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GREENER SYNTHESIS, CHARACTERIZATION OF Co-doped SnO_2 NANOPARTICLES AND THEIR BIOLOGICAL SIGNIFICANCE

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ABSTRACT

The ecofriendly method was applied to the preparation of Undoped and Cobalt doped Tin Oxide (Co-doped SnO_2) nanoparticles with different mole (1 and 3%) concentration of Cobalt using *Canna indica (C. indica)* leaf extract as a green solvent. Powder X-ray Diffraction (PXRD), Scanning Electron Microscope (SEM) and Fourier-transform Infrared spectroscopy (FTIR) are the techniques used for the characterization purpose. PXRD confirmed the tetragonal rutile phase for both undoped and Co-doped SnO_2 nanoparticles. The existence of atomic groups which are responsible for the chemical reaction taking place was analyzed by FTIR. The peak formation in the range of wavelength between 480 and 750 cm^{-1} is consigned to the Sn - O consents group. SEM morphological studies show clustered granules with spherical morphology for the samples. Potential antioxidant activity of greater than 80% was observed for undoped and Co-doped SnO_2 nanoparticles with 1,1'-diphenyl-2-picryl-hydrazyl (DPPH), Superoxide dismutase (SOD) and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonicacid) (ABTS) assays using vitamin C as reference molecule. The antibacterial investigation suggested a better activity for *Staphylococcus aureus (S. aureus)* against *Escherialia coli (E. coli)* bacterial strains.

Keywords: SnO_2 Nanoparticles, Cobalt Doping, *Canna indica*, Antioxidant, Antimicrobial Activity.

INTRODUCTION

Semiconducting metal oxide nanoparticles are effectively traced to both enhance the performance of existing and developing new significances in nanoscience and technology.[1] Among the various nano metal oxide nanoparticles, SnO_2 nanoparticles possess wide bandgap energy (3.6 eV), quantum confinement and more availability of reactive surface atoms[2]. Hence it has been utilized broadly in the arena of transistor devices[3], battery technology[4], varistors[5], as electrodes in fuel cells[6], catalysis[7], and water splitting[8]. It is mainly used in the field of adsorption as its high surface area, high reactivity for photo catalysis[9] and antimicrobial activity in the medical field.[10] Furthermore, it also has other unique optical and electronic properties in novel treatment process[11,12] and sensors for monitoring gaseous product formation.[13,14] Researchers, focusing on aggregation, accumulation and toxicity of synthesized nanoparticles, have enabled a good understanding of the effects on animate matters and environmental implications.[15] The synthesis of nanoparticles using the chemical method, in the field of nanotechnology is developing rapidly along with some severe concerns about toxicity deeds on the environment as well as the health of living organisms.[16,17] So, there is a need for the evolution of cheap and sustainable green route methods for the production of nanoparticle, to reduce hazardous effects.[18-20] The proportional degree of synthesis of nanomaterials depends on the reducing agents, capping agents used during the process of synthesis. But in the green synthesis of nanomaterials, the biomolecules existing in the plant materials acting as the reducing and stabilizing agents are highly influencing the morphology and size of the metals[21, 22]. The combined arrangement of both nanoscience and eco-friendly greener approach will reveal

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the array of bio significant and cytological companionable metal oxide nanoparticles.[23,24] *C. indica,* a medicinal plant, was used in our research as a green solvent to synthesize undoped and metal-doped metal oxide nanoparticles. Many species of *C. indica* are grownup for medication and redecoration. Ethno-medical uses of *C. indica* leaves including antimicrobial, analgesic, and anthelmintic activities.[25,26] Properties of the synthesized nanomaterials can be positively modified by introducing dopants into the parent structure. The doping of new transition metals with bio-constituents in SnO_2 nanoparticles can stimulate its properties like antibacterial, antiviral, antifungal, anti-oxidant, drug-carrying, sensing and bio-imaging ability.[27]

We have selected, well-identified and valuable medicinal plant, Cannaceae family, *C. indica* plant leaf extract for synthesizing undoped and Co-doped SnO_2 nanoparticles. In our research work, we synthesized the above-mentioned nanoparticles using leaf extracts of the plant *C. indica* as a reducing agent and capping agent in aqueous Tin (II) Chloride solutions. Resulting products were characterized by using XRD, FTIR, SEM to examine its particle size, lattice parameters, presence of functional groups, morphology, respectively. Antioxidant and antimicrobial activity of undoped and Co-doped SnO_2 nanoparticles are also discussed in detail.

EXPERIMENTAL

Materials and Method

Tin (II) chloride dihydrate, Cobalt (II) chloride hexahydrate, was acquired from Merck (Indian Company). Analytical grade chemicals were taken for the synthesis without doing purification. Leaves of freshly grown *C. indica* shrub leaves were collected from Nallur area of Tirupur district.

Preparation of Extract

C. indica leaves were properly washed using double distilled water and dried in sunlight. Dried leaves were finely trimmed into small bits and weighed up to 10 gm. This was added in 100 ml of boiling distilled water and allowed to boil for thirty minutes. The aqueous extract was detached by filtration using Whatman No. 1 filter paper and then centrifuged at 1,200 rpm for 5 min to remove heavy biomaterials.

Synthesis of Undoped and Co-Doped SnO_2 (1 and 3 mole %) Nanoparticles

Undoped and Co-doped SnO_2 nanoparticles were synthesized by adding 10 ml of *C. indica* leaf extract into 90 ml aqueous solution of 1 mM tin (II) chloride taken in 250 ml conical flask. Drop-wise addition of leaf extract and continuous stirring using magnetic stirrer was maintained until the thorough precipitation of pale yellow coloured tin oxide nanoparticles. This reaction mixture was heated at 70°C for two hours. The resulting suspension was kept at rest for 15 hours at room temperature and then filtered using deionized water to remove the remaining chloride ions. Then slightly warmed with 2ml of alcohol and dried.

A similar green route was used to synthesize 1 and 3 mole % Co-doped SnO_2, by adding the required molar amount of aqueous solution of Cobalt (II) chloride hexahydrate to the tin chloride solution (doping step). After being washed, both undoped and Co-doped SnO_2 nanoparticles can be stored in aqueous suspensions and recovered by doing centrifugation whenever necessary. This synthesis method was explained already in our previously published article.[28] Here, Undoped (sample 1) and 1, 3 mole % Co-doped SnO_2 nanoparticles were referred to as samples 2, 3 respectively.

In-vitro Antioxidant Analysis

Antioxidant behaviour of the green route synthesized samples 1 and 3 was assessed in 3 ways. Namely, (a) DPPH free radical procedure described by Blois et al[29], (b) Superoxide anion scavenging method ascribed by Srinivasan et al[30], and (c) ABTS assay for antioxidant analysis was carried out based on the methodology followed by Huang *et al*[31]. 0.1mM solution of DPPH dissolved in solvents like ethanol, methanol, petroleum ether, ethyl acetate and benzene and exactly 1 ml of this solution extract was taken with 3ml of the aqueous solution of sample 1 and 3 at various concentrations as mentioned in Fig.-3. The mixtures were shaken well and permitted to position in dark place at 34 -37°C (room temperature) for half an hour. Then the UV-VIS spectrophotometer was used to measure the range of absorbance at 517nm. Vitamin C or Ascorbic acid was taken as standard. In case of SOD assays, radical superoxide anion was

caused in 3 ml of 16 mM Tris hydrochloric acid buffer (pH 8.0) comprising 0.5 ml of nitroblue tetrazolium chloride with 0.3mM concentration and 0.5 ml of nicotinamide adenine dinucleotide (0.936 mM) solution with 1.0 ml of green synthesized nanoparticles, dissolved in above-mentioned solvents. Then 0.5 ml of phenazinemethosulfate solution (0.12mM) was added to the reaction mixture and then protected as it is at 24 - 26ºC for 5 minutes and the range of absorbance was noted at 560 nm. 100 µg of green synthesized nanoparticles dissolved in various solvents, which was reacted with ABTS stock solution (7mM) in water, potassium per sulphate (2.45 mM) and then the reaction mixture was kept aside in dark place at 35ºC for 14-16 hours. This mixture was diluted with water and added with ethanol to get a range of absorbance in 0.70 $\pm$ 0.02 at 734 nm after six minutes against standard ascorbic acid. Highly potential and remarkable free radical scavenging ability was reported due to the lesser absorbance values of the reaction mixture. Finally, the consequences were stated as trolox equivalent antioxidant capacity (TEAC). The competence to scavenge the free radical was intended by the following equation:

$$\text{Percentage of free radical scavenging activity (\%)} = [(A_o - A_i) / A_o] \times 100 \quad (1)$$

Where, A_o is the absorbance of reference and A_i is the absorbance of test samples. All the examinations were performed thrice and the effects were monitored.

Antimicrobial Assessment

Antimicrobial potential of samples 1, 2 and 3 was tested by Well diffusion assay[32]. Muller hinton agar plates inoculated culture and wells were created using 50 mm stainless sterile well puncture. 50 µL of samples 1, 2 and 3 containing a final concentration of 25, 50 and 75 µg mL^{-1} were studied against pathogenic gram-positive and negative bacterial strains. The plates were gestated at 30˚C for 24 hours and results were detailed by evaluating the zone of inhibition.

Characterization Techniques

The Powder X-ray Diffraction (PXRD) patterns of the synthesized nanoparticles were documented using the model BRUKER AXS D8 - Advanced X-ray Diffractometer Cu-Kα radiation at 2θ assessment between the range of 20° and 80°. The Fourier Transform Infrared Spectroscopy (FT-IR) of all the samples was recorded with the help of Brucker – Tensor 27, in the range from 400 to 4000 cm^{-1} to study the presence of the functional group. Model JEOL JSM – 6390 microscopes operating at 20kV equipped with EDAX attachments was used to examine the surface morphology and the elemental compositions nanoparticles. Measurements of absorbance for antioxidant analysis were done with the help of UV-VIS spectrophotometer - Genesys 10s UV: Thermo Electron Corporation.

RESULTS AND DISCUSSION

Powder X-Ray Diffraction Analysis

The structural arrangement of all the samples was studied using PXRD studies at the angle of 2θ between 20° to 70°. Figure 1(a-c) illustrates the XRD patterns of green synthesized nanoparticles. The SnO_2 nanoparticles show several Bragg reflections peaks at different 2θ angles 26.48°, 31.2°, 50.08°, 64.84°, which can be indexed to (110), (101), (211) and (112) planes respectively. The observed diffraction peaks were noticed as tetragonal rutile structure and coincided with JCPDS: 77-0451. The rutile type structure is well maintained and no foreign phases are observed, which denotes the purity of nanoparticles. The XRD peaks get broadened with rising in the doping concentration is due to the particle size reduction. According to the Debye-Scherer's equation (2),

$$D = (0.9\lambda / \beta \cos \theta) \quad (2)$$

Where, λ and β represent wavelength and Full-width half maximum of the X-ray diffraction peak, respectively and θ is the Bragg diffraction angle. The size of the particles was calculated to be around 22.5, 21.2 and 22.0 nm for both undoped and 1, 3 mole % Co-doped SnO_2 nanoparticles, respectively. The calculated lattice parameters for the sample 1 are, (a = b) = 0.5256 nm and c = 0.3587 nm. Similarly,

for sample 2 and 3, (a = b) = 0.5235 and 0.5192 nm and c = 0.360 and 0.364 nm, respectively. Moreover, the position and height of intensities display slight orderly variation with the doping of Co. The evolution of the cell parameter values of a = b and c, with the Co doping, can be observed that the values are decreasing from sample 1 to sample 3. Hence, the unit cell volume possibly may decrease with the addition of dopant concentration. The estimated cell volume of samples 1, 2 and 3 were found to be around 99.09, 98.65, and 98.12 $Å^3$ correspondingly. This slight deviation is dependable by the way of less radius value 0.58 Å of the cobalt ion than the 0.69 Å which is the radius of tin ion [33] owing to the concentration of cobalt taken for the process of doping. Hays et al[34] and Gopinathan et al[35] also reported a similar illustration on contraction in lattice parameters due to the substitution of Sn ion by Co ion in the SnO_2 thin film surface lattice. So from the XRD evaluations, we determine that the doped Co ions are substituting Sn ion in the host matrix and it contain no other impure phases in the resultant nanoparticles.

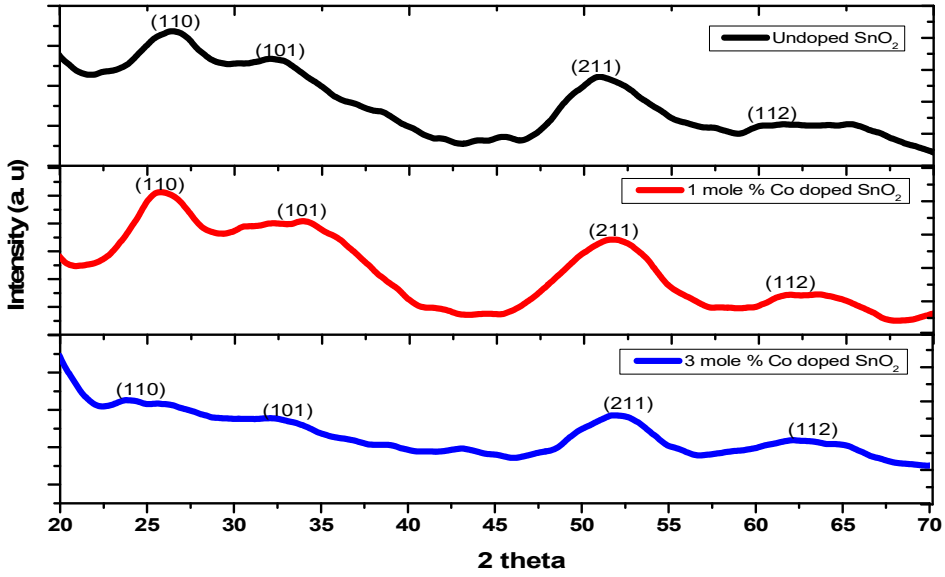

Fig.-1: XRD Pattern of Green Synthesized Nanoparticles

FTIR Analysis of Undoped and Co-doped SnO_2 Nanoparticles

The reactive group's existent in samples 1, 2 and 3 were confirmed from the FTIR spectrum and are listed in Table-1. The absorption peak at 1610 cm^{-1} and 3330 $cm^{-1}$are ascribed to the bend vibration of H-O-H and stretching vibration of O-H bond in water molecules present on the outer surface of the sample, respectively[36]. The band at 636 cm^{-1} and 495 cm^{-1} are attributed to the Sn-O stretching vibration and O-Sn-O bending vibration, respectively which confirms the presence of SnO_2 in the crystalline phase[37]. The exhibition of broad band around 1068 cm^{-1} was due to the bending vibration of Sn-OH groups. The absorption band at 500 to 700 cm^{-1} may be owing to symmetric and also asymmetric stretching vibration of Sn-O-Sn chemical groups[38, 39].

SEM Analysis of Undoped and Co-Doped SnO_2 Nanoparticles

Morphological studies of the sample 1, 2 and 3 were performed by SEM shown in Fig.-2(a-c). It is seen that the product consists of tiny, aggregated spherical shaped particles.

In-vitro Antioxidant Analysis

Antioxidant agents are the chemical constituents are used for interrupting oxidation reaction or eliminating free radical formation. The antioxidants shield the organic matter from nascent oxygen and free radicles[40]. Responsive nascent oxygen species harms biomolecules like fats, enzymes, proteins, amino acids in the cells and causes cell death. DPPH assay estimates the ability to damage the natural macromolecules[41].

Table-1: List of Functional Groups Present in Synthesized Nanoparticles

Wavelength (cm^{-1})	Assignments
3328	Stretching Vibration of -OH group
1610	bending vibration of -OH group
1163	bending vibration of N-H group
2255	Stretching vibration of C-H group
1520	bending vibration of C=C group
1431	Stretching vibration of C-C group
510 and 628	Sn-O-Sn vibrations

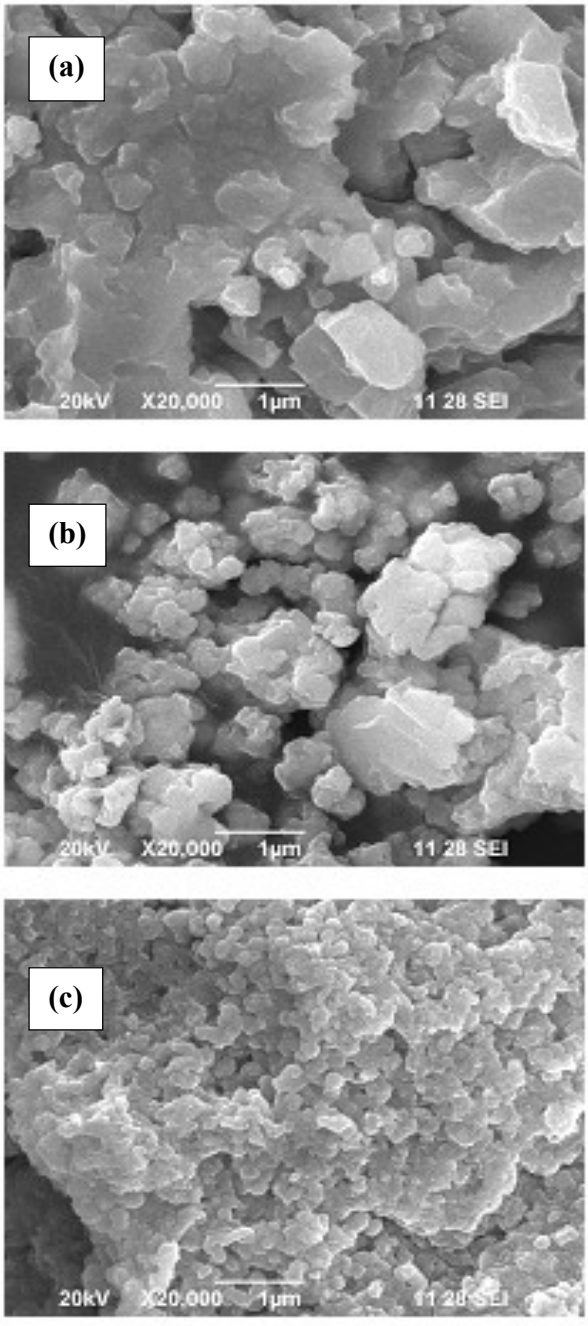

Fig.-2: SEM Images of (a) Sample 1 (b) Sample 2 (c) Sample 3

The antioxidant property of green synthesized samples 1 and 3 in scavenging the DPPH free radical were determined by using Ascorbic acid as a reference compound and their consequences in different solvents were manifested in Figure 3. Results were demonstrated that DPPH in all the solvents with samples 1 and 3 exhibits remarkably determined and considerably free radical scavenging tendency than standard ascorbic acid. While, sample 1 was found to exhibit remarkable DPPH free radical scavenging activity in the presence of petroleum ether and for sample 3 shows great antioxidant activity in Ethanol, Methanol and petroleum ether solvent. But other solvents showed the reduced DPPH free radical scavenging activity than standard Vitamin C. Figures 3a and b explores scavenging ability in percentage to that of Vitamin C (Reference). The fall of the intensity of the band at 517 nm evidenced the scavenging capacity of samples.

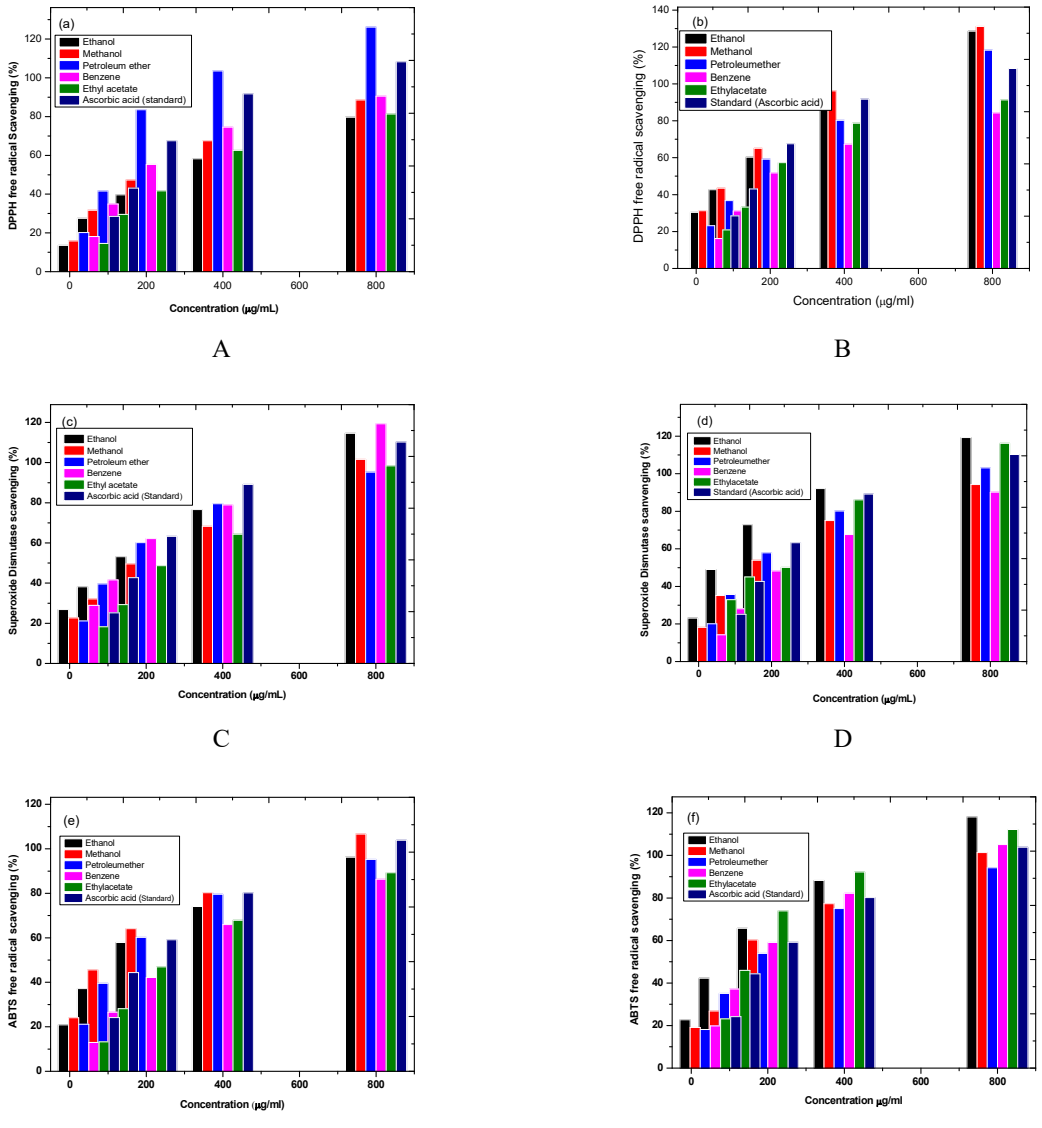

Fig.-3: Antioxidant Activity of Green Synthesized (a) Sample 1 and (b) Sample 2 with DPPH Assay, (c) Sample 1 and (d) Sample 2 with SOD Assay, (e) Sample 1 and (f) Sample 2 with ABTS Assay in Presence of Various Solvents

The presence of the phenolic compound in the sample extract resolves the capability of the sample to act as an antioxidant agent[42]. Higher the phenolic content, the stronger is the antioxidant ability. Because, the hydroxyl group in the phenolic compound, leads to donate hydrogen atom in DPPH radical, to maintain

the stability of the compound[43]. Superoxide radical scavenging capacities of synthesized nanoparticles exhibits the highest antioxidant ability in the presence of all the solvents used in the experiment than the standard ascorbic acid (Fig.-3c and d). Above 85 % of antioxidant activity was observed for both samples 1 and 3 in the various solvent used for the analysis with that of standard one at the high concentration of nanoparticle (800 µg/mL). ABTS radical cation quenching assay demonstrated great results for both samples. Results obtained in ABTS and SOD assays also confirm the presence of a strong positive test for phenols existence in the solvent extracts of samples.

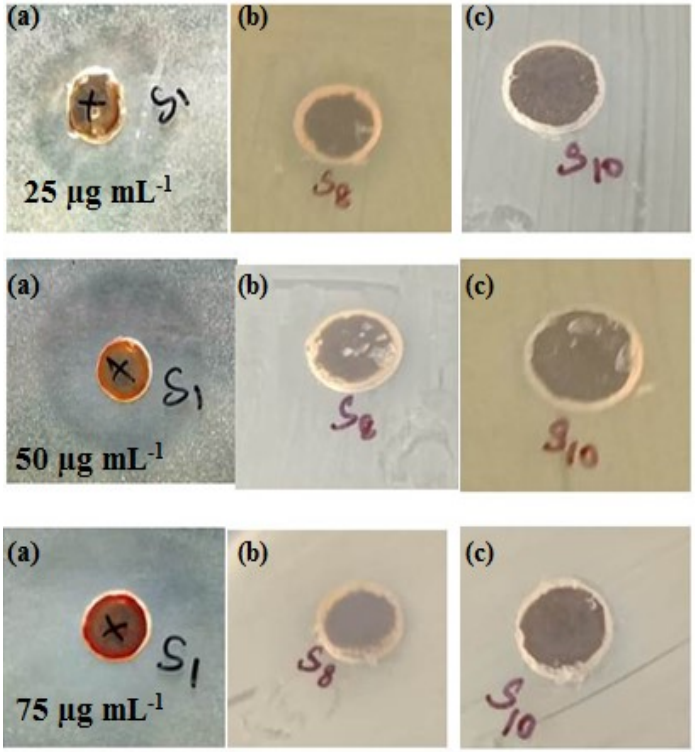

Fig.-4: Antimicrobial Potential of (a) Sample 1 (b) Sample 2 and (c) Sample 3 against *Staphylococcus aureus* with Various Concentration

The polyphenol compounds show a spirited role as antioxidants in living organisms due to the presence of hydroxyl groups in the ortho and para positions[44]. Strong positive presence of various constituents like alkaloids, phenolic compounds, carbohydrates, protein, glycosides, Tannins and saponins were confirmed by undergoing a phytochemical screening test on *C. indica* leaf extract. These nanoparticles, synthesized using this green solvent, represented potential antioxidant activity with both standards ascorbic acid at the maximum concentrations with free radical scavenging assays (Figure 3e and f). While comparing the antioxidant property of synthesized nanoparticles with DPPH, SOD and ABTS assays, doping of metal into the host material enhance the percentage of antioxidant activity, which also may be stimulated by several aspects like size, structural morphology, defect in surface and the phenolic groups present in green solvent used for the synthesis process.

Antimicrobial property of Undoped and Co-doped SnO_2 Nano particles

Figures 4 and 5 show antimicrobial testing on most common and venerable bacterial pathogens *E. coli* and *S. aureus* showed positive were tested by well diffusion assay. The bacterial growth was inhibited by SnO_2 nanoparticles. The doping of Co onto the matrix of SnO_2 with 1mole % concentration reflects no variation in the inhibition towards the bacterial growth among both gram-positive and negative bacteria. These inhibitions were found to increase with an increase in dopant concentration (3 mole %). The results demonstrate that the Co-doped host material was positively influencing the bactericidal property of green synthesized SnO_2 nanoparticles. Effectiveness of bacterial growth inhibition was found maximum with *S.*

aureus than *E. coli* which indicates the membrane diversification among the bacterial species (Table-2). The antimicrobial activity of samples 1, 2 and 3 might be due to the presence of hydroxyl ions or radicals which are directed to the formation of hydrogen peroxide, which enters into the cell and intrudes the configuration of cytoplasm, finally, the bacteria become incapable to persist.[45, 46]

Table-2: Antibacterial Potential of Sample 1, 2 and 3 against Human Pathogens

Test Organism	Sample 1			Sample 2			Sample 3		
Conc.(µg/mL)	25	50	75	25	50	75	25	50	75
E. coli	12	18	23	14	18	22	19	25	27
S. aureus	21	28	29	21	28	30	26	30	32

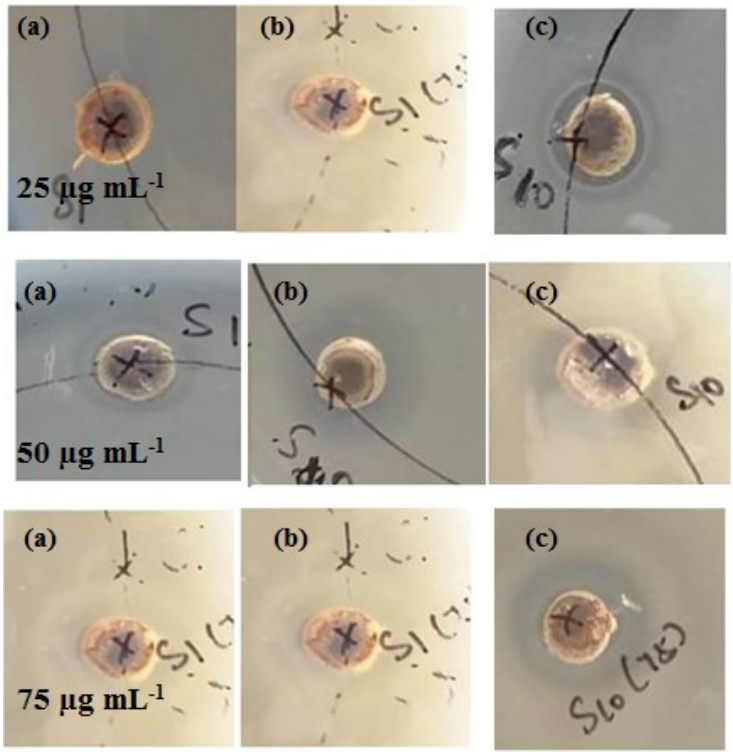

Fig.-5: Antimicrobial Potential of (a) Sample 1 (b) Sample 2 and (c) Sample 3 against *Escherichia coli* with Various Concentrations

CONCLUSION

Green synthesis of undoped and Co-doped SnO_2 using aqueous tin and cobalt chloride solutions, respectively with *C. indica* leaf extract as a reducing agent was done. Powder XRD spectra reveal the particle size of the order of ~ 22 nm. FTIR analysis confirmed that the bio-reduction of aqueous tin chloride solution to SnO_2 nanoparticles is due to the reduction by the *C. indica* leaf extract. FT-IR Spectra shows a characteristic peak at 597 and 553 cm^{-1} has been credited to Sn-O- stretching of Sn-O-Sn. SEM shows the morphology of the resulting product as clustered nanospheres along with some agglomerates. Antioxidant activity of undoped, Co-doped SnO_2 nanoparticles and ascorbic acid (reference) using DPPH, SOD and ABTS assay was carried out.

The percentages of radical scavenging effectiveness of green synthesized nanoparticles were found to increase with an increase in the dose of both undoped and Co-doped SnO_2 nanoparticles. These green synthesized nanoparticles exposed nearly 80% of radical scavenging activity in all the assays at maximum concentration. It is a comparably remarkable antioxidant activity with that of the Vitamin C (reference). This may be due to the presence of phenolic compounds. The antibacterial investigation suggests a better antibacterial activity for *S. aureus* than *E. coli* bacterial strains.

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