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Research Article

HERBAL SYNTHESIS OF IRON DOPED COBALT OXIDE NANOPARTICLE AND ITS APPLICATIONS

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ABSTRACT
Iron doped cobalt oxide nanoparticles were prepared by using *Eclipta alba* leaves extract. The structural, optical and phase analysis of the synthesized nanoparticles are investigated by X-Ray Diffraction (XRD), Ultraviolet Visible Spectroscopy (UV), and Fourier Transform Infrared Spectroscopy (FTIR) respectively. Scanning Electron microscope (SEM), Energy Dispersive X-Ray Spectroscopy (EDX) and Dynamic Light Scattering (DLS) are used to study the surface morphological, elemental analysis and the hydrodynamic size of the prepared nanoparticles. Methylene Blue (MB) and Congo Red (CR) dye degradation efficacy of the iron doped cobalt oxide nanoparticles are examined using UV. Antibacterial activity for three different bacteria was done using disc diffusion method. Capacitative property of $FeCo_2O_4$ was proved by Cyclic Voltammetry (CV) analysis. Thermodynamic properties of the herbal synthesized particle were investigated using Ultrasonic technique using propylene glycol as a base fluid.

Keywords: *Eclipta alba*, DLS, Ultrasonic technique, Antibacterial activity, Capacitative behaviour, Photocatalytic action.

1. INTRODUCTION
Iron doped cobalt oxide ($FeCo_2O_4$) has been well known because of its interesting physical properties, and it has been used as a candidate for many applications such as Li-ion storage, gas sensors, catalysts, and magnetic devices. Ferric oxide nanoparticles are of significant technological interest and have attracted more attention due to its unique properties. This transition metal oxide with a narrow band gap forms the basis of several high temperature superconductors, gas sensors, giant magneto resistance materials, solar energy transformation and preparation of organic-inorganic nanostructure composites.
With the aim of synthesizing iron doped cobalt oxide nanoparticles, a complete green approach was adopted using aqueous leaf extracts of plant *Eclipta Alba*, as an effective stabilizing and chelating agent. This process does not contain any surfactants for an ecofriendly and green synthesis. The interface of medicinal plants and biosynthesis of nanoparticles provides an exciting opportunity for wide range of biomedical applications [1].
In the present study, we are reporting the synthesis of iron doped cobalt oxide nanoparticles using Eclipta Alba leaves their characterization findings with respect to XRD, UV, FTIR, SEM, EDX, DLS, Photocatalytic activity, CV, antibacterial and reported that the thermodynamic properties of the prepared nanofluid using propylene glycol as a base fluid under various temperature.

2. MATERIAL AND METHODS
The chemical used for this study are of analytical reagent grade with 99% purity, cobaltous chloride hexahydrate ($CoCl_2.6H_2O$) was purchased from HiMedia Laboratories Pvt. Ltd., and Ferric chloride hexahydrate ($FeCl_3.6H_2O$)was purchased from Avantor performance materials India Ltd., Maharashtra, and ultrapure distilled water for aqueous solution preparation was used without

further purification. Fresh leaves of Eclipta Alba were collected from Paddy fields and brought to the laboratory.

2.1. Preparation of leaf extract

The fresh leaves of *Eclipta Alba* (50g) were thoroughly washed with tap water followed by distilled water. Chopped leaves of *Eclipta Alba* were then taken in a bowl and 200ml of ultrapure distilled water was added. The mixture was heated for 20 minutes to get the leaf extract of 100ml. The extract was then cooled and filtered using Whatman filter paper. For the synthesis of Iron doped Cobalt oxide nanoparticles, the resultant filtrate act as a reduction and capping agent.

2.2. Preparation of iron doped cobalt oxide nanoparticles

For the synthesis of Iron doped cobalt oxide nanoparticles, the freshly prepared leaf extract (100ml) was added to the 1 molar concentrated cobaltous chloride and the Ferric chloride hexahydrate. pH of the prepared product was set to neutral. The mixture was stirred over 3 hours at room temperature. After that, the solution was allowed to settle for overnight and the supernatant solution was then discarded carefully. Washing with distilled water and ethanol was carried out to remove the by-products, impurities and un-react particles that were bound to the nanoparticles. This process was repeated for 5 days. The obtained precipitate was dried using hot air oven at 120°C for 3 hours. The derived product was grained using small hand agate mortar and calcined at 500°C for 3 hours in a muffle furnace. Finally, a fine nanopowder was obtained, and collected for further characterization studies.

2.3. Preparation of nanofluid

Nanofluids are dilute liquid suspensions of nanoparticles with at least one of their principal dimensions smaller than 100 nm. Nanofluids have novel properties that make them potential applications in heat transfer including microelectronics, pharmaceutical processes, fuel cells, etc. they exhibit enhance thermal conductivity and convective heat transfer coefficient compared to the base fluid.

In the present study ultrasonicator is used for preparation of nanofluid with minimum aggregation of nanoparticles and improved dispersion behavior. Prepared dry $FeCo_2O_4$ nanoparticles are mixed with propylene glycol as base fluid in nanofluid preparation. The quantity of nanoparticles required for preparation of nanofluid of different volume concentrations is calculated using weight percentage equation. A sensitive balance (Wensar, resolution-0.001 g) is used to weigh the nanoparticles very accurately. Ultrasonication was applied for 1-2h to mix calculated amount of nanoparticles in base fluid using ultrasonic Cleaner (Smiledrive, Voltage- 220-240 V, frequency- 50Hz). The $FeCo_2O_4$ nanofluid thus prepared was kept for observation and no particle settlement was observed at the bottom of the flask even after twenty four hours. During the experimentation, the time taken to complete the experiment is less than the time required for first sedimentation to take place and hence surfactants are not mixed in the nanofluid [2]. Five different volume concentrations of 0.1%, 0.2%, 0.3%, 0.4% and 0.5% were used in the study.

3. RESULTS AND DISCUSSION

3.1. XRD pattern for iron doped cobalt oxide nanoparticles

Crystal phase of prepared $FeCo_2O$ sample was depicted in fig. 1, It shows the product is pure and well crystalline nature. The peaks positioned at 2θ values of 30.13, 31.56, 35.59, 37.24, 43.24, 53.76, 57.31 and 62.87 are indexed for the optimized $FeCo_2O_4$ nanoparticles and the respective miller indices are (220), (533), (311), (222), (400), (422), (511) and (440). These indices pointed out the cubical crystal lattice with lattice parameters a = b = c = 8.391 Å and the volume of the unit cell was found to be 590.99 $(Å)^3$. Average crystalline size of the particles is calculated as 10 nm and the parameters calculated from the XRD are tabulated in Table 1.

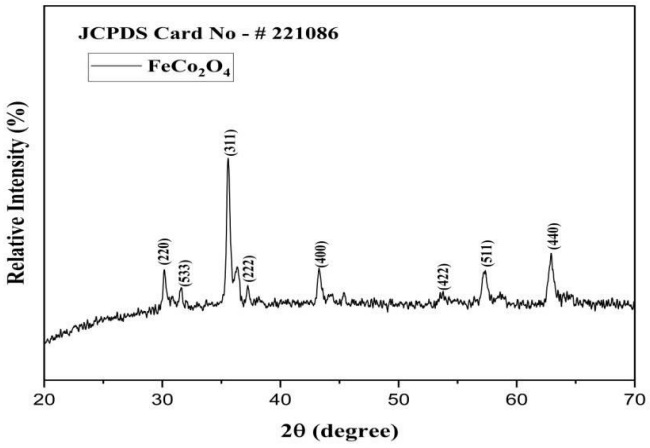

Fig. 1: XRD Pattern of $FeCo_2O_4$ nanoparticles

Table 1: Calculated parameters of $FeCo_2O_4$ nanoparticles from XRD

Sample	2θ (degree)	hkl	Crystalline Size (nm)	Volume of the unit cell (Å)^3	Cell Parameter a=b=c (Å)	D-Spacing (Å)	
						D_{cal}	D_{Te}
$FeCo_2O_4$	30.13	(220)	10	590.99	8.391	2.97	2.96
	35.59	(311)				2.53	2.52
	37.24	(222)				2.42	2.41
	43.24	(400)				2.09	2.09
	53.76	(422)				1.71	1.70
	57.31	(511)				1.61	1.61
	62.87	(440)				1.48	1.48

3.2. FTIR studies of iron doped cobalt oxide nanoparticles

Fig. 2, reveals that FTIR analysis of green synthesized $FeCo_2O_4$ nanoparticles. Broad absorption band at 3430cm^{-1} due to the adsorbed water molecules hence the nanomaterial exhibits a high surface to volume ratio and thus absorbs moisture readily. Peak at 2924 and 2851 cm^{-1} corresponds to C-H symmetry stretching vibration, bands at 1643, 1442 and 1114 cm^{-1} confirmed the presence of amide, carbonate group elements and C-O symmetric stretching vibration respectively. In fingerprint region the peak at the wave number 594 cm^{-1} gives the evidence for the formation of metal oxide.

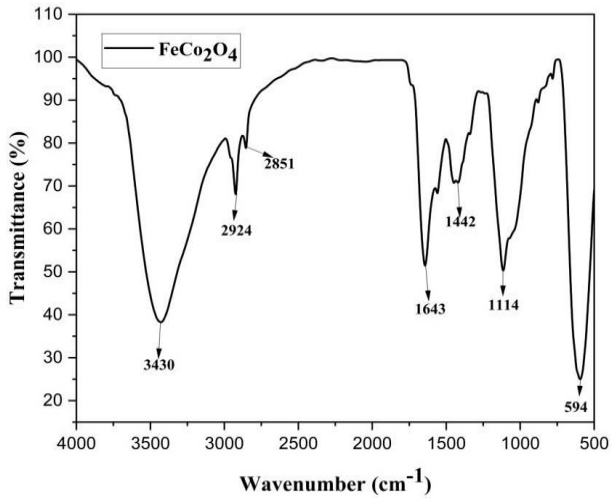

Fig. 2: FTIR Spectrum of $FeCo_2O_4$ nanoparticles

3.3. UV analysis of iron doped cobalt oxide nanoparticles

The optical spectrum and the band gap of $FeCo_2O_4$ nanoparticles was estimated from absorption coefficient (α) and photon energy (hν) using the following relation.

$$E_g = (\alpha E)^n \quad \ldots\ldots\ldots (1)$$

Fig. 3, shows the plot of $(\alpha h\nu)^2$ versus photon energy (hν). The value of band gap of Copper doped cobalt nanoparticles was measured by extrapolating the intercept line on the photon energy (hν) axis gives direct band gap (Eg) of 2.89 eV, which confirms the semiconducting properties of the nanoparticles.

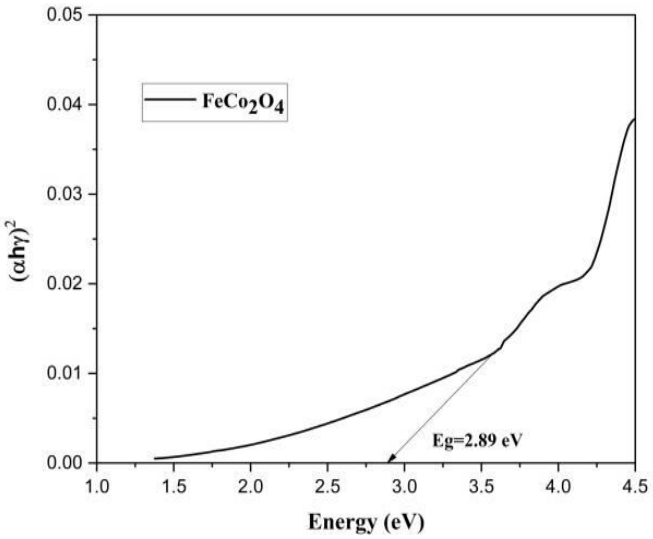

Fig. 3: Direct band gap of $FeCo_2O_4$ nanoparticles

3.4. Scanning electron microscopy

Surface morphology of the prepared $FeCo_2O_4$ was investigated using SEM analysis. From the SEM (Fig. 4), it is revealed that Iron doped cobalt oxide nanoparticles exist in highly prismatic structured morphology with low degree of agglomeration.

3.5. Energy dispersive X-ray spectroscopy

The elemental composition and purity of the as prepared iron doped cobalt oxide nanoparticle was investigated by using energy dispersive X-ray (EDX) spectroscopy it was shown in Fig. 5.

Only Oxygen, Iron and Cobalt elements was existed in the sample. The atomic percentages of Fe, Co and O were found to be 29.98%, 28.96% and 41.05%, respectively.

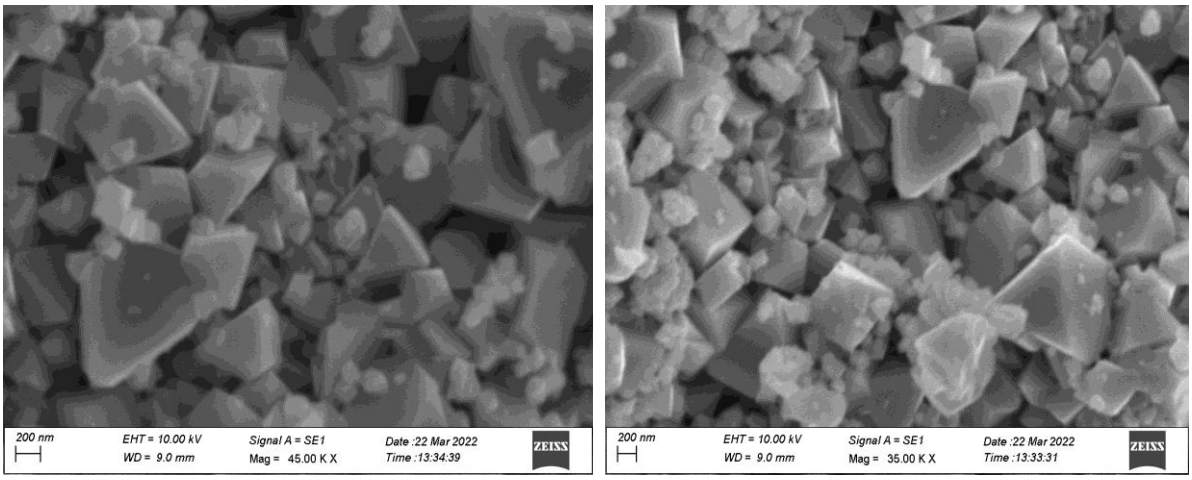

Fig. 4: SEM images of $FeCo_2O_4$ nanoparticles

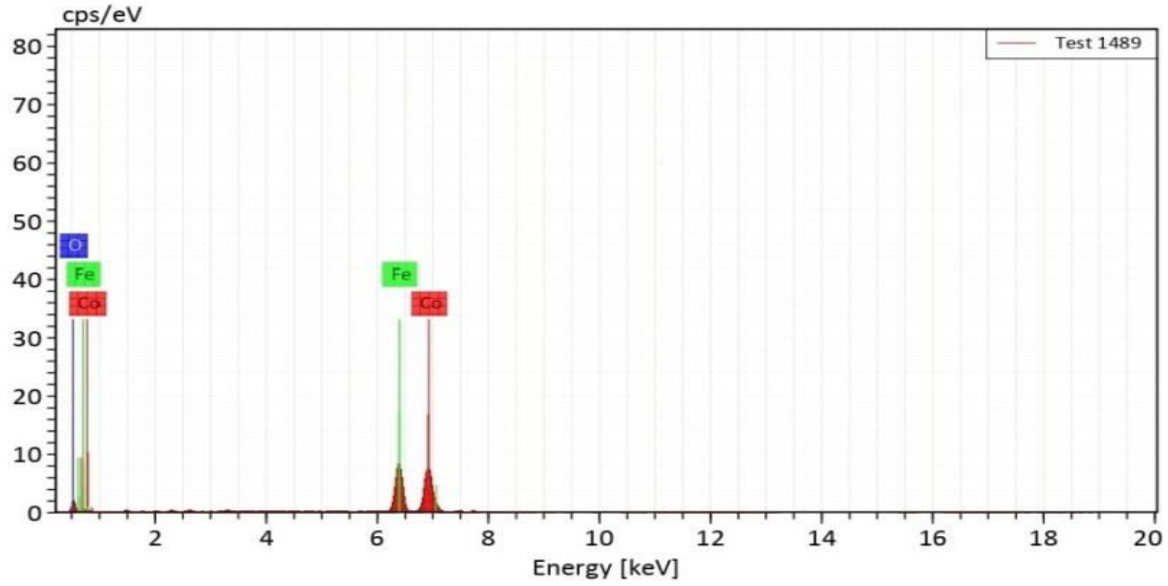

Fig. 5: EDX images of $FeCo_2O_4$ nanoparticles

3.6. Dynamic light scattering

The detection of the light scattered from the interaction of light with matter gives information related to the physical characteristics of the samples.

Typically, in light scattering experiments, a mono-chromatic beam is directed to the sample and then a detector records the scattered light at a certain angle [3]. The hydrodynamic diameter of $FeCo_2O_4$ NPs in aqueous phase was estimated by dynamic light scattering (DLS) study. The DLS profile of $FeCo_2O_4$ NPs is shown in Fig. 6. The hydrodynamic size measurement suggested that $FeCo_2O_4$ NPs had an average size of 120 nm and the polydispersity index (PI) of 0.324 in aqueous medium.

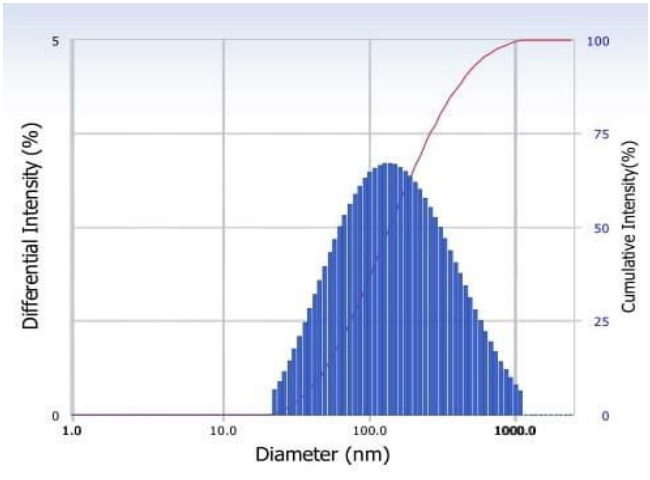

Fig. 6: DLS images of $FeCo_2O_4$ nanoparticles

4. APPLICATIONS OF $FECO_2O_4$ NANOPARTICLES

4.1. Photocatalytic activity

Photocatalytic degradation of Methylene Blue (MB) and Congo Red (CR) dye was separately carried out in the presence of $FeCo_2O_4$ nanoparticles. After irradiation with UV light for 60 minutes, the absorption intensity decreased due to discoloration of both the dyes. The reduction of initial absorbance at 664 nm and 498 nm for MB and CR in aqueous medium was also decrease upon resprective catalytic addition of NPs 5 and 10 mg (Fig. 7). The degradation efficacy of the synthetic $FeCo_2O_4$ NPs was calculated as (98% and 84%) and (34% and 98%) respectively. In the case of control there was a negligible change of absorbance for both dyes. Thus $FeCo_2O_4$ shows greater efficiency to degrade both MB and CR dyes in higher concentration.

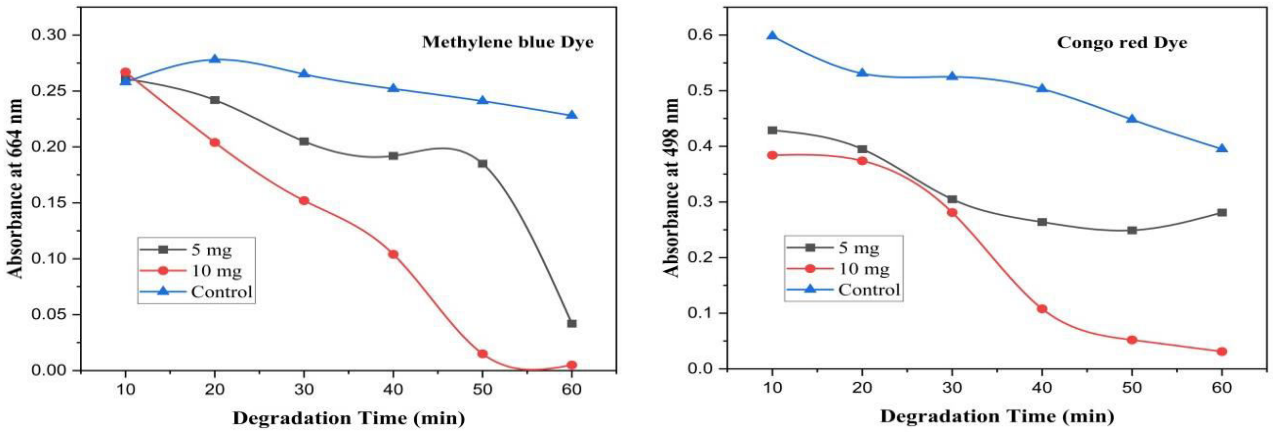

Fig. 7: Degradation of MB and CR by $FeCo_2O_4$ Nanoparticles

4.2. Thermodynamic parameters using ultrasonic techniques

In recent years ultrasonic technique has become a powerful tool in providing information regarding the molecular behavior of liquids and solids and the physiochemical properties of the medium. The thermodynamic properties of the nanofluid are extensively used to study the departure behaviour from basefluid. The nanofluid was prepared in various mole fractions (0.01, 0.02, 0.03, 0.04 and 0.05 g) and the data obtained from the experiments are used to calculate the thermodynamic properties of the nanofluid. The experiments were carried out at different temperature like 308 K, 313 K, 318 K and 323 K. The velocities of ultrasonic waves in the nanofluid have been measured using an ultrasonic interferometer working at a fixed frequency of 2MHz supplied by Mittal Enterprises New Delhi. The density of the fluid was measured using a 5cc specific gravity bottle. The viscosity of the pure propylene glycol and $FeCo_2O_4$ nanofluid were measured using an Ostwald's Viscometer.

$$\beta_a = \frac{1}{\rho U^2} \quad \text{..... (2)}$$

$$K_{nf} = 3\left(\frac{\rho N_A}{M_{nf}}\right)^{2/3} K_B U \quad \text{..... (3)}$$

Ultrasonic velocity of the nanofluid decreases with increasing temperature and concentration while at the same temperature it is observed that increasing trend of velocity with respect to increase in concentration. An opposite behaviour was observed in both adiabatic compressibility and free length. Due to electrostriction, the liquid molecules within the primary solvation shell of electrolytic solution are rendered incompressible moreover increasing concentration of ions results in more solvent molecules to engage in incompressible solvation spheres thereby decreasing the adiabatic compressibility. This shows the formation of hydrogen bonds, complex formation and there was a strong interaction between the basefluid and the nanoparticles. The decrease in compressibility brings the molecules to a closer packing resulting into a decrease of intermolecular free length. As Intermolecular free length (L_f) increases, ultrasonic velocity decreases and vice-versa, shows an inverse behavior [4].

Viscosity and density is found to increase with increasing concentration. This Increase in density with concentration is due to the shrinkage in the volume which in turn is due to the presence of solute molecules. In other words, the increase in density may be interpreted to the structure-maker of the nanoparticles

due to the added basefluid. In this case, there was a continuous increase in the density of the solution with an increase in concentration. This shows there was a strong intermolecular interaction such as dipole-dipole attraction and hydrogen bonding. The sharp decrease in density at 0.04% can be explained on the basis of a sudden increase in the volume of the basefluid with the addition of nanoparticles [5].

The nanoparticles with different characteristics have been introduced to base liquids to enhance the overall thermal conductivity. This reveals the influence of various para-meters, including base liquid, temperature, nanoparticle concentration, nanoparticle size, nano-particle shape, nanoparticle material, and the addition of surfactant, on nanofluid thermal conductivity. The thermal conductivity of nanofluids is clearly shown through plotting the thermal conductivities of nanofluids as a function of temperature and/or nanoparticle concentration on the same graphs as their respective base liquids. It has been observed that nanoparticle size and shape significantly influence the thermal conductivity of nanofluids whereas, surprisingly, nanoparticle material does not have a significant impact. It has been observed that temperature and nanoparticle volume concentration also significantly influence the thermal conductivity of nanofluids [6].

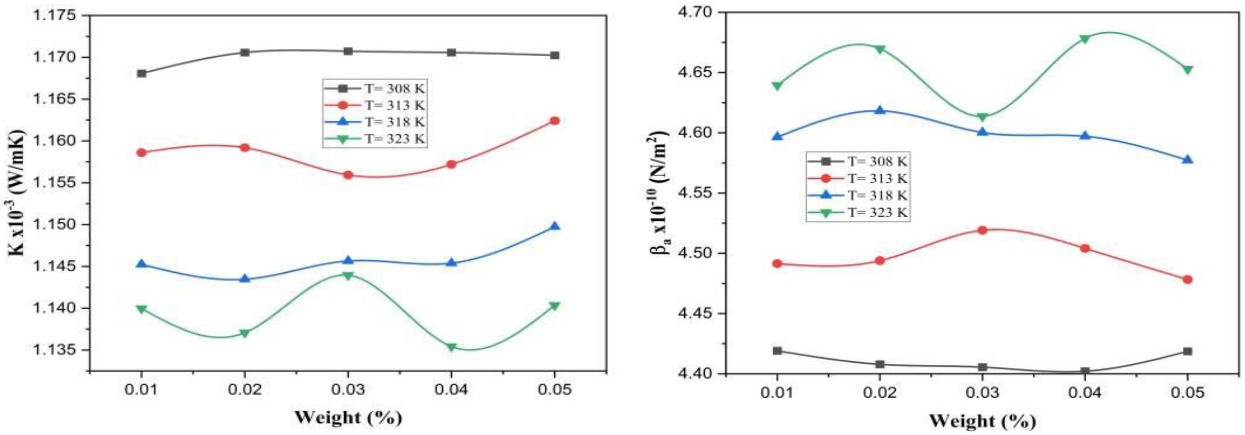

Fig. 8: Thermodynamic parameters of $FeCo_2O_4$ Nanofluid

4.3. Antibacterial activity

Antibiotic resistance development is increasingly a serious trend in pathogenic bacteria [7]. Hence, advancement of antibacterial compounds has become a vital goal in research. Based on chemical properties of the examined sample, antibacterial compounds are of two categories, such as organic antibacterial compounds and inorganic antibacterial compounds. Unlike organic antimicrobial compounds, inorganic antibacterial compounds offer environment-friendly safe and long duration action, although organic antibacterial compounds provide superior, short-term, and rapid performance [8]. Presently, nanomaterial science techniques have gained much attention by using inorganic nanoparticles, especially metal oxides nanoparticles with antibacterial properties: for example, Ag_2O, ZnO, SiO_2, CuO, MgO, and CaO [9, 10]. Among them, iron doped cobalt oxide shows highest activity against both Gram-negative (*Pseudomonas aeruginosa, Escherichia coli*, etc.) as well as Gram-positive species (*Bacillus subtilis, Candida albicans*, etc.) [11, 12].

Metal oxide NPs generally diffuse into the bacterial cell by adsorption process and release metal ions that damage DNA leading to cell death. After ingesting metal oxide NPs, surface area of bacterial cells increased significantly and interacted with intracellular enzymes [13].

An antibacterial study of iron doped cobalt oxide nanoparticle was carried out by using disc diffusion method, nanoparticles have small size with high surface area and hence it possesses strong antibacterial activities. The synthesized nanoparticles showed remarkable antibacterial activities against *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *K. Pneumoniae* with the inhibition of 28, 19 and 18 mm respectively even at a minimum dose. $FeCo_2O_4$ shows a high antibacterial activity compared to Chloramphenicol. Fig. 9, shows the results of antibacterial studies of $FeCo_2O_4$ nanoparticles using disc diffusion method.

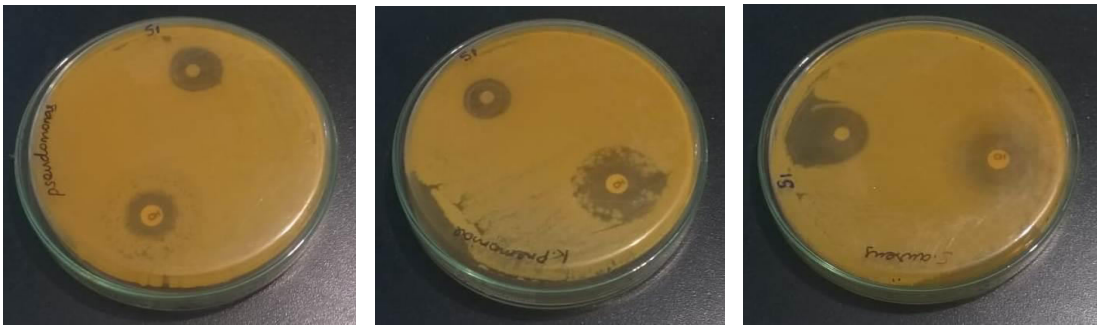

Fig. 9: Antibacterial activity of $FeCo_2O_4$ Nanofluid

4.4. Cyclic voltametry

Cyclic voltammetry is considered to be an ideal tool for indicating the capacitive behavior of any material. Modified iron doped cobalt oxide-glassy carbon electrode was employed as the working electrode. A Calamol electrode acted as the reference electrode, a platinum wire as the counter electrode and 0.1 M KCl was used as an electrolyte.

To investigate the electrochemical performance of modified iron doped cobalt oxide-glassy carbon electrode, cyclic voltammetry (CV) was employed over a potential range from +2 to -2 volt. The CV loops result due to the reaction between $FeCo_2O_4$ and electrolyte, which is mainly governed by the intercalation and deintercalation of K+ from electrolyte into $FeCo_2O_4$. The shape of the CV loop of the sample indicates that good charge propagation takes place at the electrode surface [14].

From cyclic voltammetric studies the metal oxide nanoparticles exhibited good electrocatalytic activity and the rate of reaction is determined by the diffusion of analyte to the surface of electrode are diffusion controlled. From this investigation the metal oxide can be used as a potential, electrode material for further electronic applications.

Fig. 10, shows the cyclic voltammograms for $FeCo_2O_4$ electrode with potential window of 2V to - 2V at various scan rates 10, 20, 30, 50, 60, 80,100 and 150 mV/sec.

From the CV curves, it is observed that the reduction and oxidation peaks are visible. This indicates that the electrochemical capacitance of the $FeCo_2O_4$ electrode mainly results from pseudo capacitance Fig. 13, Shows the graph of specific capacitance versus scan rate $FeCo_2O_4$ electrode exhibited a common trend of decreasing specific capacitance values against an increasing scan rate. It is well known that for very low scan rates, the specific capacitance values are higher because the ions have a much longer time to penetrate and reside in the electrode pores and form electric double layers, which are needed to generate higher capacitance [15]. The specific capacitance of 873 Fg^{-1} obtained at minimum scan rate of 10mVs^{-1}.

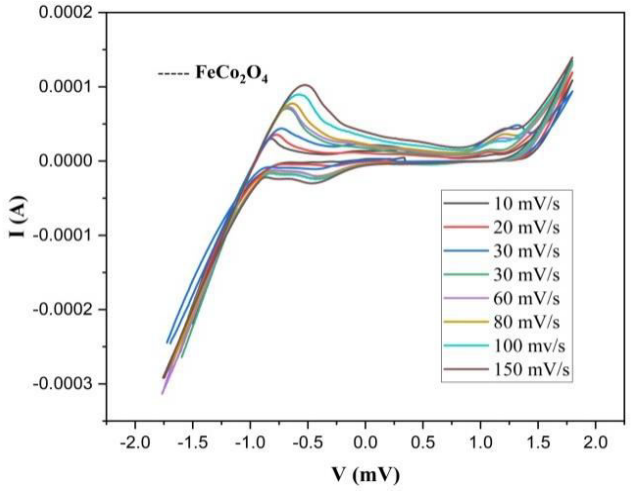

Fig. 10: Cyclic Voltammograms of $FeCo_2O_4$ Nanoparticles

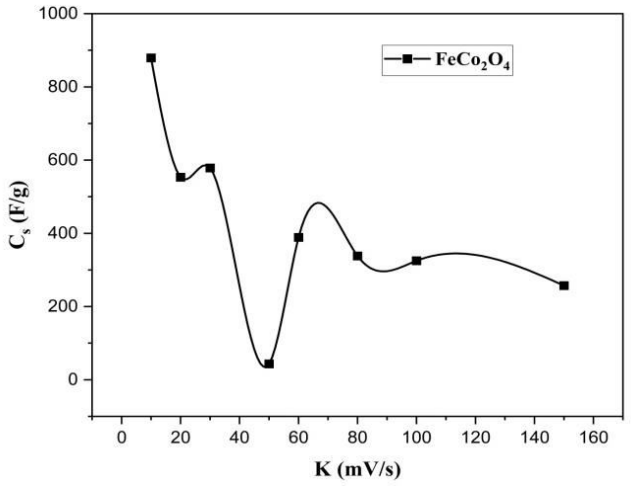

Fig. 11: Scan rate versus Specific capacitance

5. CONCLUSION

In this research work, green synthesis method using *Eclipta alba* leaves extract was used for the doping of Fe into cobalt oxide nanostructures. The doped material was characterized by XRD, UV, FTIR, SEM, EDX and DLS techniques. The effect of doping on the structural and morphological properties was investigated. Further, the effect of doped material on the catalytic performance of Methylene Blue and Congo red dye was examined. The doped material showed excellent degrading efficacy. The disc diffusion techniques were used for the measurement of antibacterial activity against *K. Pneumoniae, S. Aureus* and *Pseudomonas* and it was found that $FeCo_2O_4$ nanoparticles shows a very high antibacterial activity. From the investigation of CV the synthesized metal oxide can be used as a potential, electrode material for electronic applications with the maximum specific capacitance of 873 Fg^{-1}. Thermodynamic properties of the bio synthesized nanomaterials were examined using ultrasonic techniques and the interaction between the particle-fluid was successfully explained.

6. ACKNOWLEDGMENTS

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Conflict of interest

None declared

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