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The Novel Simple Path for Preparation of Fe_3O_4, ZnO, NiO and Co_3O_4 Nano-Crystallites Using Curcumin Transition Metal Complexes as Single-Source Precursors (SSP) and their Antimicrobial Activity

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ABSTRACT

The Use of single-molecule precursors (also known as single-source precursors =SSP) for preparation of nano-crystallites is very interesting as it contains desired element in same molecule. The synthetic method adopted can change the shape, phase, purity and morphology of the materials. The controlled properties of materials make them suitable for the technological applications. Nano-dimensions of the materials give rise to new interesting properties due to size Confinement. Metal oxides have great importance due to their applications as catalysis and battery cathode. Curcumin is used as traditional Ayurvedic medicine. It is yellow coloured powder and have β-di-keto moiety which is considered as powerful chelating agent.

Herein, we report the preparation of curcumin transition metal complexes of type M(L=Cu= curcumin) (where M= Fe, Zn, Ni, Co) which were used as single source precursors for preparation of nano-crystallites. The precursors were characterized by elemental analysis, UV, IR and NMR spectroscopy which implies formation of 1:1 complex.

The products obtained by pyrolysis of the above precursors were characterised by powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersive analysis by X-rays (EDAX). The effect of decomposition conditions on the morphology of nano-crystallites are also studied.

However, the curcumin is water insoluble where as complexes are water soluble and shows enhanced biological activity with *S aureus*, *B subtilis* and *E coli* as test cultures.

Keywords: *Curcumin; single-source precursors; transition metal nano-crystallites; antimicrobial activity*

INTRODUCTION

There are numerous applications of these transition metal oxide nanoparticles since they are current hot area of research[7a-f]. Literature survey reveals that Fe_3O_4 and Co_3O_4 are used as label in biomedical applications as they are biocompatible[1,2,3]. They show catalytic activity eg. Co_3O_4 as peroxidase used in preparation of lithium batteries. ZnO having wide band gap semiconductor (3.37eV), are used as mechanical actuators, piezoelectric sensors[9]. Zinc oxide nanoparticles have been studied extensively because of their wide band gap (3.36 eV) which has broadened their potential applications in various feilds including catalysis. They find applications in gas sensors, cosmetics, storage, optical devices, window materials for displays, solar cells, biomedicine, photo catalysts and photoluminescence[4,5]. NiO is the p- type transparent semiconductor used in preparing smart windows, as super capacitors, as dye- sensitized photo cathodes[6]. Iron oxides are a unique family of materials that have been investigated for decades from a variety

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of angles, both to satisfy the quest for fundamental understanding and because of their potential use in emerging technologies. The main attention has switched over time to magnetic iron oxide nanoparticles because of their high surface-to-volume ratio and different physical and chemical characteristics from bulk systems. Iron oxide nanoparticles are specifically used in drug imaging (MRI), in cancer therapy, as a corrosion protective pigments in paints and also coatings. In protein purification it is utilised for biological separation, as a catalyst and in drug delivery systems as magnetic resonance storage material, in spintronic based devices ferromagnetic to antiferromagnetic material shows the superparamagnetism, i.e. their magnetization is zero, in the absence of an external magnetic field and they can be magnetized by an external magnetic source[7]. The band gap of Fe_3O_4 is 2.00-3.00eV. This property provides additional stability for magnetic nanoparticles in solutions. Iron oxide available in various forms such as wustite (Fe_3O_4), haematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4) [2]. Iron oxide possesses +2 and +3 oxidation state and with oxygen it gives polymorphs (α to δ). Also Fe_4O_5, Fe_7O_9, Fe_5O_6, Fe_5O_7 have being reported[2]. Many transition metals complexes with various ligands have been reported namely semicarbazone [8], curcumin [9], 2-hydroxy-1-naphthaldehydedato [10], p-hydroxybenzoate [11] and diketones [12].Curcumin is a polyphenol having diketo functional group *[Figure.1]*. and shows keto-enol tautomerism [Figure 2]. It derived from the rhizome of *Curcuma longa*Curcumin has long been used as a spice in curry, a natural colouring agent and as an Indian traditional medicine. Curcumin has been found to have multiple actions like anti-inflammatory action through inhibition of NF-kB; anti-cancer action through cell-cycle arrest, induction of apoptosis, and inhibition of angiogenesis; anti-oxidant action through removal of free radicals and an increased intracellular concentration of glutathione; anti-viral action; and cytoprotective action[12]. But it is not soluble in water. Curcumin is good ligand which can co-ordinate with empty d orbitals of transition metals via its oxygen atom. Present work focuses on synthesizing such curcumin transition metal complexes which may solve the solubility problem and enhance the antimicrobial activity. These complexes are further used as single source precursor for preparation of nano-crystallitees.

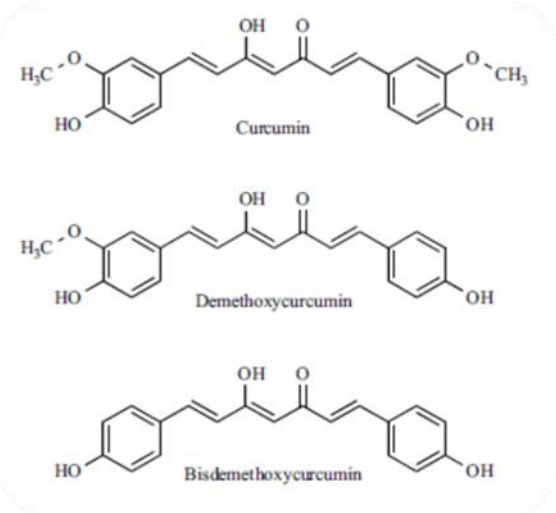

Figure 1. Constituents of Curcumin

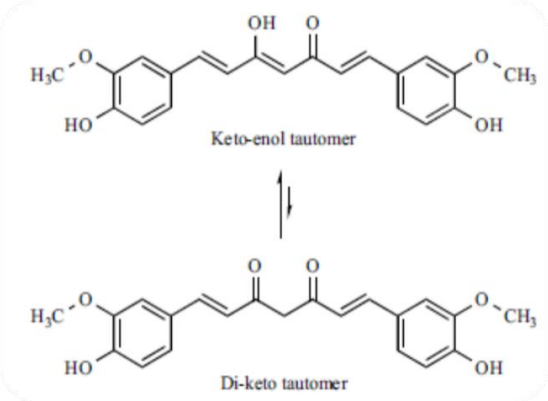

Figure 2. Tautomerism in Curcumin

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MATERIALS AND METHODS

SYNTHESIS OF SINGLE SOURCE PRECURSOR (SSP)

A.R grade $FeCl_3$ $CoCl_2$ $Zn(CH_3COO)_2$ $NiCl_2$ and methanol were used from sigma-Aldrich and Curcumin obtained from Konark Herbals Limited, Mumbai with 99% purity. In a typical synthesis, (Figure 3.) in a 20 cm^3 round bottom flask 0.307 mmole of iron chloride was dissolved in methanol and in another round bottom flask 0.694 mmole of Curcumin was dissolved in methanol. Ligand solution was added drop-drop and reaction mixture is stirred at room temperature for 24 hours[Table 1][Cu= Curcumin]

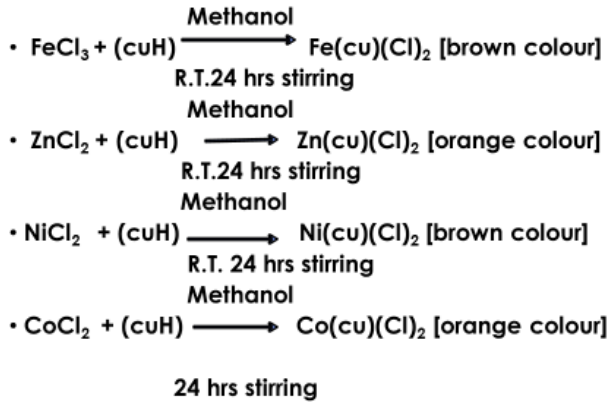

Figure 3. Synthesis of single source precursor

Metal salt	Metal salt in mmoles	Curcumin in mmoles
$FeCl_3$	0.307	0.694
$CoCl_2$	0.513	0.689
$Zn(CH_3COO)_2$	0.445	0.747
$NiCl_2$	0.477	0.740

Table 1. Synthesis of single source precursor.

SYNTHESIS OF NANOCRYSTALLITES

For the synthesis of nano-crystallites 0.350g $Fe(Cu)Cl_2$ single source precursor was weighed, transferred in silica crucible and placed in horizontal tube furnace. Temperature was raised to 470 ℃ and it was kept in the furnace at same temperature for annealing process. After two hours, furnace was allowed to attain room temperature. The product was air dried which weighed 0.070g. The practical yield was in agreement with the theoretical yield for iron oxide. Same procedure was repeated for the preparation cobalt oxide, zinc oxide and iron oxide nano-crystallites.

CHARACTERIZATION OF SINGLE SOURCE PRECURSOR

UV-Visible Spectroscopy(UV-Vis): For UV-Vis spectroscopy, the SSP was re-suspended in ethanol and spectrum scan was performed using Smart UV-Vis Double Beam Spectrophotometer 2203 from Systronics, in the wavelength range of 200-400nm.

Fourier Transform Infrared Spectroscopy (FTIR): FTIR of SSP was carried out using Agilent Technologies – Cary 630 Sr. No 150166.

The elemental analysis was done by using CHNS (O) Analyzer of Thermo finnigan, Italy make, FLASH EA 1112 series model which is based on the principle of Dumas method.

X-ray diffraction (XRD): Powder XRD of transition metal nanocrystalites were carried out by using Panalytical Xpert PRO X Ray Diffractometer, Model: Xpert Pro MPD, Anode : Copper, Wavelength: 1.5405 Angstorm, Power: 40KV /30mA, Detector : Xcelerator Detector with Diffracted Beam Monochromator.

Nuclear Magnetic Resonance (NMR) Spectroscopy: NMR of SSP was carried out using Bruker Avance III HD NMR 500 MHz.

Transmission Electron Microscopy (TEM): TEM analysis was carried out by sonicating 5 mg of nanoparticles in 10 cm^3 of methanol for half an hour. 2 drops was taken on copper grid by using TEM CM 200, Make : PHILIPS, Model : CM 200, Operating voltages : 20-200 kv. Grid is air dried and the images were recorded.

ANTIBACTERIAL ACTIVITY OF SSP

Antibacterial activity of the synthesized SSP was performed against both Gram positive (*S.aureus, B. subtilis*) and Gram negative (*E. coli*) bacteria. The antibacterial activity was done by agar cup method. 0.2 ml of 18 hours old actively growing culture of test organism was added in sterile molten Mueller-Hinton agar (MHA) (Hi-Media, Mumbai, India) butts and poured in sterile petri dishes. After the plates were solidified, 4 cups were made/ plate with the help of a sterile borer (8mm). Distilled water was used as solvent to prepare suspension of SSP and Ligand Curcumin. Curcumin used as internal standard and Reference. The standard Strength of SSP and ligand Curcumin was used 10 mg/ml i.e. 1% solution of SSP was used for *in-vitro* antibacterial assessment. 50 µl of SSP solution was loaded into each well. After addition of SSP, plates were incubated at 4ºC for 30 min to allow effective diffusion of SSP and control. Later, they were incubated at 37±1ºC for 24 hours. After overnight incubation, the zone of inhibition was measured. Solvent blank was maintained as negative control.

RESULTS AND DISCUSSION

The lambda max of Curcumin ligand is 418 nm and that for complexes is 420-425 nm which indicates the formation of complex[Figure 4]. FTIR spectra shows frequency C-O binding in 1564-1600 cm^{-1}, M-O 440-480 cm^{-1} indicates coordination through oxygen atom [Figure 5]. In proton NMR no peak was observed for –O-H group which implies existence of enol form of curcumin when it co-ordinated to metal[Figure 6]. The elemental analysis was done by using CHNS (O) Analyzer of Thermo finnigan, Italy make, FLASH EA 1112 series model which is based on the principle of Dumas method.

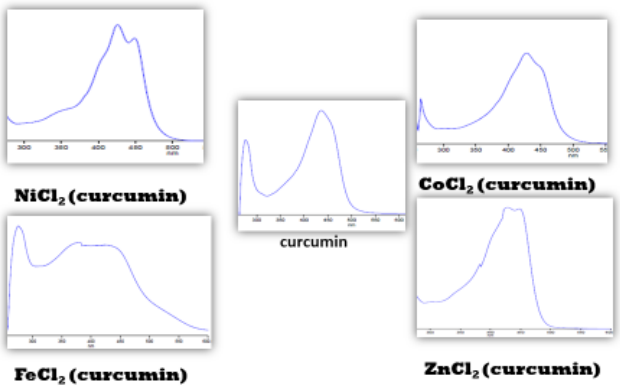

Figure 4. UV-VIS- spectra of single source precursor

The complex was opened in aquaregia and evaporated nearly to dryness. Estimation of metal was carried out by titrating iron, cobalt, zinc and nickel with ethylene diammine tetracetic acid (complexometric titration) and chorine was estimated by Volhards method. Elemental analysis of complex observed (calculated):

For $Fe(Cu)Cl_2$ - Fe: 11.27% (11.33%), C:51.10% (51.14%), H: 3.64% (3.65%), O: 19.50% (19.49%), Cl: 14.40% (14.41%), Melting point of complex: 314ºC, Melting point of ligand:183 ºC, Yield: 87.57%. Conductance:0.317,

For $Co(Cu)Cl_2$ - Co: 11.85% (11.88%), C:50.82.% (50.82%), H: 3.64% (3.63%), O: 19.35% (19.36%), Cl: 14.30% (14.32%), Melting point of complex: 317ºC , Yield: 90.17%. Conductance:0.308,

For $Zn(Cu)Cl_2$ - Zn: 13.00% (13.01%), C: 50.14.% (50.16%), H: 3.55% (3.58%), O: 19.10% (19.12%), Cl: 14..11% (14.11%), Melting point of complex: 314ºC , Yield: 90.77%. Conductance:0.490,

For Ni(Cu)Cl_2 - Ni: 11.85% (11.84%), C:50.84.% (50.85%), H: 3.66% (3.65%), O: 19.35% (19.37%), Cl: 14.32% (14.32%), Melting point of complex: 310ºC, Yield: 92.79%. Conductance:0.617.

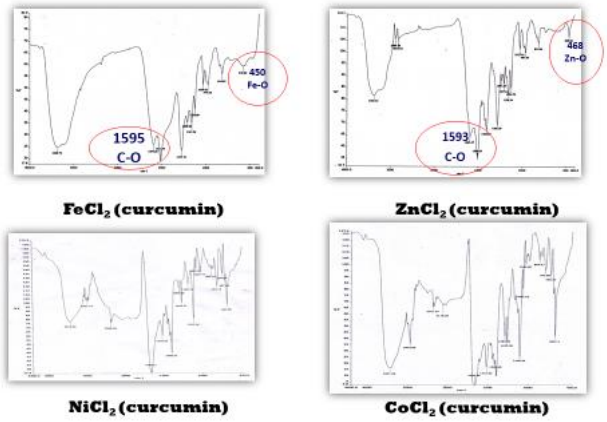

Figure 5. FTIR spectra's of single source precursor

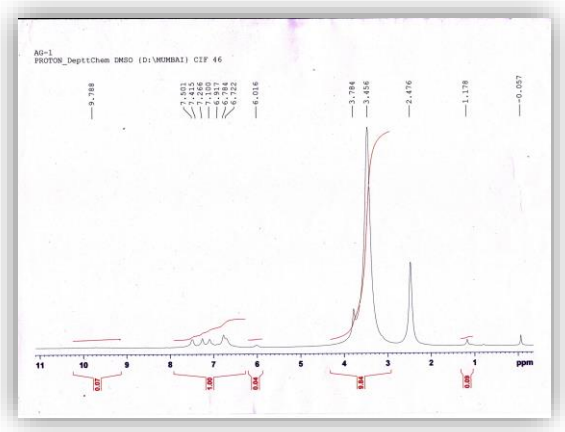

Figure 6. Representative proton NMR spectra of $FeCl_2$ (curcumin)

The PXRD was carried out transition metal nanocrystallites shows for iron oxide (220)(311)(222)(400)(423)(511)(440) matches with (220)(311)(222)(400)(423)(511)(440) (JCPDS 19-0629); Fe_3O_4, (111), (200), (220) and (222) matches with(111), (200), (220) and (222); Nickel Oxide (JCPDS:78-0643) cubic phase, (101)(102)(110)(103) (200) (112) and (211 matches with (101)(102)(110)(103) (200) (112) and (211); Zinc oxide(JCPDS 79-0205) hexagonal phase,(,(111)(220)(311)(400)(440)(422)(511) matches with(111)(220)(311)(400)(440)(422)(511) Cobalt oxide (JCPDS 76-1802). [Figure 7].

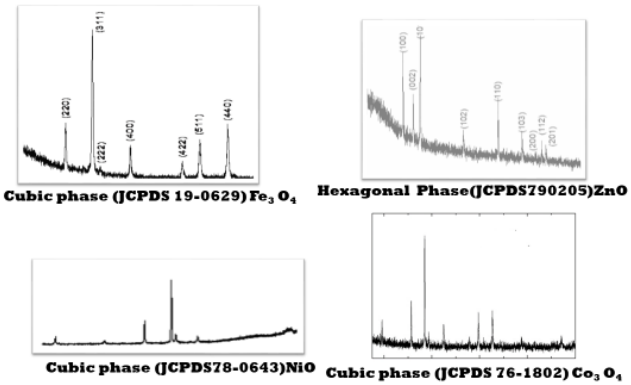

Figure 7. Powder XRD of prepared nano-crystallites

SAED pattern and PXD shows Cubic phase iron oxide (220)(311)(222)(400)(423)(511)(440) (JCPDS 19-0629) Fe_3O_4, (111), (200), (220) and (222) Nickel Oxide (JCPDS:78-0643) cubic phase, (101)(102)(110)(103) (200) (112) and (211) Zinc oxide (JCPDS 79-0205) hexagonal phase, (111)(220)(311)(400)(440)(422)(511) cobalt oxide (JCPDS 76-1802) [Figure 8].

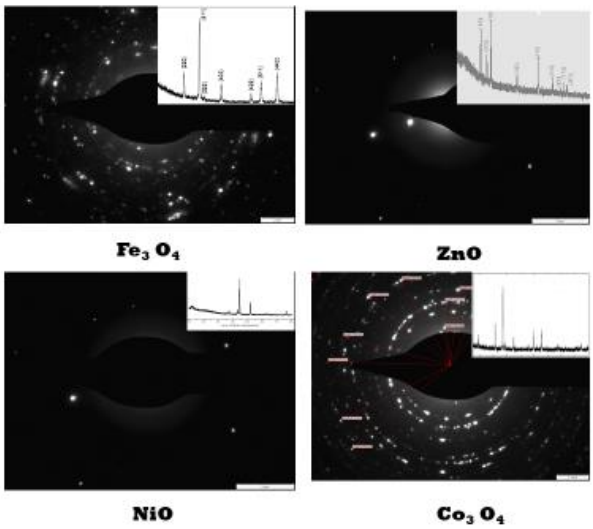

Figure 8. SAED pattern and powder XRD of prepared nao-crystallites

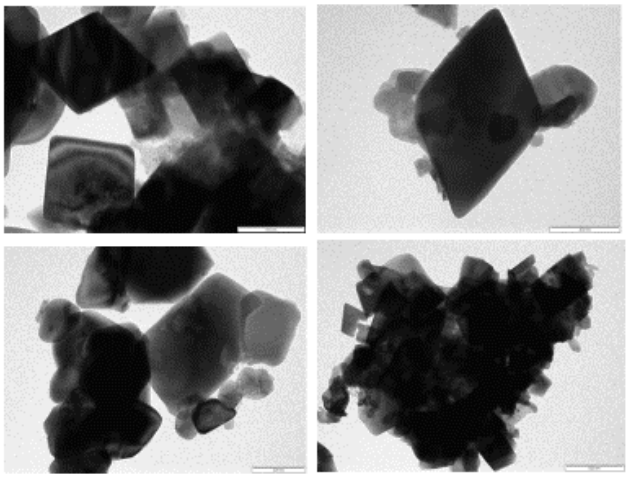

Figure 9. TEM images of Iron oxide nano-crystallites

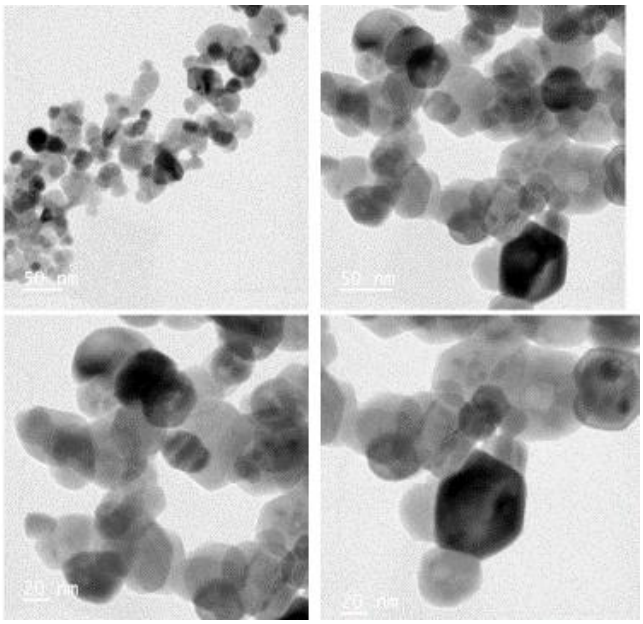

Figure 10. TEM images of Zinc oxide nano-crystallites

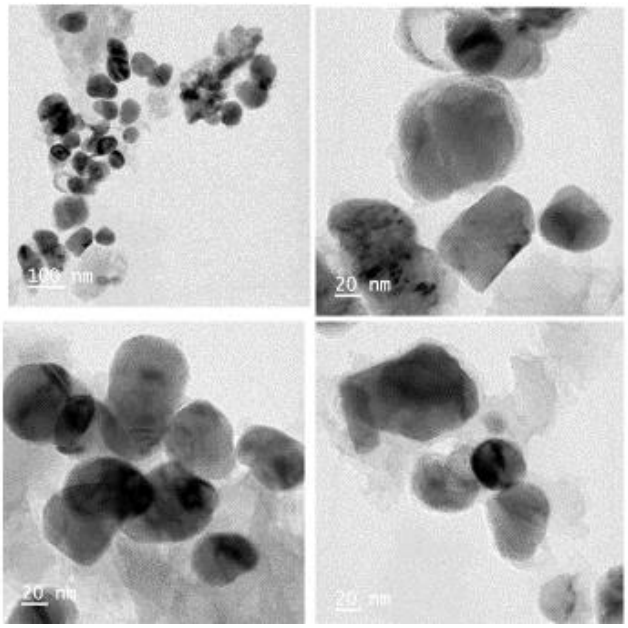

Figure 11. TEM images of Nickel oxide nano-crystallites

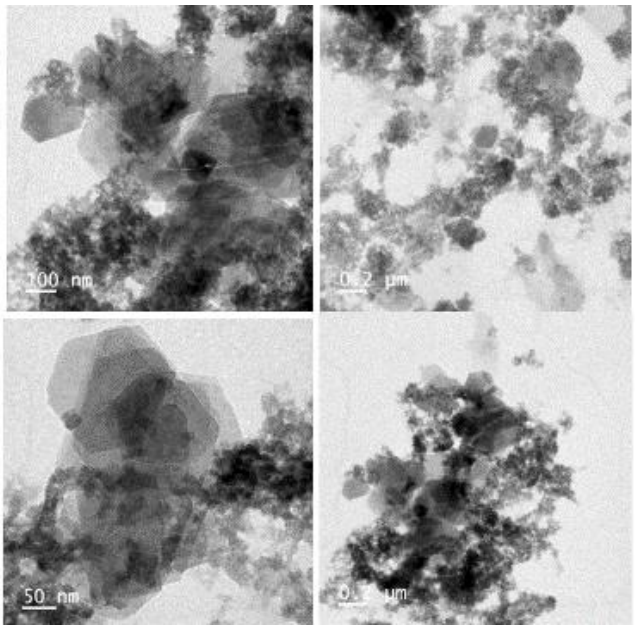

Figure 9. TEM images of Cobalt oxide nano-crystallites

Antibacterial effect of curcumin and all four SSP were visualized against both Gram positive (*B. subtilis* & *S. aureus*) and Gram negative (*E. coli*) bacteria. Ethanol and distilled water was used for the dispersion of curcumin and SSPs respectively. Only ethanol was maintained as control. SSPs showed best antibacterial activity better antibacterial activity against Gram positive organisms compared to Gram negative organisms. The following table 2 depicts the zone of inhibition (mm) by SSPs and curcumin for *B. subtilis*, *S. aureus* and *E. coli.* No antibacterial effect was observed by curcumin as well as ethanol.

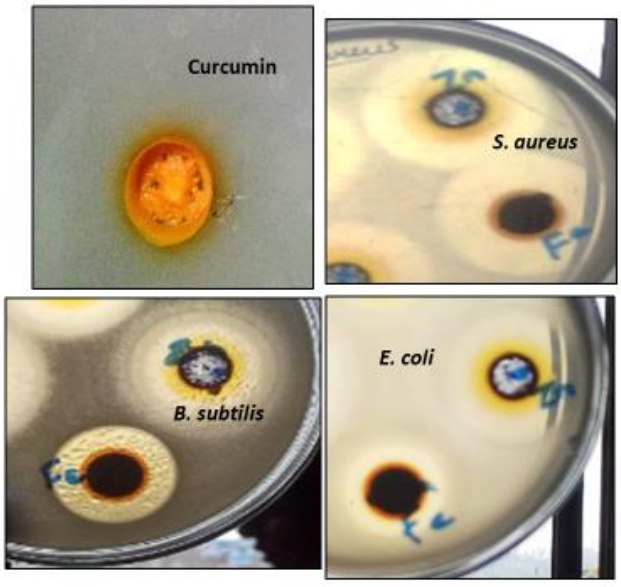

Figure 13. The Antibacterial activity of single source precursor compared with ligand

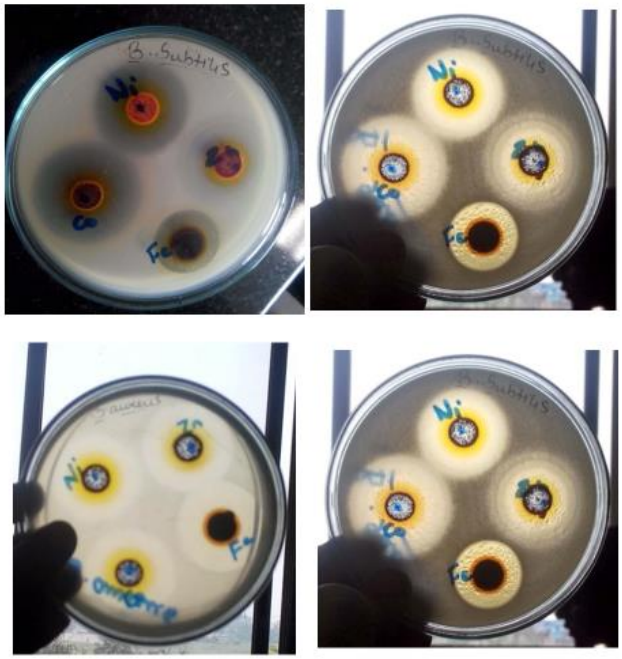

Figure 14. The Antibacterial activity of single source precursor complexes of transition metals

SSP'S	S. aureus	E. coli	B. subtilis
$FeCl_2$ (Curcumin)	30mm	16mm	32mm
$NiCl_2$ (Curcumin)	30mm	18mm	28mm
$CoCl_2$ (Curcumin)	30mm	16mm	32mm
$ZnCl_2$ (Curcumin)	32mm	18mm	23mm
Curcumin	7mm	7mm	7mm

Table 2: The Antibacterial activity of single source precursor

Here in our present studies indicate that biological activity of curcumin increases with metal complex formation. The single source precursor used in all the above studies was prepared in 1:1 stoichiometry. Studies clearly reveal that antibiotic activity of prepared curcumin complexes was higher as compared to the Antibacterial activity of curcumin.

CONCLUSION

The transition curcumin complexes found to be good single source precursor for preparation of metal oxide nano-crystallites. The transition curcumin complexes are good candidate for preparation of nano-crystallites. Work demonstrate simple and easy path for preparation of metal oxide-nano-crystallites. These complexes show good Antibacterial activity as compare to curcumin due to trans effect.

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