FINAL REPORT OF
UGC MINOR RESEARCH PROJECT
(**F.MRP-6358/16 DT.30.06.2017**)

Green Synthesis of trivalent Chromium from hexavalent Chromium present in tannery effluents

SUBMITTED TO

SUBMITTED BY

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To

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Sir,

Sub : Submission of Consolidated UC and Final Report of UGC Minor Research Project
Scheme and Other documents - **F.MRP-6358/16 Dt.30.06.2017 -**Reg

Warm Greetings. I wish to express my heartfelt thanks for approving the UGC minor Research Project entitled "Green Synthesis of trivalent Chromium from hexavalent Chromium present in tannery effluents" (F.MRP-6358/16 Dt.30.06.2017). I am here by submitting the consolidated Utilisation Certificate and Final project report for the year 2017-2019 along with Annexure III, Annexure IV, Annexure V, Annexure VI and Annexure VII. Kindly acknowledge the same.

Thanking you

Yours Sincerely

(**K.JEGATHEESAN**)

Green Synthesis of trivalent Chromium from hexavalent Chromium present in tannery effluents

1.Introduction

The branch of science that deals with very small nanosized particles of less than 100 nm are known as the nanotechnology and they are all involved in the synthesis, characterization of materials. Nanoparticles research is an important aspect in the field of nano technology due to its innumerable application. In the present study chromium nanoparticles are synthesized from the tannery effluents using plant extracts.

Chromium is the 7[th]most abundant metal in earth's crust and an important environmental contaminant released in to the atmosphere due to its huge industrial use. Among the entire industrial waste tannery effluents are ranked as the highest pollutant and which includes compounds like Arsenic, Cadmium, Cobalt, Copper, Chromium, Nickel, Lead, Phenol, Chloride, Sulphide, tannin and formaldehydes. Among these chromium plays a major role in polluting water environment. Chromium exists in nine valence states ranging from -2 to +6 of these states, only the Trivalent chromium [Cr(III)] and Hexavalent chromium [Cr(VI)] have primary environmental significance because they are the most stable oxidation forms in the environment. Both are found in various forms of water and wastewater. Hexavalent chromium and trivalent chromium species have different chemical and biological characteristics.

Cr (VI) is comparatively more toxic than Cr (III) due to the characteristic like high solubility, rapid permeability through biological membranes and subsequent interactions with nucleic acids & intercellular protein. Cr (VI) more toxic, it is usually associated with oxygen such as chromate (CrO_4) and dichromate ($Cr_2O_7^{-2}$) due to solubility and mobility in soil environment and water. Moreover, Cr (III) is in the form of oxides, hydroxides or poorly soluble sulfates by which it is less mobile. Cr (VI) is a strong oxidizing agent and in the presence of organic matter is reduced to Cr (III); this transformation is faster in acidic environment. However, chromium is one of the important essential elements for plants and animals. But in higher amount it becomes toxic. The maximum level of Cr permitted in wastewater is 5mg/L for trivalent chromium and 0.05mg/L for hexavalent chromium. But the effluents of these industries contain chromium at concentrations ranging from tenths to hundreds of milligrams per liter.

In order to reduce the toxicity, it is essential for industries to treat their effluents to reduce the Cr to acceptable levels. Due to more Stringent environmental regulations, most of the wastewater produced in huge quantities, laden with Cr. Several methods have been used for removal of toxic metal ions from the effluent. The most commonly used conventional processes to remove Cr (VI) are Precipitation, although ion exchange and adsorption. However, these technologies have certain limitation such as high operation cost, low removal efficiency, generation of toxic sludge and requirement of high energy. Therefore, Recent developments in nanoscience and nanotechnology pave the way to solve the technological constraint of water purification.

The nanoparticles are synthesized through physical, chemical and biological methods. The physical and chemical methods are extremely pricey. The biological methods of nanoparticles synthesis would assist to remove ruthless processing conditions, by allowing the synthesis at physiological pH, temperature, pressure, and at the same time, at negligible cost. During the past decade, it has been demonstrated that many biological systems, including plants can transform metal ions into metal nanoparticles via the reductive capacities of the proteins and metabolites present in them. It is significant that the nanoparticle production using plants have an important advantages over other biological systems(algae, diatoms, bacteria, yeast, fungi and human cells).Plants are able to reduce the metal ions, especially those which have strong metal ions hyper accumulating reducing capacity and so plant extracts have been used for green synthesis of Nanoparticles.

In an effort towards minimizing the use of toxic chemicals and reduce the generation of hazardous waste while obtaining metal nanoparticles, CSIR–Central Leather Research Institute (CLRI), Chennai has found suitable biosynthetic and/or biomimetic processes of metal nanomaterial synthesis for environmental and biomedical applications. Hence, the present study has been aimed at Chromium Nanoparticles Synthesis using leaf extracts of *Murraya koenigii* leaf extracts and *Raphanus sativus*(tuber) extracts from Potassium dichromate, Potassium Chromate and tannery effluents.

2.METHODOLOGY
2.1. COLLECTION OF THE TANNERY EFFLUENTS
The effluents samples were collected from discharge site of the leather in the Dindigul District.

2.2. PHYSICAL AND CHEMICAL PARAMETERS

The physicochemical properties such as appearance, odor, pH, Electrical conductivity(EC), Biological oxygen demand (BOD), total dissolved (TDS),Total hardness, Total alkalinity, Heavy metal such as chromium were also analysed.

(i) Determination of pH

The pH is determined by measurement of the electromotive force (emf) of a cell comprising of an indicator electrode (an electrode responsive to hydrogen ions such as glass electrode) immersed in the test solution and a reference electrode (usually a calomel electrode). The emf of this cell is measured with pH meter.

(ii) Determination of Electrical Conductivity(EC) :

The EC is determined by measuring the effluents ability to conduct an electric current. It was measured using digital conductivity meter.

(iii)Determination of Dissolved Oxygen (DO):

The DO is the measure of oxygen dissolved in the effluents.

(iv)Determination of BOD, TDS:

BOD of an effluent is the milligram of oxygen required to biologically stabilize one liter of that effluent (by bio-degradation of organic compounds with the help of micro-organisms).

Total solids include **(TSS)** and **(TDS).** It gives the measure of the turbidity of the effluents. Suspended solids cause the water to be milky or muddy looking due to light scattering from very small particles in the samples.

(v) Determinatin of Salinity and Conductivity:

Salinity is the total concentration of all dissolved salts in water and Conductivity is the measure of water's capability to pass electric flow.As such, Salinity is a strong contributor to Conductivity.All the above mentioned parameters are measured using Water Analysis Kit -371.

(vi) Determination of Total Hardness

Hardness is to find the mineral content dissolved in the effluent sample. The hardness of the sample is determined by titrating the sample with EDTA of known value of pH, volume and concentrations.

Reagents: EDTA, Standard $CaCO_3$ solution, Erichrome black-T indicator, Buffer solutions (NH_4Cl & NH_4OH) were used.

Procedure:

Take 20ml of Sample in a conical flask , add 5ml of buffer solution and few drops of Erichrome black-T indicator. The solution appears wine red color then titrate with EDTA solution in the Burette, till the wine red color changes to blue which is the end point. Note the volume of titrant and calculate using the formula.

Total Hardness(mg/L) = $\dfrac{\text{Volume of EDTA} \times 100}{\text{Volume of Sample(ml)}}$

(vii) Determination of Alkalinity

Alkalinity is the capability of the water to neutralize acid. Measuring alkalinity is important to determine neutralize acidic pollution in the effluent released from the tannery industry. The alkalinity of sample can be determined by titrating the sample with sulphuric acid or hydrochloric acid of known value of pH, volume and concentrations.

Reagents:

Sulfuric acid(H_2SO_4), Phenopthaline and Methyl orange indicator.

Procedure:

Take 50ml of Sample in a conical flask then add two drops of Phenolphalein indicator. If pink color appears titrate it against the acid titrant (H_2SO_4) until it turns colorless (end point).Note the volume of titrant. If pink color doesn't appear, Add Methyl orange and continue titration till the color changes from yellow to orange (end point) note the volume of titrant and calculate using the formula.

PA(mg/L) = $\dfrac{\text{A} \times \text{Normality of HCl} \times 100 \times 50}{\text{Volume of sample}}$

MA(mg/L)= $\dfrac{\text{A} \times \text{Normality of HCl} \times 100 \times 50}{\text{Volume of Sample}}$

A = Vol of Sulfuric Acid used

PA = Phenolphalein Alkalinity

MA = Methyl orange Alkalinity

Total Alkalinity (mg/L) = PA+MA

(viii) Estimation of Chromium (Diphenylcarbazide method)

The hexavalent chromium is determined spectrophotometrically by reaction with diphenylcarbazide in acid solution.

Reagents:

- **Stock Chromium Solution**

    Dissolve 141.4 mg of $K_2Cr_2O_7$ in water and dilute to 100 ml (1.0 ml = 500 μg of Cr).

- **Standard Chromium Solution**

    Dilute 1.0 ml of stock chromium solution to 100 ml; (1.0 ml = 5.0μg of Cr).

- **Sulphuric Acid**

- **Diphenylcarbazide Solution**

    Dissolve 250 mg of 1, 5-diphenylcarbazide (1,5-diphenylcarbohydrazide) in 50 ml acetone. Store in an amber bottle. Discard when the solution becomes discolored.

Procedure

Preparation of Calibration Curve

Pipette out measured volumes of standard chromium solution ranging from 2 to 20 ml(to give standards for 10-100 μg of Cr), into 100 ml beakers. Make up the volume to about 50 ml with water. Use 0.2 μ H_2SO_4 and a pH meter to adjust the pH of each solution to 1.0 ± 0.3. Transfer quantitatively each of these solutions into 100 ml volumetric flasks and add 2.0 ml of diphenylcarbazide solution. Dilute to 100 ml with water, mix and let these stand for 5 to 10 min for full color development. Meanwhile, reagent blank also prepared in an identical manner using 10 ml of water. The absorbance of the standard solutions were measured at 540 nm, using reagent blank as reference solution. Calibration curve was constructed by plotting absorbance values against micrograms of chromium in 100 ml of the final volume.

Determination of Hexavalent Chromium (Cr^{6+})

Pipette out a portion of filtered sample (filtered through 0.45 μm membrane filter), containing 10 to 100 μg of Cr into a 100 ml beaker. Make up the volume to about 50 ml with water. Adjust pH of this solution to 1.0 ± 0.3 using 0.2N H_2SO_4, and a pH meter. Transfer quantitatively in to a 100 ml volumetric flask; add 2.0 ml of diphenylcarbazide solution. Dilute to 100 ml with water, mix well and allow to stands for 5 to 10 min. Measure absorbance at 540 nm, using reagent blank as reference solution. From the absorbance data, determine the micrograms of chromium present in 100 ml of the final solution using the calibration curve. From the absorbance data, determine the micrograms of Cr present in 100 ml of the final solution using the calibration curve.

2.3. PLANT MEDIATED SYNTHESIS OF CHROMIUM NANOPARTICLES

2.3. a. Selection of Plant Materials

The plant materials selected for present study are *Murraya koenigii* and *Raphanus sativus.*

2.3b. Preparation of Plant extracts:

The plant materials such as leaves of *Murraya koenigii*and tubers of *Raphanus sativus* were washed thoroughly in tap water. 1g of the leaves were weighed using the electronic balance and ground using the mortar and pestle with 10 ml of water and centrifuged at 3000 rpm 2 mins. After that the supernatant were taken and made upto 50ml.The supernatant was used as the broth solution. Extracts of Curry leaf and Radish were prepared separately and used for Nanoparticles Synthesis.

2.3. c. Preparation of Potassium Dichromate ($K_2Cr_2O_7$) solution:

0.1M of $K_2Cr_2O_7$ solution was prepared by dissolving 0.141g in 100ml of distilled water. An orange colour potassium dichromate solution was obtained.

2.3. d. Preparation of Potassium Chromate solution:

0.1M of K_2CrO_4 solution was prepared by dissolving 1.94g in 100ml of distilled water. A yellow colour Potassium chromate solution was obtained.

2.3. e. Preparation of Chromium Nanoparticles:

50ml of plants extracts obtained from the leaves of *Murraya koenigii* and tubers of *Raphanus sativus* mixed separately with Potassium Dichromate, Potassium Chromate and Tannery Effluents. This reaction mixture was incubated at the room temperature for 5 minutes and subjected for analysis.

S.No	Reaction Mixtures
1	*Murraya koenigii*& $K_2Cr_2O_7$
2	*Murraya koenigii*& K_2CrO_4
3	*Murraya koenigii*& Tannery effluents
4	*Raphanus sativus*& $K_2Cr_2O_7$
5	*Raphanus sativus*& K2CrO4
6	*Raphanus sativus*& Tannery effluents

2.4.CHARACTERIZATION TECHNIQUES:

The characterization of chromium nanoparticles were done by UV-spectroscopy(UV-Vis,FTIR and SEM Anlaysis.

2.4. a. Sample preparation for UV-Vis Spectroscopy

A small aliquot of liquid samples was taken and used for the Characterization of Chromium Nanoparticles a UV-Vis spectrometer.the absorbance was measured in the wave length ranging between 400 and 700 nm.

2.4. b. Sample preparation for FTIR and SEM Analysis

The powdered Samples were prepared in a easiest way by placing the samples in between the calcium chloride salts in an air tight container, hence the moisture will be absorbed by $CaCl_2$ salt and the samples are completely dried and then powder were collected from it scrubbing the dried sample sticking on the surface of the beakers. The collected powders were used for FTIR and SEM Analysis.

3. RESULTS AND DISCUSSION

Tannery effluents constitute the bulk of the industrial effluents of the Dindigul area. In the present study, the effluents were collected, analysed for Physico-Chemical parameters. Finally attempts were with the chromium present in the effluents

3.1. Analysis of Effluents:

The effluents collected from the tannery industries around Dindigul areas are subjected to physical analysis.

3.2. Colour&Appearance:

The present investigation shows that the effluents were yellow in color with an offensive odor. The Color of the of the sample resembles the potassium chromate solution.(**Fig-1**)Our results were not in consonant with the findings of Sugasini and Rajagopal (2015) who observed the color of the effluents was blackish in color. Yellow colour of the effluent may be due to the absence of biodegradable and non-biodegradable high molecular weight organic compounds and in organic chemicals.

Fig 1:- Tannery Effluent

3.3. Physio-chemical parameters:

The tannery effluents were subjected to Physio-chemical analysis such as pH, EC,TDS, Total Hardness, Total alkalinity, DO, BOD, Salinity, Conductivity. The results are tabulated below in (**Table-1**).

3.3.a Temperature:

The observed temperature of the samples was 29.4∘C less than the atmospheric temperature of the Dindigul district. Similar results were reported by Farhad Ali *et al*., (2014) in the tannery effluents in Bangladesh.

3.3.b. pH:

The present study observed the average value pH of the effluent sample as 12.13 and hence the sample was found to be highly alkaline in nature. The observed pH values were deviated

from the standard values quoted by the Environmental (Protection) rules,1986. Similar study was also reported by Farhad Ali *et al.,* (2015) in the tannery effluents of Bangladesh who attribute the alkaline condition of the sample to industrial waste of effluents.

3.3.c.Electrical Conductivity (EC):

The electrical conductivity of water or Sample is its ability to conduct electric current and it depends on the presence of ions, their total concentration and temperature of water. In the present study, effluents EC value is 1924.75 µs/cm which exceeds the limits prescribed by WHO (1400 µs/cm) which indicates that discharge of cations and anions were higher in effluents. This higher conductivity alters Chelating properties of water bodies and creates an imbalance of free metal availability for flora & fauna (Akan *et al.,* 2008). Sugasini & Rajagopal (2013) and Farhad Ali *etal.,*(2015) reported the high electrical conductivity similar to the present investigation.

3.3.d.Total Dissolved Study (TDS) :

The entire TDS value evaluation of entire combination of minerals and salts can be known by Nivruti *et al.,* (2013). In this research the TDS values of the tannery effluent (5340mg/L) were higher than the standard one(2100mg\L).

3.3.e.Hardness:

The Hardness of the effluent reported in the present study was found to be less (6mg\l).

3.3.f.Alkalinity:

According to Saxena and Shrivastava(2002), alkaline nature of the tannery effluent may be due to the presence of carbonates and bicarbonates present in the effluent. The investigation reveals that alkalinity of the Sample is 210mg/l

3.3.g.DO:

The Sample contains 8.76 mg/L of Oxygen dissolved and it varies based on the changes in the temperature.

3.3.f.BOD:

In the present Study, BOD was found to be .83 mg/L. The microbes present in the effluents Consumes particular amount of Oxygen to break down the waste.

3.3.h.Salinity and Conductivity:

Salinity is the total concentration of all dissolved salts in the effluents. The Salinity of the effluent was 7.02ppt and therefore, salinity is the strong Contributor to Conductivity and so 9.89ms in the measured Conductivity value in the effluents.

S.No	Parameters	Values
1	Temperature	29.4°C
2	pH	12.13
3	EC µs/cm	1924.75
4	TDS(ppt)	5340
5	Hardness(mg/l)	6
6	Alkalinity(mg/l)	210
7	DO(mg/l)	8.7
8	BOD (mg/l)	.83
9	Salinity (ppt)	7.02
10	Conductivity(ms)	9.89

Table:1 – Physio-chemical parameters of effluents

3.4.Determination Of Hexavalent Chromium:

The hexavalent Chromium present in the effluents were determined using the Diphenylcarbazide method, Dichromate and Chromate Solutions were used as the standard for determination of Hexavalent Chromium present in the effluents.
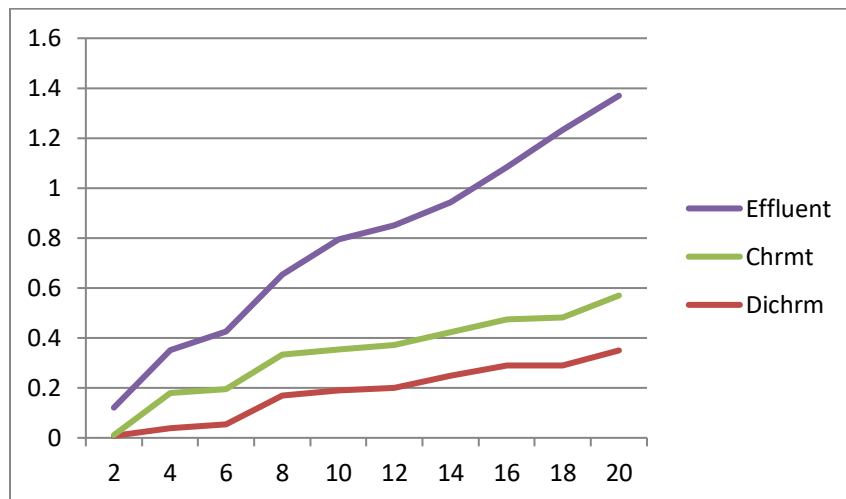
Fig:-2 Shows that the Sample Contained Hexavalent Chromium

3.5. Synthesis and Characterization of Chromium Nanoparticles

In the present study the tannery effluent were mixed with the Extracts of *Murraya koenigii, Raphanus sativus,* $K_2Cr_2O_7$, K_2CrO_4 for the synthesis of chromium Nanoparticle and are subjected to Spectrometric Analysis, FTIR Analysis, and SEM Analysis.

3.5.1. Spectrometry

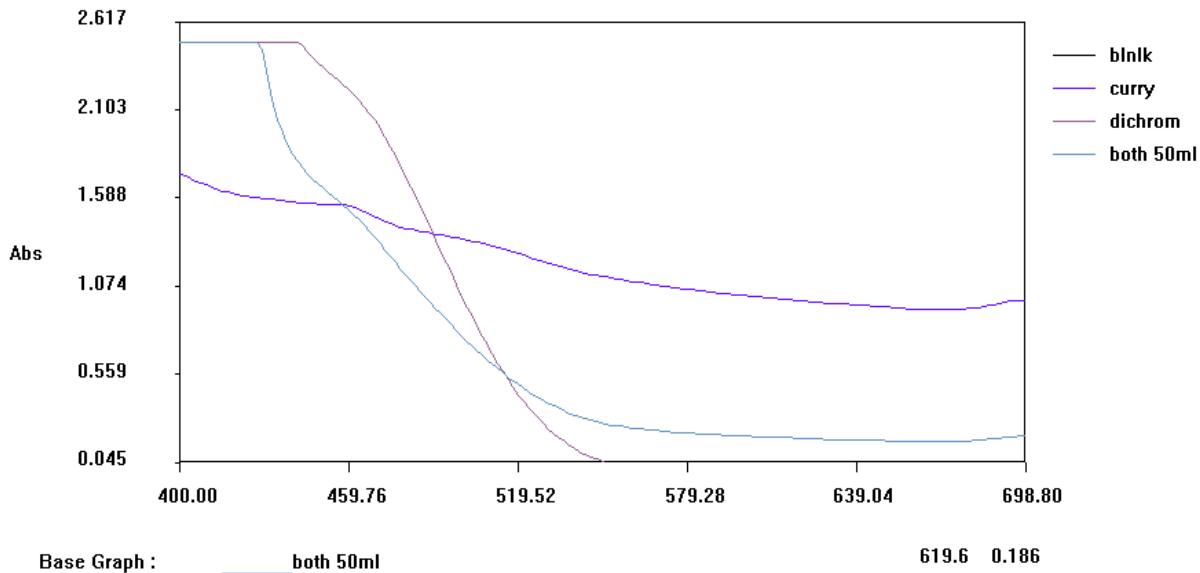### 3.5.1.a. Synthesis and Characterization of Chromium Nanoparticles from $K_2Cr_2O_7$ and *Murraya koenigii*

Fig 3:-Absorstion Spectrum of $K_2Cr_2O_7$ and *Murraya koenigii*

Fig 3 shows the Absorption Spectrum of dichromate solution which had λ max 445nm upon mixing with the *Murraya koenigii* λmax shifts to 438nm.The observed Shift of plasmon peak in an indication of production of Chromium Nanoparticles.

3.5.1.b.Synthesis and Characterization of Chromium Nanoparticles from K₂CrO₄ and _Murraya koenigii_

UV-VIS SPECTROPHOTOMETER: 119

Abs

Base Graph : _____ both

— blank
— leaf
— chrom
— both
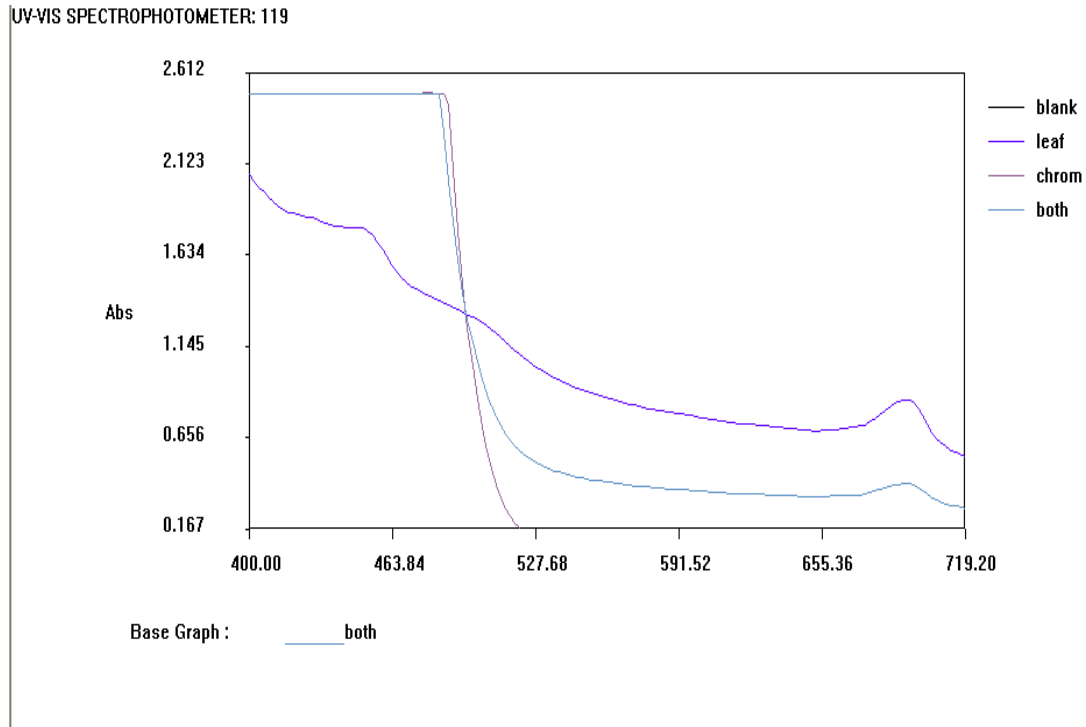
Fig 4:-Absorbtion Spectrum of K₂CrO₄ and _Murraya koenigii_

Fig 4 shows that Absorption Spectrum of Chromate solution which had λ max 474nm upon mixing with the _Murraya koenigii_ λ max shifts to 470nm.The observed Shift of plasmon peak in an indication of production of Chromium Nanoparticles.

3.5.1.C. Synthesis and Characterization of Chromium Nanoparticles from Tannery Effluents using the Extracts of *Murraya koenigii*


UV-VIS SPECTROPHOTOMETER: 119

Abs

2.622
2.085
1.549
1.013
0.477
-0.059

400.00   459.76   519.52   579.28   639.04   698.80

blnlk
curry
efflu
cureff 50

Base Graph :   cureff 50
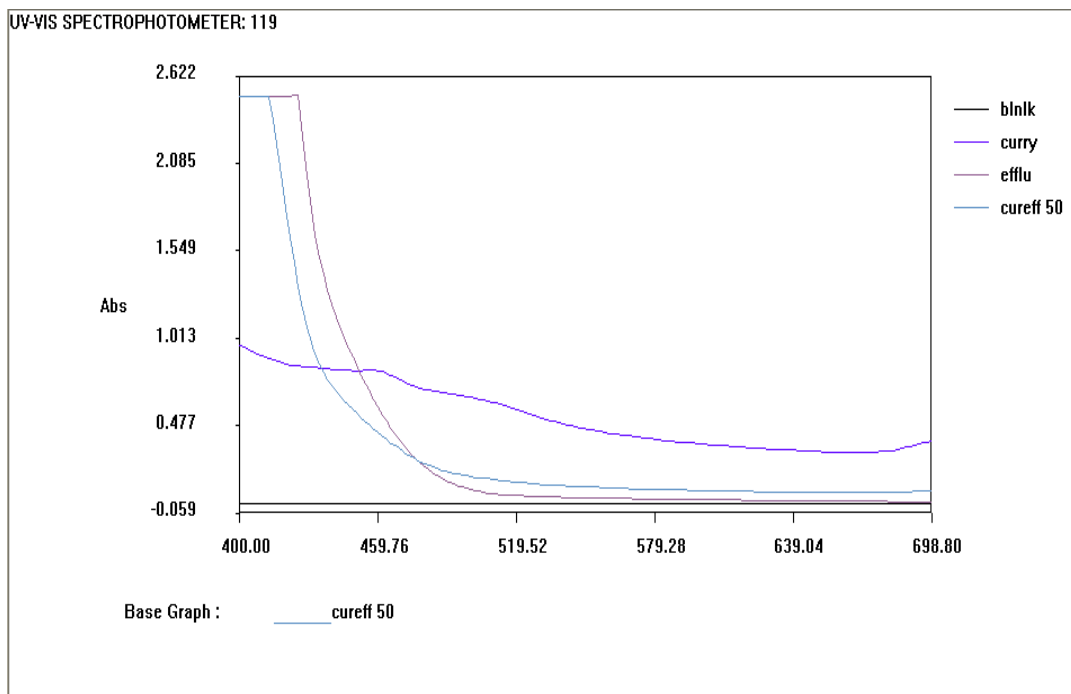
Fig.5 Absorption Spectrum of Tannery Effluents & *Murraya koenigii*

From the **Fig.5** It was quite interesting to note that the λ max of effluent was found to be 421nm and shifted to 410nm in the reaction mixture of *Murraya koenigii* and tannery effluent after the incubation. The observed shift of Plasmon peak is an indication of production of chromium nanoparticles.

3.5.1.d.Synthesis and Characterization of Chromium Nanoparticles from K$_2$Cr$_2$O$_7$ and
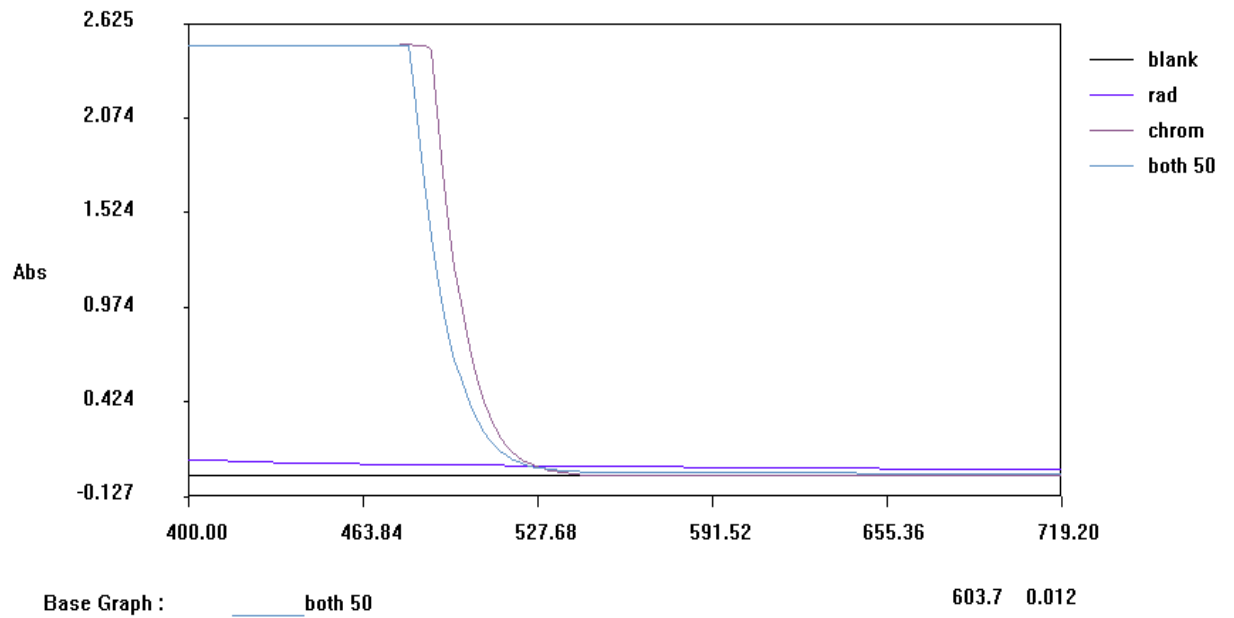
Raphanus sativus
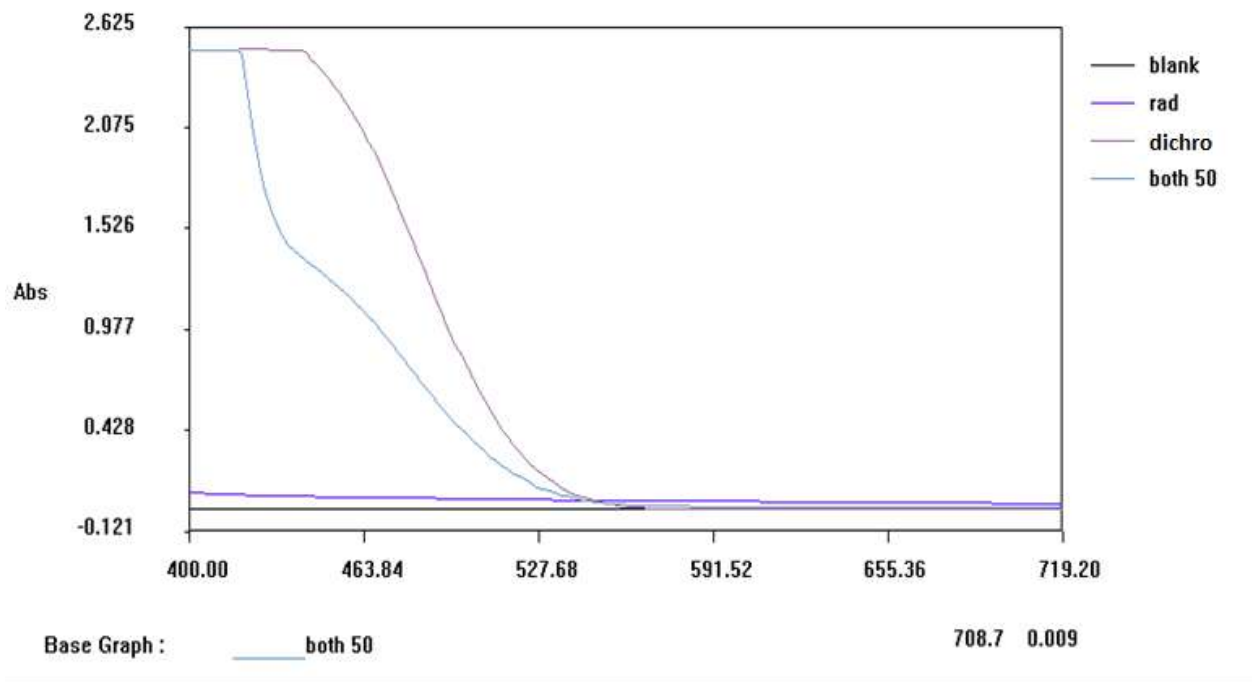
Fig .6 Absorption Spectrum of K$_2$Cr$_2$O$_7$ and *Raphanus sativus*

Fig 6 shows that Absorption Spectrum of dichromate solution which had λ max 442nm upon mixing with the *Raphanus sativus* λ max shifts to 430nm.The observed Shift of plasmon peak in an indication of production of Chromium Nanoparticles.

3.5.1.e.Synthesis and Characterization of Chromium Nanoparticles from K$_2$CrO$_4$and

Raphanus sativus

Fig.7Absorption Spectrum of K$_2$CrO$_4$and *Raphanus sativus*

Fig 7 shows that Absorption Spectrum of Chromate solution which had λ max 468nm upon mixing with the *Raphanus sativus* λmax shifts to 475nm.The observed Shift of plasmon peak in an indication of production of Chromium Nanoparticles.

3.5.1.f. Synthesis and Characterization of Chromium Nanoparticles fromTannery Effluents Using the Extracts of *Raphanus sativus*
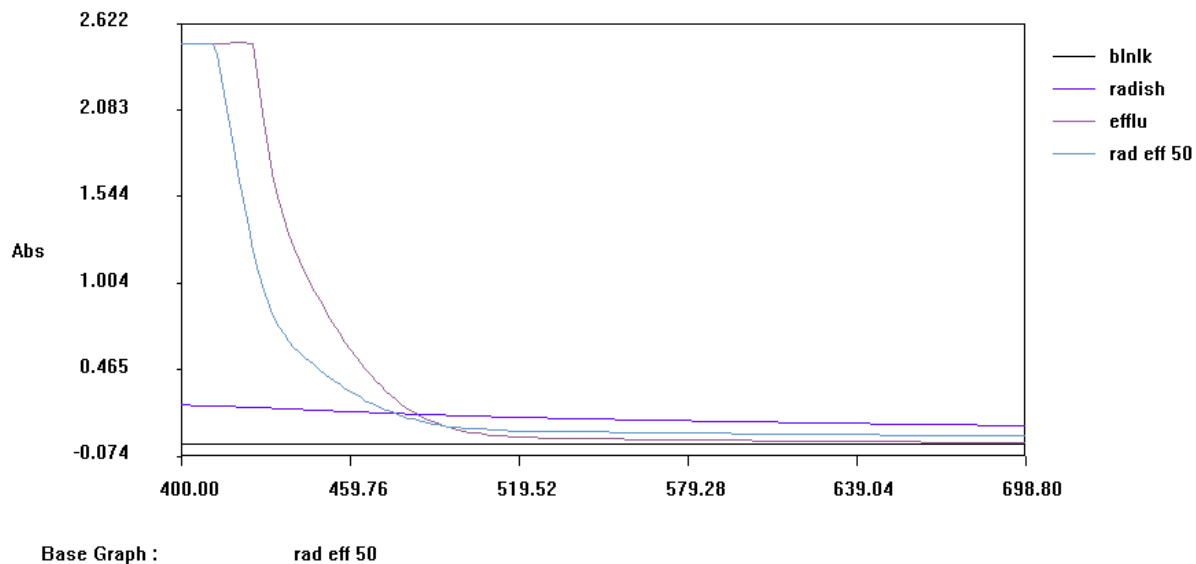
Fig.8 Absorption Spectrum of Tannery Effluents and *Raphanus sativus*

From Fig 8 It is quite interesting to note that the λmax of tannery effluent was found to be 425nm and shifted to 409nm in the reaction mixture *Raphanus sativus* and tannery effluent after the incubation. The observed shift of Plasmon peak is an indication of production of chromium nanoparticles.

3.5.2. FTIR spectroscopic analysis

FTIR spectroscopy is widely used to study the nature of surface absorbents in nanoparticles. Since the nanoparticles possess large surface area, the modification of the surface by a suitable absorbate can generate different properties. The FTIR spectra of the nanoparticles, which contain some absorbates, possess additional peaks in comparison with the FTIR pattern of a bare nanoparticle. So the property change with different absorbates can easily be detected with FTIR Spectroscopy. FTIR analysis of respective leaf broths of *Murraya koenigii, Raphanus sativus*, Tannery effluent, Reaction mixture of Dichromate solution &*Murraya koenigii,* Chromate solution &*Murraya koenigii,* Tannery effluent & *Murraya koenigii*, Dichromate solution &*Raphanus sativus,* Chromate solution &*Raphanus sativus,* Tannery effluent &*Raphanus sativus* and were done using FTIR spectrometer

3.5.2.a. FTIR Spectroscopic analysis of Reaction mixture of Dichromate solution & *Murraya koenigii*

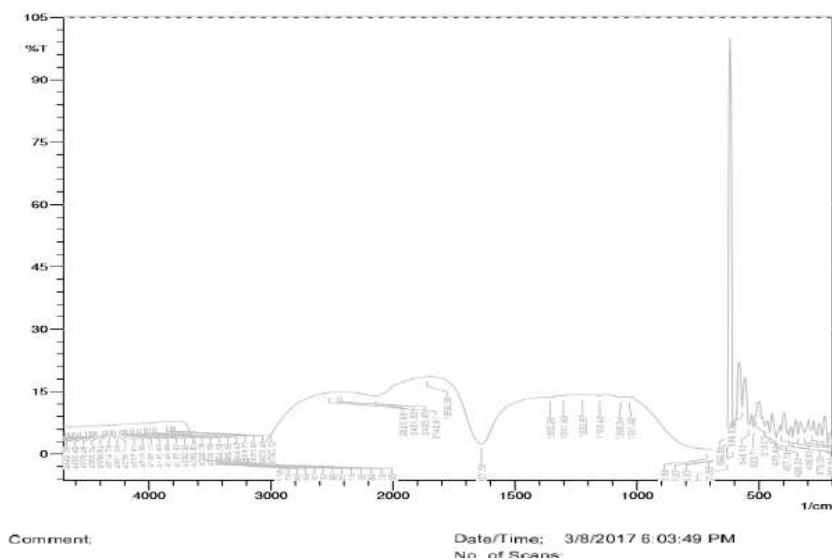FT-IR Analysis of Dichromate solution &*Murraya koenigii* were done using FTIR Spectrometer is given below.**Fig.9**

Fig.9 FTIR Spectrum of Reaction mixture of Dichromate solution &*Murraya koenigii*

The characteristics of Chromium Nanoparticles were observed FTIR spectrum. Fig.9 Shows the peak at 542 cm^{-1},569cm^{-1}, 1301.95 cm^{-1}, 3417.86 cm^{-1} in the region 400cm^{-1}-4000cm^{-1}. The peak at 3417.86cm^{-1} is the characteristic band of hydrogen bonded OH groups present in aqueous phase. The peak at1301.95cm^{-1} indicates the presence of (-COO-) carboxylate ions, responsible for stabilizing the Chromium Nanoparticles. The peak at 569cm^{-1} and 542 cm^{-1} indicates that Cr=O and Cr-O vibration of Chromium Nanoparticles.

3.5.2.b. FTIR Spectroscopic analysis of Reaction mixture of Chromate solution &*Murraya koenigii*

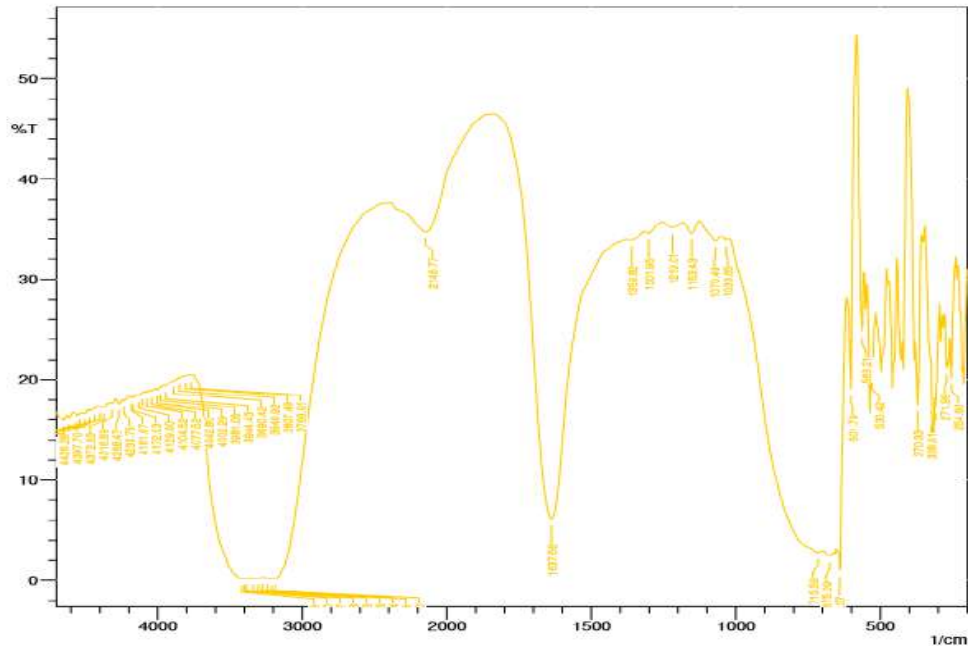FT-IR Analysis of Chromate solution &*Murraya koenigii* were done using FTIR Spectrometer is given below.

Fig.10 FTIR Spectrum of Reaction mixture of Chromate solution &*Murraya koenigii*

The characteristics of Chromium Nanoparticles were observed FTIR spectrum. Fig.10 Shows the peak at 563 cm^{-1}, 1301.95 cm^{-1} 1359.82 cm^{-1} , 3419.86 cm^{-1} in the region 400cm^{-1}-4000cm^{-1}. The peak at 3419.86cm^{-1} is the characteristic band of hydrogen bonded OH groups present in aqueous phase. The peak at 1359.82 cm^{-1} and 1301.95cm^{-1} indicates the presence of (-COO-) carboxylate ions, responsible for stabilizing the Chromium Nanoparticles. The peak at 563cm^{-1} indicates that Cr=O and Cr-O vibration of Chromium Nanoparticles.

3.5.2.c. FTIR Spectroscopic analysis of Reaction mixture of *Murraya koenigii*& Tannery Effluent.

FT-IR Analysis of *Murraya koenigii*and Tannery effluent were done using FTIR Spectrometer is given below
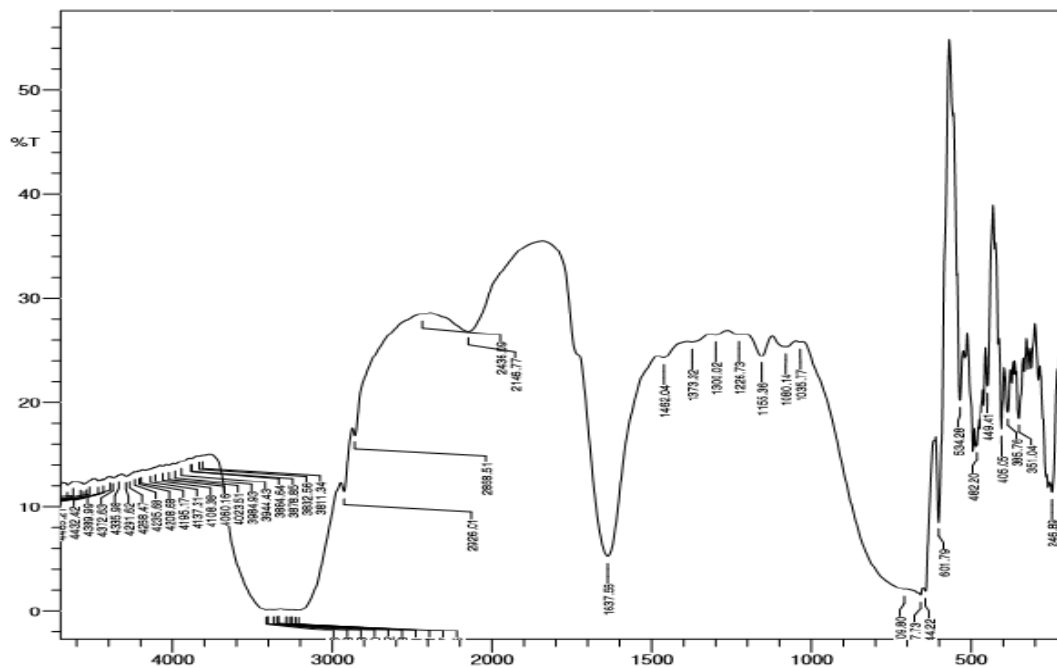

Fig.11 FTIR Spectrum of Reaction mixture of *Murraya koenigii*& Tannery Effluents

The characteristics of Chromium Nanoparticles were observed FTIR spectrum. Fig.11 Shows the peak at 534 cm^{-1},601.79cm^{-1}, 1300.02 cm^{-1} 1373.32 cm^{-1} , 3412.08 cm^{-1} in the region 400cm^{-1}-4000cm^{-1}. The peak at 3412.08cm^{-1} is the characteristic band of hydrogen bonded OH groups present in aqueous phase. The peak at 1373.32 cm^{-1} and 1300.02cm^{-1} indicates the presence of (-COO-) carboxylate ions, responsible for stabilizing the Chromium Nanoparticles. The peak at 534cm^{-1} and 601.79cm^{-1} indicates that Cr=O and Cr-O vibration of Chromium Nanoparticles.

3.5.2.d. FTIR Spectroscopic analysis of Reaction mixture of Dichromate solution &*Raphanus sativus*

FT-IR Analysis of Dichromate Solution and *Raphanus sativus* and were done using FTIR
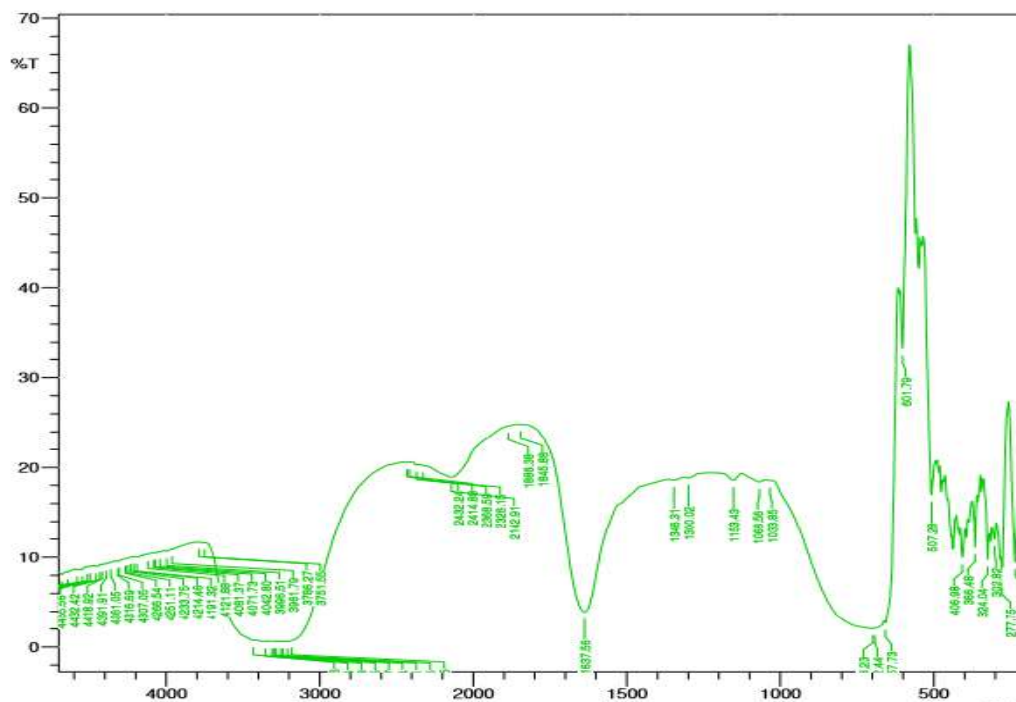
Spectrometer is given below

Fig.12 FTIR Spectrum of Reaction mixture of Dichromate solution &*Raphanus sativus*

The characteristics of Chromium Nanoparticles were observed FTIR spectrum. Fig.12 Shows the peak at 601.79cm^{-1}, 1300.02 cm^{-1} , 1346.31 cm^{-1}, 3431.36 cm^{-1} in the region 400cm^{-1}-4000cm^{-1}. The peak at 3431.36cm^{-1} is the characteristic band of hydrogen bonded OH groups present in aqueous phase. The peak at 1346.31 cm^{-1} and 1300.02cm^{-1} indicates the presence of (-COO-) carboxylate ions, responsible for stabilizing the Chromium Nanoparticles. The peak at 601.79cm^{-1} indicates that Cr=O and Cr-O vibration of Chromium Nanoparticles

3.5.2.e. FTIR Spectroscopic analysis of Reaction mixture of Chromate solution &*Raphanus sativus*

FT-IR Analysis of Chromate solution and *Raphanus sativus* and were done using FTIR Spectrometer is given below
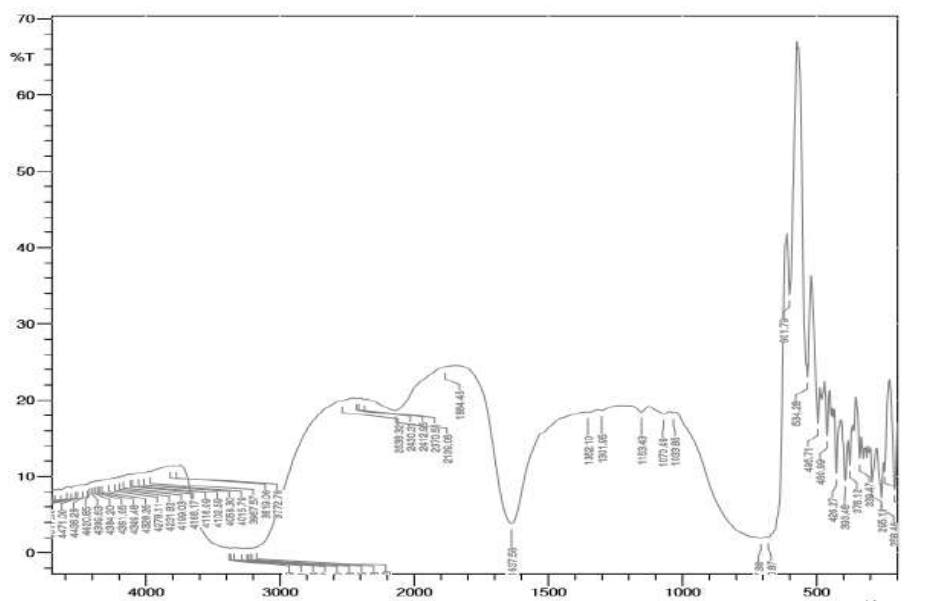

Fig.13 FTIR Spectrum of Reaction mixture of Chromate solution &*Murraya koenigii*

The characteristics of Chromium Nanoparticles were observed FTIR spectrum. Fig13: Shows the peak at 534.28 cm-1, 601.79cm^{-1}, 1301.95 cm^{-1} , 1352.1 cm^{-1}, 3379.29 cm^{-1} in the region 400cm^{-1}-4000cm^{-1}. The peak at 3379.29cm^{-1} is the characteristic band of hydrogen bonded OH groups present in aqueous phase. The peak at 1352.1 cm^{-1} and 1301.95 cm^{-1} indicates the presence of (-COO-) carboxylate ions, responsible for stabilizing the Chromium Nanoparticles. The peak at 534.28 cm-1 and 601.79cm^{-1} indicates that Cr=O and Cr-O vibration of Chromium Nanoparticles.

3.5.2.f. FTIR Spectroscopic analysis of Reaction mixture of *Raphanus sativus*& Tannery Effluent.

FT-IR Analysis of *Raphanus sativus* and Tannery Effluents were done using FTIR Spectrometer is given below
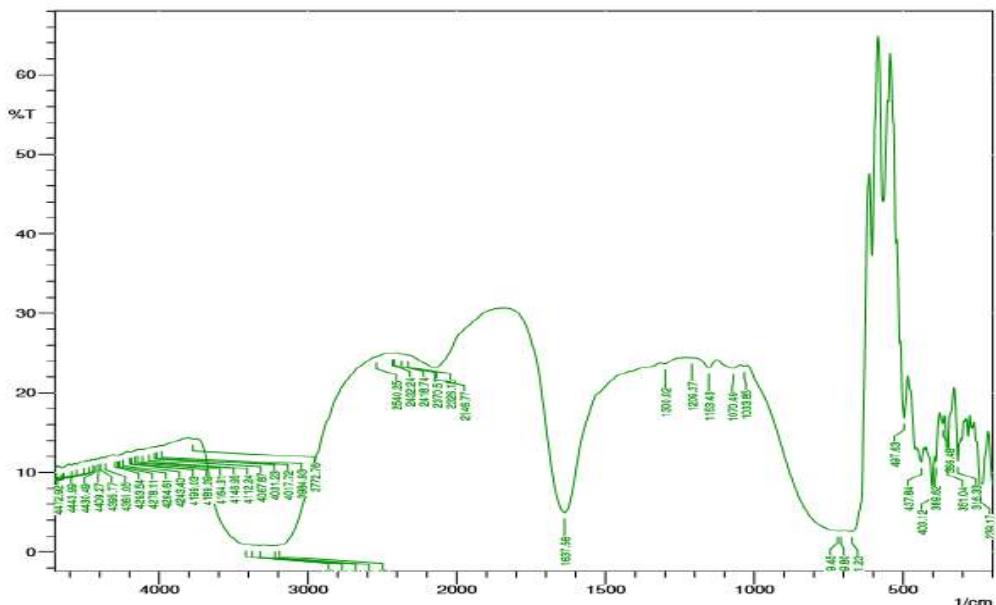

Fig.14 FTIR Spectrum of Reaction mixture of *Raphanus sativus* and Tannery Effluents

The characteristics of Chromium Nanoparticles were observed FTIR spectrum. Fig.14: Shows the peak at 497.63 cm^{-1}, 671.23cm^{-1}, 1300.02 cm^{-1}, 3417.86 cm^{-1} in the region 400cm^{-1}-4000cm^{-1}. The peak at 3417.86cm^{-1} is the characteristic band of hydrogen bonded OH groups present in aqueous phase. The peak at 1300.02cm^{-1} indicates the presence of (-COO-) carboxylate ions, responsible for stabilizing the Chromium Nanoparticles. The peak at 497.63 cm^{-1} and 671.23cm^{-1} indicates that Cr=O and Cr-O vibration of Chromium Nanoparticles. Similar Study of FTIR Analysis of Chromium Nanoparticles were reported by Farzaneh and Najafi(2011).

3.5.3.Scanning Electron Microscopic Studies

SEM analysis of Chromium nanoparticles that were synthesized from the reaction media was done using Scanning electron microscopy. It is a type of electron microscope that images the sample surface by scanning it with high energy steams of electrons in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. The most common SEM mode is detection of secondary electrons emitted by atoms excited by electron beam. By scanning the sample and collecting the secondary electrons that are emitted using a special detector, an image displaying the topography of the surface is created.
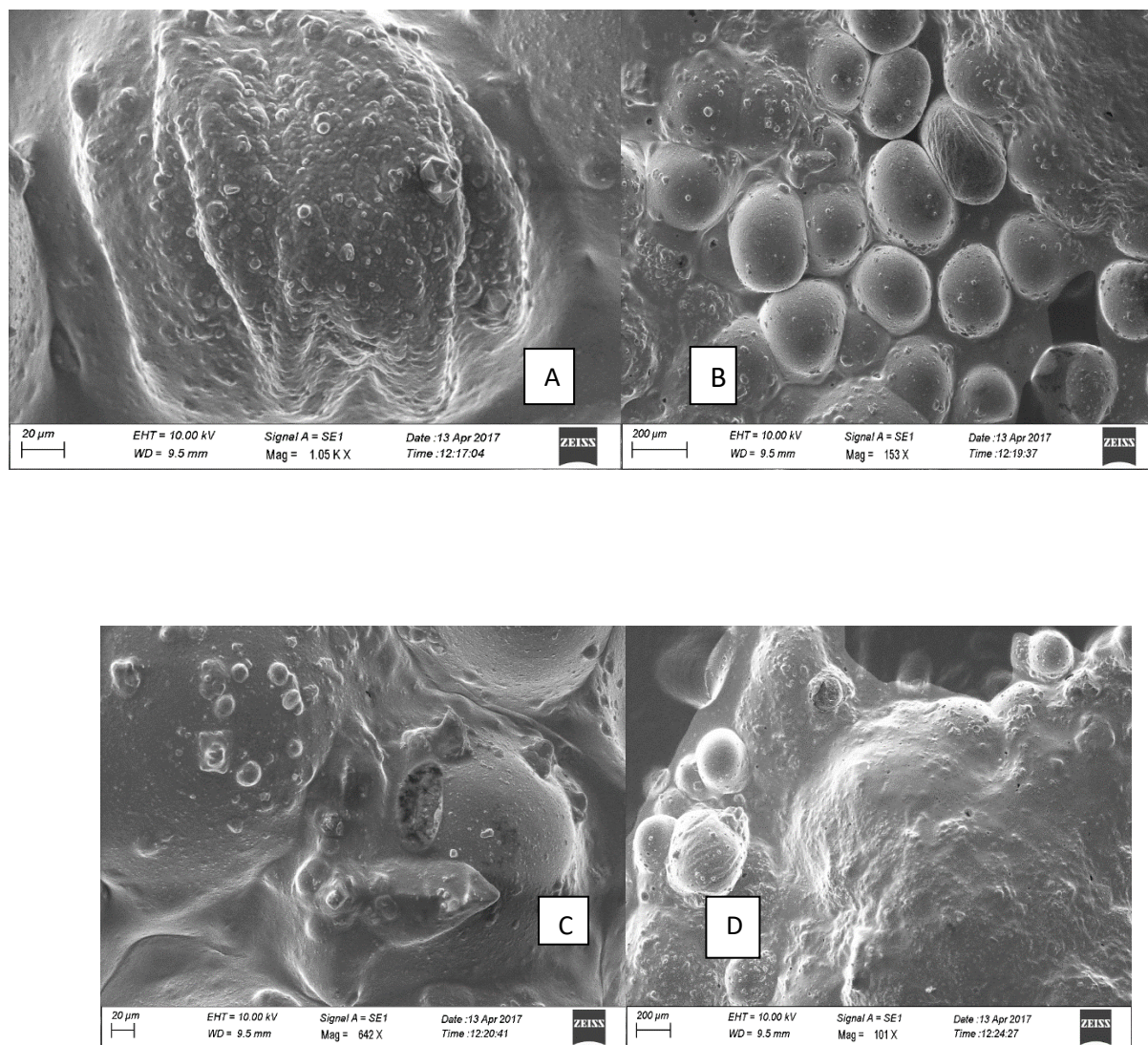

Fig 15. (A-D) SEM Image of Chromium Nanoparticles Synthesized from *Murraya koenigii* & Dichromate Solution
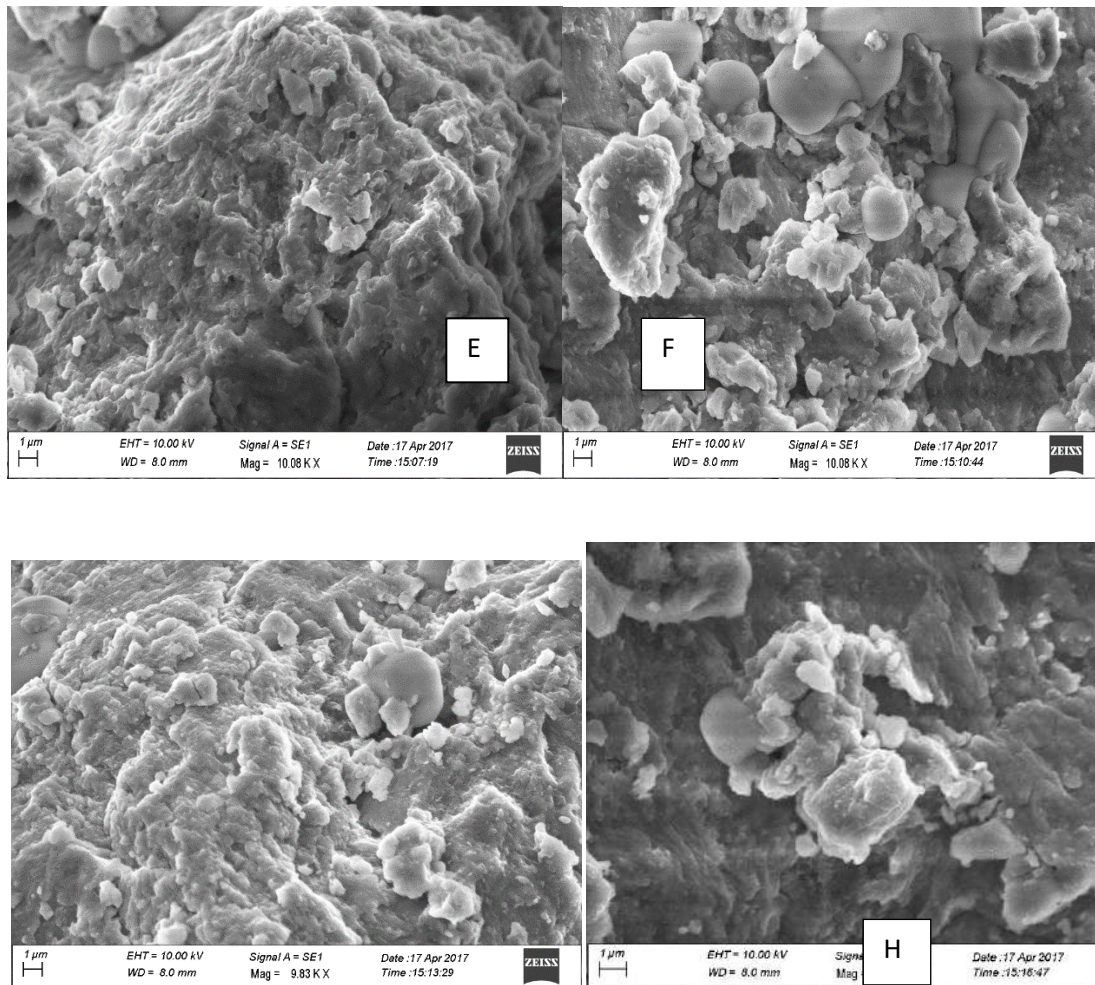
Fig 15 (E-H).SEM image of Chromium Nanoparticles Synthesized from *Murraya koenigii*

& Tannery Effluent

From the SEM Analysis it has been found that the Size of the Chromium Nanoparticles ranged from20-900nm. Further Studies are warranted to have the size Controlled production of Nanoparticles.

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