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Preparation and some characterization of curcumin-silica materials by sol-gel method

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ABSTRACT: In this research prepartion of curcumin-silica materials using sol-gel method (bio-based materials)by reaction phenolic hydroxy group of curcumin with silanol group of silica . Tetraethoxysilane (TEOS) was used as the silica precursor, hydrochloric acid (HCl) ,as the catalyst .Curcumin form as the organic precursor, Curcumin was dissolved in THF (concentration of 10 wt%). 1 gm curcuim dissolved 10 ml THF , The mixture was stirred under nitrogen until the curcumin dissolved completely to give a clear yellow solution. TEOS + HCl (0.1M)) solution was added drop by drop to the cucumin solution under continuous stirring to give four different organic/inorganic ratios (15%,25%,35%, and 50% v/v). The results show that the absorption peak shift with red shift and the Fluorescence Spectrophotometer ,silica-curcumin materials were showed ablue shifted peak. DTA thermograph shows sharp endothermic peak this can be attributed to the vaporization of water and ethanol.

KEYWORDS: Silica,Curcumin ,Sol-Gel,FTIR,UV.VIS.,DTA

I. INTRODUCTION

In recent years, new kinds of inorganic-organic materials have been prepared using sol-gel process. The new class of bio-based materials when curcumin organic phase(biocompatible and biodegradable) and silica inorganic phase(thermalstablity and rigidity) [1]. The sol-gel process is of interest in preparing these materials due to its mild conditions such as low temperature and pressure[2]. This process provides a convenient route to combine inorganic and organic components as a homogeneous hybrid material. Many researchers have demonstrated that, monolithic transparent hybrid materials without macroscopic phase separations can be prepared by controlling properly the conditions of hydrolysis and condensation of sol-gel materials such as tetraethoxysilane (TEOS)[2]. Silica-polymer hybrid materials have received much attention, due to their wide application in adhesion, biomaterials, protective coatings, composites, microelectronics, thin-films [3].
Silicon dioxide (SiO2) is one of the most abundant components of the crust of the earth. Combined with the oxides of magnesium, aluminum, calcium, and iron, SiO2 forms the silicate minerals in rocks and soil (Bergna, 1994). Silica is an interesting ceramic material in the field of materials science due to its low cost, availability and particular properties [4]. Curcumin (1,7–bis(4–hydroxy–3–methoxyphenyl)–1,6–heptadiene–3,5–dione) [5] is a natural polyphenol and it is the main constituent of the Indian cooking spice turmeric [5].

II.CHEMISTRY OF THE SOL-GEL METHOD

The sol-gel method is based on hydrolysis of liquid precursors to form colloidal sols and their subsequent condensation to obtain the gel. The precursors are usually organosilicates (TEOS) yielding silicate sol-gel materials. However, the method is not restricted to the silicon compounds, for example compounds of zirconium, vanadium, titanium can be used as precursors leading to materials possessing different physico-chemical properties. The synthesis of silica from tetra-functional alkoxides can be described by the following three general reactions: hydrolysis, water condensation and alcohol condensation, as presented in equations (1) to (3), respectively [6].

Hydrolysis

$$Si\text{-}OR + H_2O \rightleftharpoons Si\text{-}OH + ROH \quad \ldots\ldots\ldots\ldots (1)$$

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Alcohol condensation

$$Si\text{-}OR + HO\text{-}Si \rightleftharpoons Si\text{-}O\text{-}Si + ROH \quad \text{(2)}$$

alcoholysis

Water condensation

$$Si\text{-}OH + HO\text{-}Si \rightleftharpoons Si\text{-}O\text{-}Si + H2O \quad \text{(3)}$$

Hydrolysis

Where R is an alky-group (-CxH2x+1).[6]

III. BONDING OF THE ORGANIC WITH THE INORGANIC IN HYBRIDS

The interaction at the interface of the inorganic and organic phases is an important criterion in the synthesis of hybrid materials [7]. Inorganic-organic hybrid materials are generally prepared by either the covalent bonding of the inorganic and organic components, or by specific intermolecular interactions between the inorganic and the organic moieties, which includes van der Waals forces, hydrogen bonding or electrostatic forces [8]

IV.EXPERIMENTAL PART

A. Materials:-

Tetraethoxysilane (TEOS) ,Sigma-Aldrich (Germany) , the Molecular Formula Si(OC2H5)4, Molecular Weight (g/mol) 208.3 , density =0.933, Purity >98%,State of Raw Material liquid. Curcumin (98%) and tetrahydrofuran (THF) were obtained from Acros Organics. Hydrochloric acid (HCl) BDH , Molecular Weight (g/mol) =36.46, density= 1.19 ,purity= 37% , Liquid. Deionized Water (H_2O) ,University of Baghdad/ College of Science/Laboratory of service , Molecular Weight (g/mol) = 18,density = 1 ,high degree of purity/empty of additionalions ,Liquid .

B. Synthesis of the Silica / Curcumin :-

Tetraethoxysilane (TEOS) was used as the silica precursor, hydrochloric acid (HCl) ,as the catalyst .Curcumin form as the organic precursor, Curcumin was dissolved in THF (concentration of 10 wt%). 1 gm curcuim dissolved 10 ml THF , The mixture was stirred under nitrogen until the curcumin dissolved completely to give a clear yellow solution. TEOS + HCl (0.1M)) solution was added drop by drop to the cucumin solution under continuous stirring to give four different organic/inorganic ratios (15%,25%,35%, and 50% v/v). The solution was stirred for 1 h at room temperature and later transferred to closed glass tube were opened to allow the solvent to slowly evaporate at room temperature. Figure (1) sample of curcumin /silica . Figure (2) the chemical structure of curcumin

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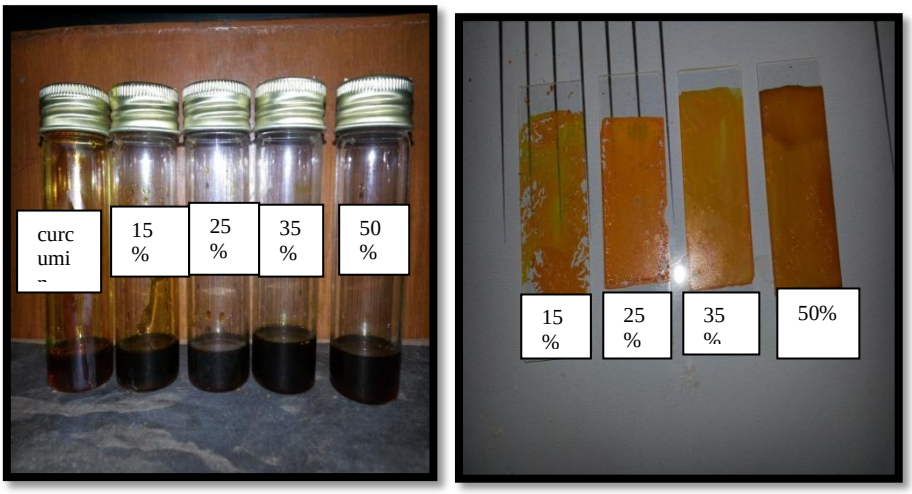

(a) (b)

Figure (1) sample of curcmin /silica hybrid

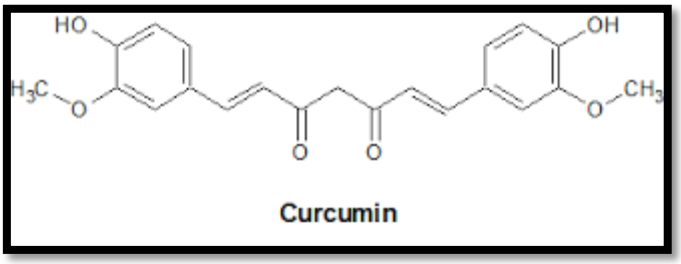

Figure (2) chemical structure of curcumin[9]

V.CHARACTERIZATION TECHNIQUES

A. Fourier transform infrared spectroscopy (FTIR) :

FTIR-Spectrometer, supplied by Shimadzu(Japan) ,Mid-IR spectra, from 4000 to 400 cm^{-1}, were obtained for all samples using, on KBr pellets of the samples.

B. UV-Visible Spectrophotometer

By using UV spectrophotometer (UV-1800/SHIMADZU) was measured transmission spectra of the hybrids samples.

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C. Fluorescence Spectrophotometer:-

RF-5301PC Spectrophotometer, (Shimadzu\Japan). The emission wavelengths range (250 - 900) nm, was used for fluorescence spectra measured of sample with Xenon CW lamp as the excitation source.

D. Differential thermal analysis (DTA)

The temperatures range of 0 to 1200°C at a heating rate of 10°C /min. the samples were ground into fine powder .The measurements were taken using 3-5mg samples.

VI.RESULTS AND DISCUSSION

A.Fourier transform infrared spectroscopy (FTIR) :

FTIR spectrum of curcumin figure (3) shows the peak at 3444.6 cm $^{-1}$ represent O-H stretching . The peak at 3008.7 cm^{-1} represent C-H stretching and the peak 1595cm^{-1} represent C ═ C symmetric aromatic stretching . the peak 1514 cm^{-1} represent C═ O stretching and the peak 970.13 cm $^{-1}$ represent bending vibration .which agree with Harshal Pawar et al. [9]

Figure (4) shows the FTIR spectra of silica-curcumin hybrid .The peak observed at 3456.2-3525.6 cm^{-1} is represent of the phenolic – OH group. The peak at 2933.5-3114.8 cm^{-1} represent to the C–H methyl stretch of the curcumin molecule. The peak at 1625-1687.6 cm^{-1} corresponds to the C=C aliphatic stretch and the peak at 1510-1600.8 cm^{-1} corresponds to the C=C aromatic stretch of the curcumin molecule. These representative peaks in the silica-curcumin hybrid confirm the presence of curcumin in the hybrids.

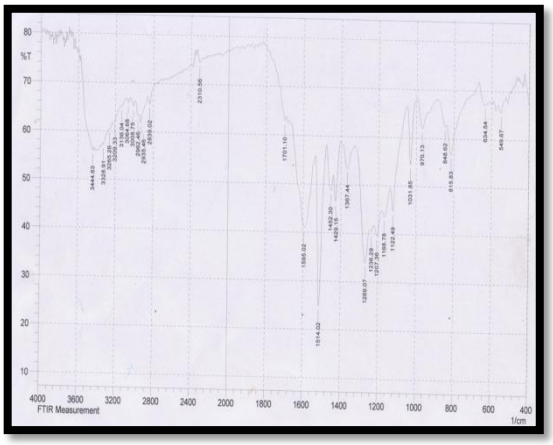

Figure (3) FTIR of curcumin

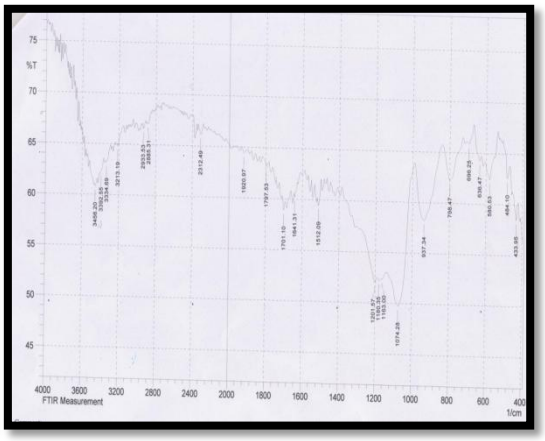

Figure (4-a) FTIR of silica & 15% curcumin

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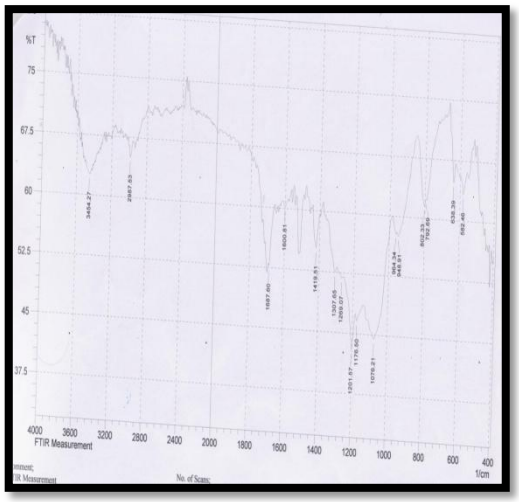

Figure (4-b) FTIR of silica & 25% curcumin

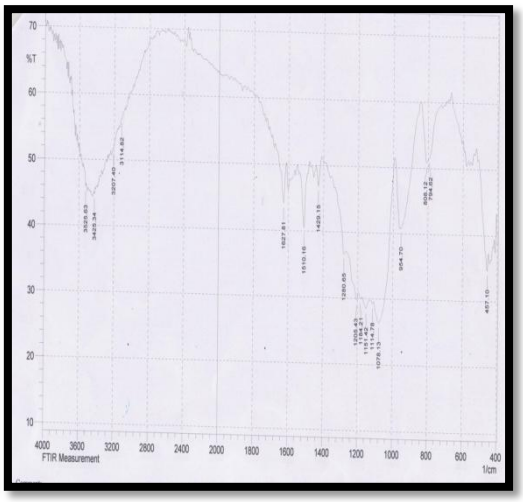

Figure (4- c) FTIR of silica & 35% curcumin

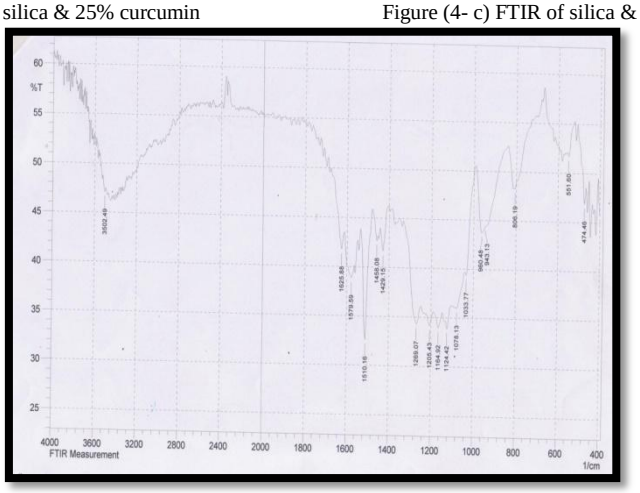

Figure (4-d) FTIR of silica & 50% curcumin

B.UV-Visible Spectrophotometer :-

Figure (5) shows the absorption spectria of curcumin in THF solvent. The absorption is well extended to the visible region. curcumin showed a strong and intense absorption band in the 275 –550 nm wavelength region. when add ratios of curcumin with silica the absorption peak shift with red shift .

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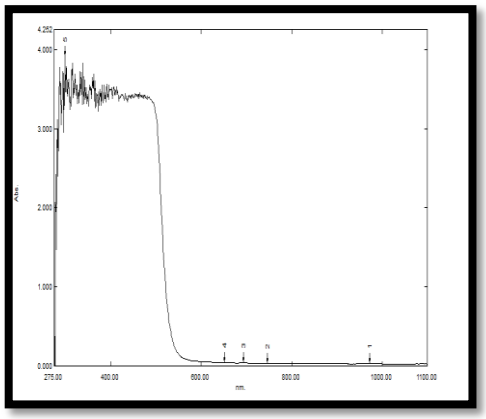

Figure (5) uv.vis. of curcumin

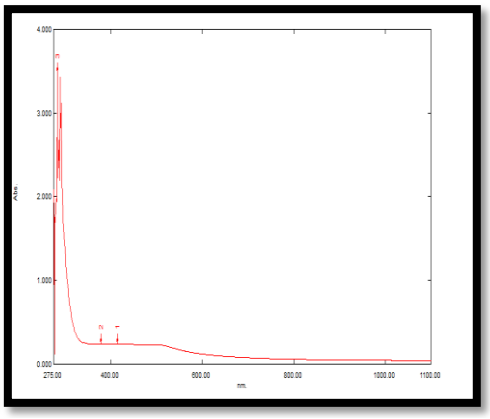

Figure (6-a) uv.vis. of silica &15% curcumin

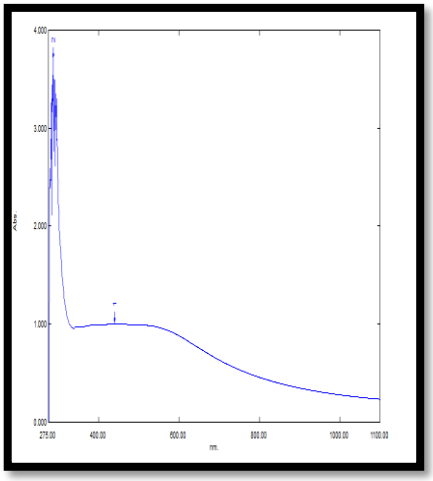

Figure (6-b) uv.vis. silica&25%curcumin

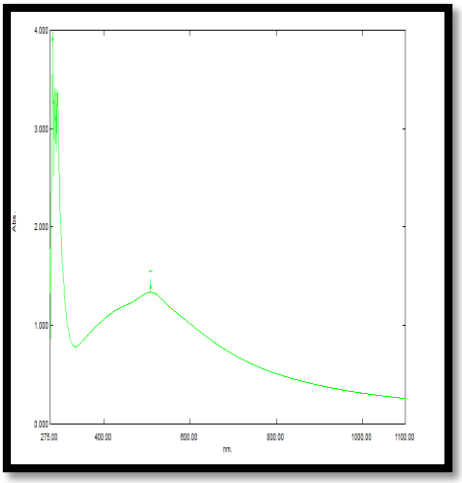

Figure (6-c) uv.vis. silica &35% curcumin

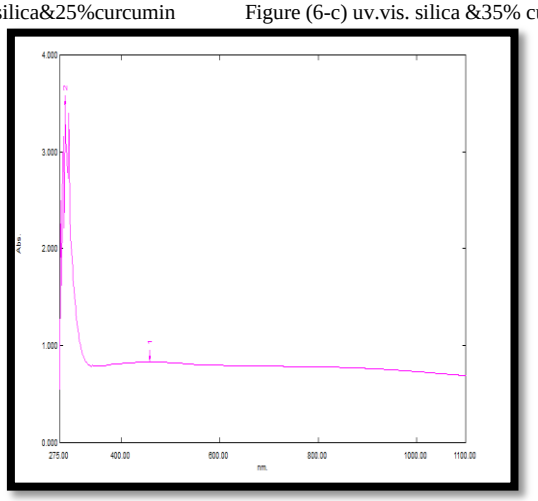

Figure (6-d) uv.vis. silica &50%curcumin

C. Fluorescence Spectrophotometer :- Figure (7) Fluorescence spectra of pure curcumin in THF showed a fluorescence peak at 500 nm which agree with Digambara Patra and Christelle Barakat [10] . The silica-curcumin materials were showed ablue shifted peak at 440-460 nm. A shift in the fluorescence peak suggests binding of the curcumin molecule with other substrates [11]. The covalent bonding of the organic curcumin phase to silicate in the hybrid materials.

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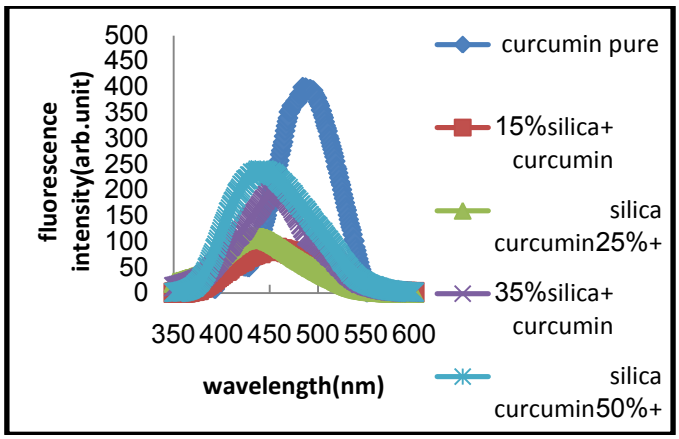


Figure(7) fluorescence spectrum of curcumin and hybrid silica &curcumin

D.Differential thermal analysis (DTA) :-

The DTA thermograph of pure curcumin is shown in Figure (8) It shows a sharp endothermic peak at 180°C. This endothermic peak corresponds to the melting point of curcumin [12]. However, in the DTA thermographs of the hybrid materials Figure (9), this sharp endothermic peak is absent. There is a endothermic peak at 130°C. This can be attributed to the vaporization of water, ethanol and un-reacted ethoxy groups present due to incomplete sol-gel reactions [13]. The DTA thermograph of a physical mixture of silica (sol-gel synthesized from TEOS) and curcumin is shown in Figure (9) The absence of this melting peak in the hybrid materials possible silicate–curcumin covalent bonding

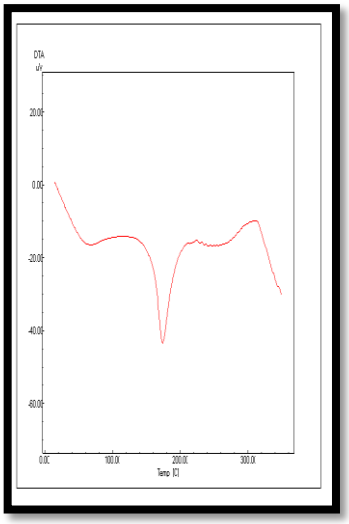
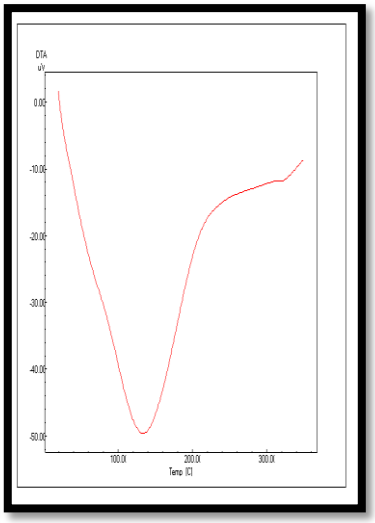
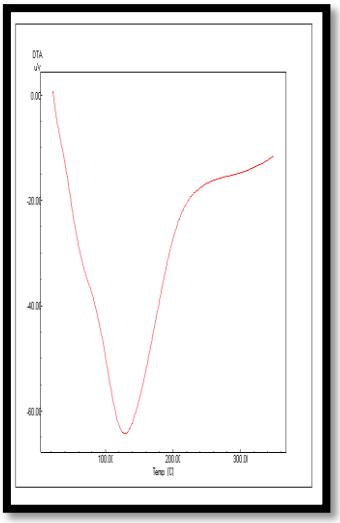


Figure (8) DTA of curcumin



(a) DTA of 15% curcumin



(b) DTA of 25% curcumin

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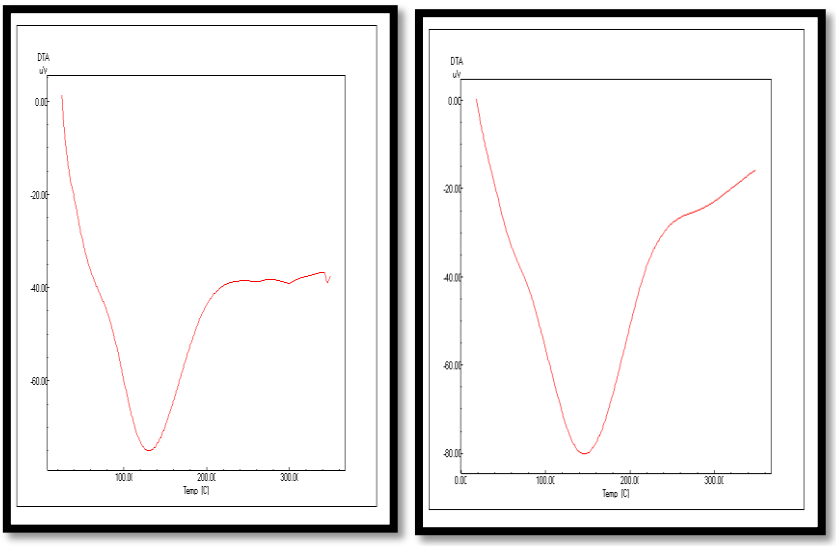

(c) DTA of 35% curcumin (d) DTA of 50% curcumin

Figure (9) DTA of hybrid silica & curcumin

VII.CONCLUSIONS

Silica –curcumin materials was prepared using sol-gel method.curcumin was inducted in the silica matrix (tetrarthlorthosilicate as the silica precursor)by reaction phenolic hydroxy group of curcumin with silanol group of silica. The absorption spectria of curcumin with silica the absorption peak shift with red shift and the covalent bonding of the organic curcumin to silicate inorganic . The silica-curcumin materials were showed ablue shifted peak. DTA thermograph shows sharp endothermic peak,this can be attributed to the vaporization of water,ethanol and un-reacted ethoxy groups present due to in complete sol-gel reaction. In this work represent a new class of bio-based materials ,where the curcumin(organic materials) is highly biocompatible and biodegradable . The silica (inorganic materials) is thermal stablity and rigidity.

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