the exchanger bed. 0.1 M sodiumnitrate solution was used to elute the $H^+$ ions from the exchanger with a flow rate of 0.2 ml $min^{-1}$. The released $H^+$ ions were determined titrimetrically using a standard 0.01 molar sodium hydroxide solution. The ion exchange capacity values of the samples were calculated and are given in table -3

**ii) Selection of the sample:**

Ion-exchange capacity of CIT-1 sample was found to be maximum out of the eight samples, therefore this sample was selected for detailed study.

**iii) Synthesis in bulk:**

CIT-1 was synthesized again in large amount by the same method as given earlier in order to study the exchanger in detail. This exchanger hereinafter shall be referred as CIT-1-II.

**iv) Determination of Ion Exchange Capacity:**

**(a) Column method :**

When ion-exchangers are utilized for analytical purposes, the solution is percolated through a fixed bed of ion exchanger packed in a column. Ordinarily the column is operated downflow by running the solution through the exchanger from top to bottom. The solution which enters the column is called the influent, and the filtrate from the column the effluent.

The first operation in an exchange cycle is the sorption step. At the beginning of this step the exchanger contains normally only one kind of exchangeable ions. The influent, which may contain one or several exchangeable ions, is passed through the column. After this column is rinsed with water. The exchanger contains the exchangeable ions from the solution as well as a certain amount of the ions originally present in the exchanger.

The ion exchange capacity of the exchanger CIT-1-II synthesized in bulk was determined by column method. Ion exchange capacity value was found to be close to the earlier value.

**(b) pH Titration Method :**

Ion exchange capacity of the exchanger was also determined by pH titration method. pH titration studies of Cerium(IV) iodotungustate (cation exchanger) was done by the added salt method (NaCl, NaOH). Eleven equal portions of the exchanger were placed in eleven different beakers containing equal volumes of the solutions of NaCl & NaOH in ten different ratios (TAble-4). The beakers were shaken occasionally and then kept as such for twenty four hours to establish the equilibrium. After twenty four hours pH of all the samples were recorded. The graph was plotted between pH & hydroxyl ion concentration (Fig-1). This graph was used to calculate the ion exchange capacity of the exchanger.

**v) Thermal Stability:**

For thermal stability determination of seven equal portions (500ml each) of the exchanger (CIT-1-II) were heated for one hour at different temperatures in the muffle furnace and the the ion exchange capacity of all the above was determined as usual by the column process (TAble-5).

**vi) Chemical Stability:**

The stability of eleven equal portions of the exchanger was determined in different acid and base solutions. HCl, KOH, $HNO_3$, $H_2SO_4$, NaOH and $CH_3COOH$ solutions were used. 25 ml of each solution was poured on a 500mg of the exchanger taken in the eleven different 50ml beakers with continuous shaking for 6 hours and then kept them as such for twenty four hours at room temperature. Detailed quantitative studies regarding the stability of the exchanger, were made in different solutions as shown in (Table-6).

**Distribution Studies:**

Kd values for different metal ions were determined by batch method. 500mg of Cerium(IV) iodotungustate (CIT-1-II) in $H^+$ form was kept in 25ml of metal ion solution at 25ºC for 6 hours, with intermittent shaking to rech equilibrium. Then the solution was kept as such for 24 hours. After 24 hours the solution was filtered and metal in concentration was determined using appropriate indicator by EDTA method. The concentration of the metal ion in the solution was also determined before treating with the ion exchanger.

The difference of metal ion concentration was calculated. Different metal ion solution's were treated in the same way as above. The Kd values were calculated by the following equation.

$$Kd = \left[\frac{(1-F)}{F}\right]\frac{V}{W}\,(mlg^{-1})$$

Where, I and F are initial & final burette readings

V is volume of solution in ml taken & W is the dry mass of the ion exchanger in gm. Kd values are given in table-7

**X-ray analysis (XRD):**

X-ray diffraction (XRD) pattern was obtained in an aluminium holder for the exchanger CIT-1-II in the original form using a pW 1148/89 based differactometer with Cu, Cd radiations. The study was done between 10º to 80º 2Q values with the spectrum of CIT-1-II as given in fig.-3

**Fourier transform infrared (FTIR) Study) :**

The Fourier transform infrared spectrum of CIT-1-II in original form dried at 40ºC was taken by KBr disc method at room temperature. The strong and broad absorption bad in the region 3600-3000cm-1 may be assigned to interstitial water molecules and free hydroxyl groups (Fig.4).

**Thermogravimetric TGA study :**

TGA graph of the synthesized ion exchanger is also obtained, in which we study the loss of water molecules & other components at different temperatures. Thermogravimetric analysis (TGA) data of the inorganic ion exchanger are present in Fig.-5.

## III. Results & Discussion:

Cerium(IV) iodotungustate was obtained in all the ten samples (Table-1). The ion exchange capacity of sample number-1 was found to be maximum (Table-3). The ion exchange capacity of sample number-1 was found to be 1.00 meq/g. Therefore sample number-1 was selected for detailed study.

The pH titration curve (Fig.1) shows that $OH^-$ ions increases on increasing the volume of NaOH solution to the system. The ion exchange materials released $H^+$ ions. The effect of temperature on ion exchange capacity of cerium(IV) iodotungustate shows that the ion exchange capacity decreases with increases in temperature, in this study the effect of temperature on ion exchange capacity of cerium(IV) iodotungustate for $Na^+$ ions was studied. Data shows that loss in ion exchange capacity causes, effect on colour and loss in weight. The graph was plotted between temperature & ion exchange capacity as shown in (Fig-2).

The chemical stability studies (Table-6) shows that CIT-I-II samples are highly stable in acids and bases. However, in acidic and basic media with the concentrations higher than 0.1 $mol^{-1}$ the exchanger is completely dissolved.

Distribution studies were done with different metal salt solutions.

The study revealed that cerium(IV) iodotungustate is more selective for $Pb^{2+}$ and least selective for $Cu^{2+}$. The obtained values of Kd are given in table-7. The X-ray diffraction pattern of cerium(IV) iodotungustate exhibited weak peaks indicating its amorphous form (fig.3). In order to further characterize the material its FTIR study (fig. 4) was obtained. The thermogram (fig-5) of CIT-I-II shows weight loss which is initially due to the removal of external water molecular from exchanger.

## Conclusion:

Amorphous ion exchanger CIT-I-II was found to have good ion exchange capacity. High chemical & thermal stability.

**Acknowledgement :**

The authors are thankful for assistance provided by the Indian Institute of Technology, New Delhi to carry the research work.

**Table-1**
**SYNTHESIS OF TEN CIT SAMPLES**

| Serial Number | Sample Number | Inter-Mixing Ratios | | | pH Value | Yield (gm) | Colour of ppt. | Colour of ppt after drying |
|---|---|---|---|---|---|---|---|---|
| | | Ammonium Ceric Nitrate solution | Potassium Iodate Solution | Sodium-tungustate Solution | | | | |
| 1 | CIT-1 | 1 | 1 | 1 | 0-1 | 1.21 | Yellowish | Yellowish |
| 2 | CIT-2 | 2 | 1 | 1 | 0-1 | 2.24 | Yellowish | Yellowish |
| 3 | CIT -3* | 1 | 2 | 1 | 0-1 | - | Yellowish | - |
| 4 | CIT -4 | 1 | 1 | 2 | 0-1 | 1.11 | Yellowish | Yellowish |
| 5 | CIT -5 | 2 | 2 | 1 | 0-1 | 3.11 | Yellowish | Yellowish |
| 6 | CIT -6 | 1 | 2 | 1 | 0-1 | 0.75 | Yellowish | Yellowish |
| 7 | CIT -7 | 2 | 1 | 2 | 0-1 | 2.99 | Yellowish | Yellowish |
| 8 | CIT -8 | 3 | 1 | 1 | 0-1 | 3.29 | Yellowish | Yellowish |
| 9 | CIT -9* | 1 | 3 | 3 | 0-1 | - | Yellowish | - |
| 10 | CIT -10 | 1 | 1 | 3 | 0-1 | 1.03 | Yellowish | Yellowish |

**Note : 1 = 40ml, 2 = 80ml, 3 = 120 ml**
**CIT = Cerium(IV) iodotungustate**
**ppt = Precipitate**
*** = Precipitates penetrated the filter paper**

**Table 2**
**GRANULIZATION**

| Serial Number | Sample number | C.O.G.B.G. | C.O.C.G. |
|---|---|---|---|
| 1 | CIT-1 | Yellowish | Yellowish |
| 2 | CIT-2 | Yellowish | Yellowish |
| 3 | CIT -3* | - | - |
| 4 | CIT -4 | Yellowish | Yellowish |
| 5 | CIT -5 | Yellowish | Yellowish |
| 6 | CIT -6 | Yellowish | Yellowish |
| 7 | CIT -7 | Yellowish | Yellowish |
| 8 | CIT -8 | Yellowish | Yellowish |
| 9 | CIT -9* | - | - |
| 10 | CIT -10 | Yellowish | Yellowish |

**Note : C.O.G.B.G.= Colour of granules before generation,**
**C.O.C.G. = Colour of charged granules**
*** CIT-3, 9= No Granules**

**Table 3**
**ION-EXCHANGE CAPACITY**

| Serial Number | Sample number | C.O.T.E. | I.E.C. (meq/g) |
|---|---|---|---|
| 1 | CIT-1 | Yellowish | 1.00 |
| 2 | CIT-2 | Yellowish | 0.40 |
| 3 | CIT -3* | - | - |
| 4 | CIT -4 | Yellowish | 0.80 |
| 5 | CIT -5 | Yellowish | 0.64 |
| 6 | CIT -6 | Yellowish | 0.80 |
| 7 | CIT -7 | Yellowish | 0.88 |

| | | | |
|---|---|---|---|
| 8 | CIT -8 | Yellowish | 0.36 |
| 9 | CIT -9* | - | - |
| 10 | CIT -10 | Yellowish | 0.84 |

**Note : C.O.T.E. = Colour of the exchanger**
**I.E.C. = Ion-exchange capacity**
*** = Ion-exchange capacity could not be determined because of insufficient amount of the precipitates**

### Table 4
### pH TITRATION

| Serial Number | Sample number | NaOH–NaCl System: NaOH solution (ml) | NaOH–NaCl System: NaCl solution (ml) | pH Values |
|---|---|---|---|---|
| 1 | CIT-1II | 0 | 50 | 3.42 |
| 2 | CIT-1II | 5 | 45 | 4.18 |
| 3 | CIT-1II | 10 | 40 | 5.64 |
| 4 | CIT-1II | 15 | 35 | 6.26 |
| 5 | CIT-1II | 20 | 30 | 7.14 |
| 6 | CIT-1II | 25 | 25 | 8.82 |
| 7 | CIT-1II | 30 | 20 | 9.64 |
| 8 | CIT-1II | 35 | 15 | 9.56 |
| 9 | CIT-1II | 40 | 10 | 10.24 |
| 10 | CIT-1II | 45 | 5 | 10.62 |
| 11 | CIT-1II | 50 | 0 | 11.83 |

**CIT-1II = Cerium(IV) iodotungustate which was synthesized in bulk.**

### Table 5
### THERMAL STABILITY

| Serial Number | Sample number | IAOIE (mg) | Temp. | FAOIE Temp. (mg) | WLOIE (mg) | Colour | I.E.C. (meq/g) |
|---|---|---|---|---|---|---|---|
| 1 | CIT-1II | 500 | R.T. | 500 | 00 | Yellow | 1.000 |
| 2 | CIT-1II | 500 | 100 | 476 | 24 | Yellow | 0.880 |
| 3 | CIT-1II | 500 | 200 | 468 | 32 | Yellow | 0.702 |
| 4 | CIT-1II | 500 | 300 | 442 | 58 | Light Yellow | 0.506 |
| 5 | CIT-1II | 500 | 400 | 396 | 104 | Light Yellow | 0.401 |
| 6 | CIT-1II | 500 | 500 | 384 | 116 | Gray | 0.203 |
| 7 | CIT-1II | 500 | 600 | 378 | 122 | Black | 0.108 |

**Note :**
**IAOIE – Initial amount of Ion-exchanger, FAOIE- Final amount of ion-exchanger,**
**WLOIE – Weight loss of ion-exchanger, I.E.C. – Ion-exchange capacity,**
**R.T. – Room temperature, Temp.- Temperature**

### Table 6
### CHEMICAL STABILITY

| Serial Number | Sample number | IAOIE (mg) | DABS: Solution | DABS: Concen-tration | WLOIE (mg) | FAOIE (mg) | Colour | I.E.C. meq/g) |
|---|---|---|---|---|---|---|---|---|
| 1 | CIT-1II | 500 | HCl | 1 M | 416 | 84 | Yellow | 0.8264 |
| 2 | CIT-1II | 500 | HCl | 2 M | 382 | 118 | Light Yellow | 0.6131 |
| 3 | CIT-1II | 500 | KOH | 1 M | 420 | 80 | Yellow | 0.9642 |
| 4 | CIT-1II | 500 | KOH | 2 M | 398 | 102 | Gray | 0.8268 |
| 5 | CIT-1II | 500 | $HNO_3$ | 1 M | 406 | 94 | Yellow | 0.9416 |
| 6 | CIT-1II | 500 | $HNO_3$ | 2 M | 396 | 104 | Gray | 0.7012 |
| 7 | CIT-1II | 500 | $H_2SO_4$ | 1 M | 436 | 64 | Yellow | 0.6618 |
| 8 | CIT-1II | 500 | $H_2SO_4$ | 2 M | 407 | 93 | Light Yellow | 0.8621 |
| 9 | CIT-1II | 500 | NaOH | 1 M | 401 | 99 | White | 0.7241 |
| 10 | CIT-1II | 500 | NaOH | 2 M | 386 | 114 | White | 0.6218 |
| 11 | CIT-1II | 500 | $2CH_3COOH$ | 1 M | 412 | 88 | Yellow | 0.5218 |

**Note :**

| | |
|---|---|
| **IAOIE – Initial amount of Ion-exchanger,** | **DABS- Different acid base solution,** |
| **WLOIE – Weight loss of ion-exchanger** | **I.E.C. = Ion-exchange capacity** |
| **FAOIE – Final amount of ion-exchanger** | |

**Table 7**
**Kd Values of Different Metal Ion solutions in DMW**

| Serial Number | Sample number | Different Metal | Initial EDTA Reading | Final EDTA Reading | kd Value (mlg$^{-1}$) |
|---|---|---|---|---|---|
| 1 | CIT-1II | Lead | 25.4 | 7.3 | 30.99 |
| 2 | CIT-1II | Zinc | 26.6 | 24.4 | 1.12 |
| 3 | CIT-1II | Cadmium | 22.4 | 8.6 | 20.05 |
| 4 | CIT-1II | Copper | 25.2 | 24.7 | 0.25 |
| 5 | CIT-1II | Thorium | 26.6 | 20.5 | 3.71 |
| 6 | CIT-1II | Calcium | 29 | 20. | 5.62 |
| 7 | CIT-1II | Magnesium | 26.1 | 20.6 | 3.62 |

**Note : EDTA = Ethylenediaminetetraacetic acid**
**DMW = Demineralised water**

**Fig 1**
**pH TITRATION CURVE**

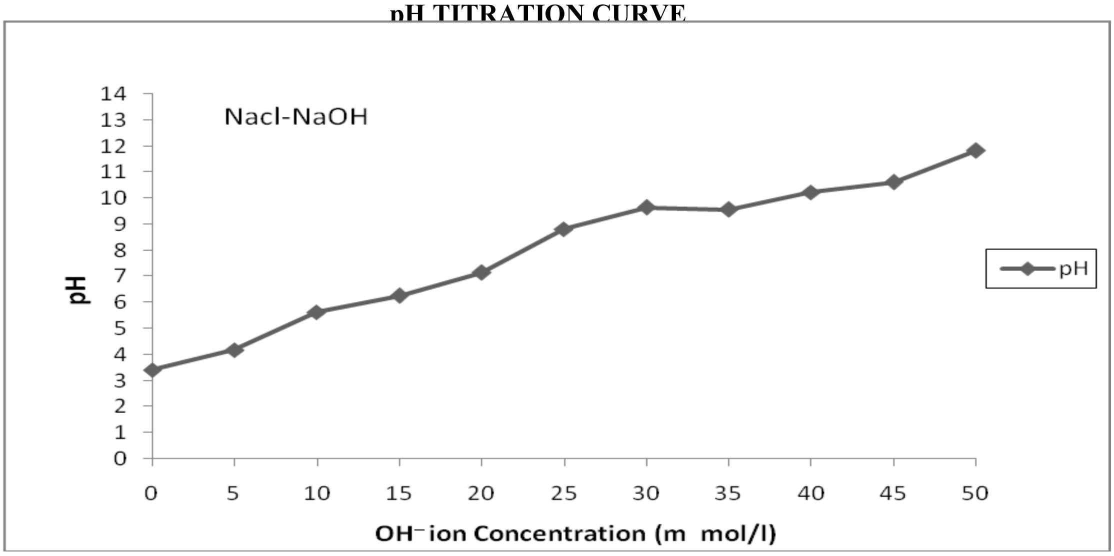
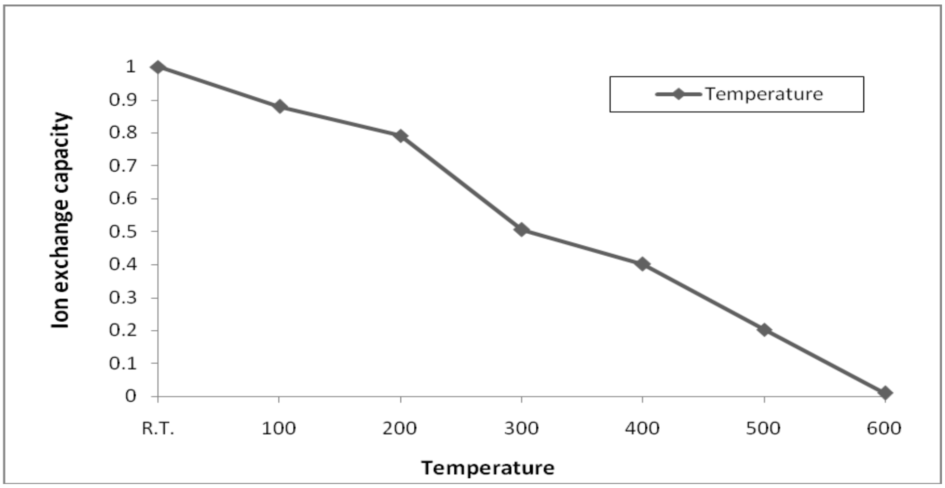


**Fig 2**
**THERMAL STABILITY CURVE**



***Note : R.T.= Room Temperature***

**Fig 3**

**X-RAY ANALYSIS**

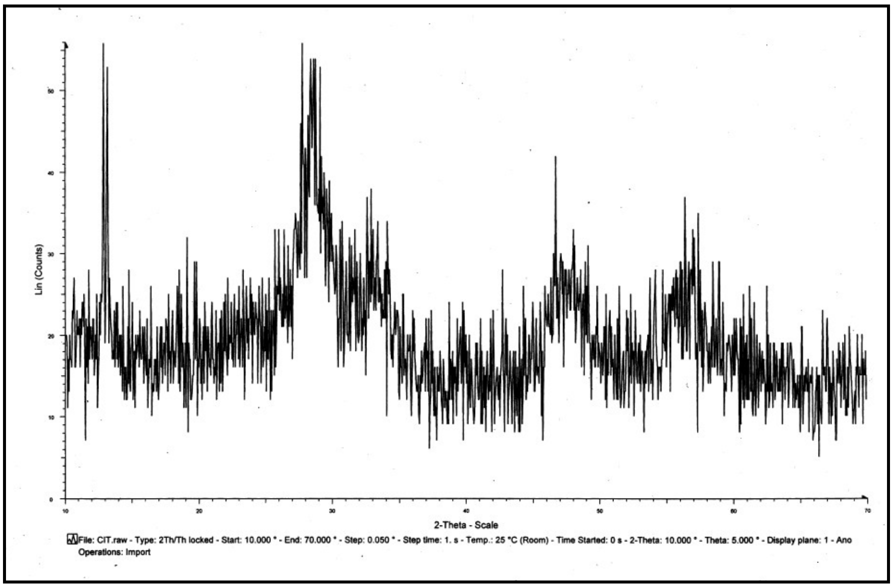


**Fig 4**

**FOURIER TRANSFORM INFRARED SPECTRUM**

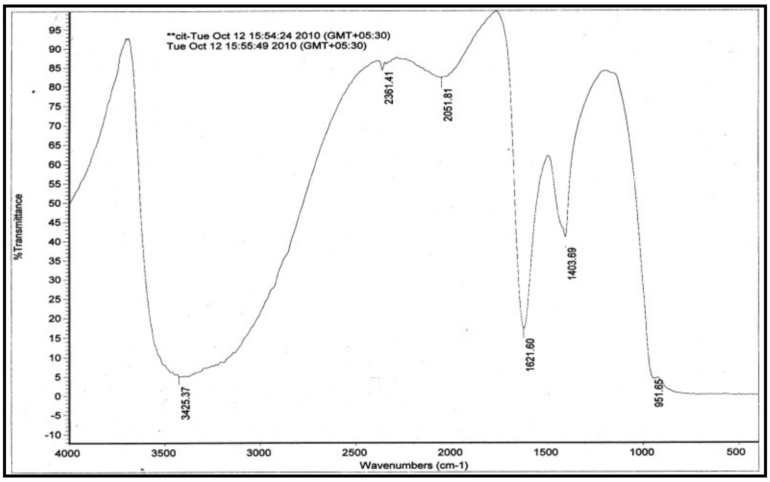
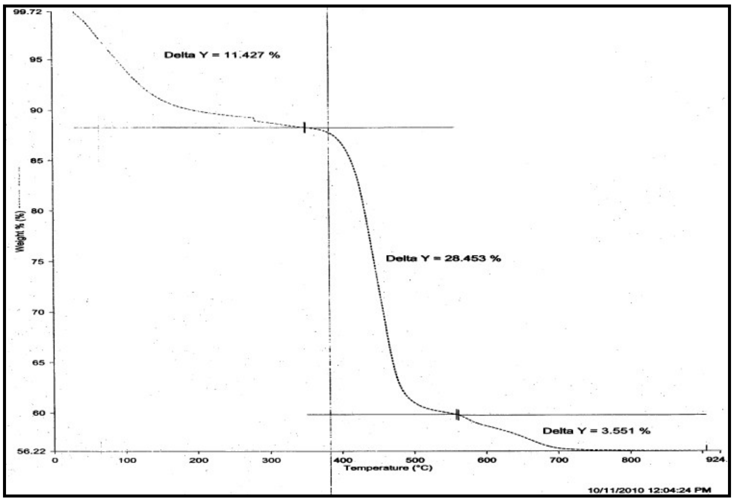


**Fig 5**

**THERMAL GRAVIMETRIC ANALYSIS**



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