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Research Papers

ANALYTICAL INVESTIGATION OF AMARANTHUS CRUENTUS SPP EXTRACT AS A POTENTIAL NUTRACEUTICAL FOR ANTIOXIDANT AND ANTIDIABETIC APPLICATIONS

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ABSTRACT

As global interest in traditional medicines continues to rise, the increasing demand for nutraceuticals necessitates rigorous analytical validation to ensure safety, efficacy, and standardization for pharmaceutical and functional food applications. Amaranthus cruentus has recently attracted attention for its potential health benefits, particularly antioxidant and antidiabetic properties, which were systematically evaluated through an analytical approach.

High-performance thin-layer chromatography (HPTLC)-DPPH scavenging assay and ferric reducing antioxidant power (FRAP) assay were employed to assess its radical scavenging capacity, while total phenolic content quantification provided insight into its bioactive composition. Its antidiabetic potential was examined using an in-vitro glucose uptake assay with a yeast suspension model, simulating possible antihyperglycemic effects.

The findings revealed significant antioxidant activity and glucose-lowering potential, reinforcing its applicability as a nutraceutical ingredient. Given its ease of cultivation, adaptability to diverse climates, and cost-effective large-scale production, A. cruentus presents a sustainable dietary alternative. This study verifies its bioactive potential and contributes to bridging the gap between plant-derived functional foods and pharmaceutical applications.

Keywords: Bioactives, HPTLC, Antioxidant, Antidiabetic, Nutraceutical, Sustainability.

INTRODUCTION

A substantial portion of the population in developing nations, including India, consumes traditional food plants as a dietary staple. Recent phytochemical investigations have revealed that many of these plants serve as rich sources of nutraceuticals. With increasing consumer awareness of nutrition and health, both herbal medicine and nutraceuticals have gained popularity.

Ethnobotanical studies indicate that approximately thirty species within the Caryophyllales order are consumed as food plants and widely utilized in traditional medicine for treating conditions such as fever, hepatic disorders, cancer, nervous system ailments, and cardiovascular diseases [1]. *A. cruentus*, commonly referred to as a pseudo-millet, exhibits nutritional properties comparable to traditional millets. Notably, its consumption is recommended for celiac disease patients due to its gluten-free nature, making it suitable for diabetic individuals as well [2]. Hence, *Amaranthus cruentus L.* species of the Amaranthaceae family (Caryophyllales) are the subject of this study.

A healthy biological system possesses natural antioxidant mechanisms [3], including enzymatic antioxidants (glutathione peroxidase, catalase, superoxide dismutase) and non-enzymatic antioxidants (glutathione, tocopherol, and ascorbic acid) [4]. Plants with therapeutic applications often contain bioactive compounds such as alkaloids, glycosides, tannins, flavonoids, saponins, phenolics, and vitamins, which contribute to their biological activity. Oxidative stress, caused by reactive oxygen species (ROS), has been implicated in diseases such as cancer, cardiovascular disorders, osteoporosis, and neurodegenerative diseases. Natural antioxidants have gained attention for their ability to neutralize free radicals, chelate catalytic metals, and scavenge reactive oxygen species, thereby mitigating oxidative damage and disease progression [5]. Most antioxidant phytochemicals, like resveratrol, anthocyanins, and curcumin, reduce inflammation by inhibiting prostaglandins, nuclear factor-κB, and enzymes while boosting cytokine production [6]. Likewise, As synthetic antidiabetic drugs can lead to insulin dependency, plant-based antidiabetic drugs do not serve as a substitute for insulin; rather, they naturally aid in stimulating its production.

Numerous reviews have highlighted the antihyperglycemic and antidiabetic properties of a diverse range of plant species [7]. Previous studies highlight the nutritional richness of *A.*

cruentus, supporting its inclusion in daily diets to address nutritional deficiencies and combat lifestyle diseases. However, the specific bioactive compounds responsible for its antioxidant and antidiabetic properties remain underexplored. To bridge this gap, the present study aims to evaluate the antioxidant and antidiabetic potential

of *A. cruentus* using a series of validated analytical assays, provide scientific evidence supporting its role as a functional food ingredient and offer insights into the bioactive compounds underlying its therapeutic properties.

MATERIALS AND METHODS

Plant Collection and Processing
Fresh red amaranth (commonly known as lal math) was sourced from the local market, Matunga, India. Leaves and stems were separated, air-dried for 24 h, then oven dried at 45°C for 2-3 days before being pulverised into fine powder.

Extraction Techniques
The pulverised powder of leaves was then subjected to Soxhlet extraction to obtain the extract of phytoconstituents. 20 gm of sample powder was wrapped in a thimble of muslin cloth and soaked in 200 mL of methanol for 3-4 days. Extract was then subjected to centrifugation at 3000 rpm for 10 minutes. The centrifuged samples were filtered into another set of tubes using Whatman Filter Paper no. 41. This collected, filtered extract was then subjected to further analysis pertaining to the research work.

Antioxidant Assays
The electron-donating capacity is a key characteristic of antioxidants. Ferric Reducing Antioxidant Power (FRAP) assay evaluates the reducing power of antioxidants by measuring their electron donating ability. While the HPTLC-DPPH assay assesses their potential to scavenge free radicals. Together, these complementary assays provide a comprehensive analysis of a plant's overall antioxidant potential.

The reducing power was assessed using a reaction mixture consisting of 500 µL of Soxhlet extract of *Amaranthus cruentus* with ascorbic acid as the standard, 2 mL of 0.2 M sodium phosphate buffer (pH 6.6), and 2.5 mL of 1% (w/v) potassium ferricyanide [$K_3Fe(CN)_6$]. The mixture was incubated at 50°C for 20 minutes, followed by the addition of 2.5 mL of 10% (w/v) trichloroacetic acid. Subsequently, 2.5 mL of distilled water was added, and the solution was mixed with 0.5 mL of 0.1% (w/v) freshly prepared ferric chloride ($FeCl_3$). The absorbance was measured at 530 nm against a blank using a colorimeter.

Along with that, The DPPH radical scavenging activity was assessed following the method described by MK Islam, 2020 et al. [8]. To optimize the assay, the mobile phase was standardized for improved resolution. Initially, a mobile phase of Toluene: Ethyl Acetate: Formic Acid (6:5:1, v/v) failed to resolve the antioxidant activity bands (components) on HPTLC plate. The scavenging of free radicals (decolorization) was only visible near the application position. Therefore, an optimized mobile phase of Ethyl Acetate: Methanol: Formic Acid: Water (20:2.5:0.5:2, v/v) was selected. Two TLC plates were developed using the optimized mobile phase and manually spotted with gallic acid (two bands) and ascorbic acid (three bands) using a TLC capillary. After development, both plates were derivatized by spraying with 0.4% DPPH. One plate was incubated in the dark at room temperature for 20–30 minutes, while the other was heated in an oven at 115°C for 10 minutes. The plate incubated in the dark provided better results; in this manner, the time and temperature for DPPH derivatization were optimized. The optimized method was implemented on the primary working plate. Since the initial sample was too concentrated, it was diluted 1:2 with methanol to improve resolution. A standard stock solution of gallic acid (200 ppm) was prepared in methanol. The derivatization reagent was prepared by dissolving 0.2 g of DPPH chemical from Sisco Research Laboratories Pvt. Ltd (assay min. 95%), in 50 mL of absolute ethanol (99.9% pure). The derivatization of the plate was carried out by spray-plate method.

HPTLC METHOD PARAMETERS

Parameters	Description
Stationary Phase	Merck Silica gel 60 F_{254} TLC pre-coated plates
Plate size	20.00 cm x 10.00 cm
Mode of separation	Normal phase
Mobile phase	Ethyl acetate: Methanol: Formic acid: Water in the ratio of 20: 2.5: 0.5: 2 v/v
Development chamber	Camag twin trough chamber
Chamber saturation	20 min
Sample applicator	Camag Linomat 5 TLC Applicator
Syringe	Camag Linomat 695.0014, 100.0 µL
Application volume (sample)	1:2 diluted plant extract, with application volumes of 2 µL (for bracketing the sample bands) and only 4 µL in triplicates.

Application volume (standard)	Standard gallic acid (200 ppm) was applied in volumes of 1 µL, 2 µL, 3 µL, 4 µL, 5 µL, 6 µL, 7 µL, and 8 µL.
Band length	7.0 mm
Band space	8.0 mm
Rate of sample application	120nL/sec
Development distance	85.0 mm
Derivatization	Non-destructive derivatization under UV 254 nm and 366 nm as well as Destructive Derivatization using DPPH.
Densitometric scanner	Camag TLC scanner 181207 equipped with win CATS Planar Chromatography manager software version 1.4.7
Lamp and wavelength	D2, Hg and W for 254 nm, 366 nm and 520 nm respectively.

Antidiabetic Assay

In-vitro yeast glucose uptake assay is a feasible assay to perform antidiabetic studies on plant samples. Yeast cells are simple, inexpensive and are easily available, they can be genetically modified to mimic specific aspects of human glucose metabolism. In-vitro studies avoid ethical concerns associated with animal testing. Overall, this assay is an ethical and efficient tool for studying this activity.

MATERIALS AND METHODS

Yeast Suspension Preparation

One gram (1 g) of commercially available baker's yeast was dissolved in 100 mL of 0.85% saline and incubated in a shaker-incubator for 24 hours at room temperature. The suspension was centrifuged (3500 rpm, 10 min, R-8M Plus centrifuge), and the supernatant was discarded. Cells were washed by resuspending in saline, repeating the centrifugation twice or thrice until a clear supernatant was obtained. The final pellet was resuspended in saline, and 1 mL of this suspension was diluted to 100 mL for further analysis.

Preparation of Standard Drug Solution

A standard solution of metronidazole drug (10 mg/mL) was prepared in saline (pH 6.8) to contain 4 mg of API.

DNSA Reagent Preparation

Solution A: 30 g of sodium potassium tartrate was dissolved in 50 mL of distilled water.

Solution B: 1 g of 3,5-dinitrosalicylic acid was dissolved in 20 mL of 2M NaOH.

Both solutions were mixed, and the final volume was adjusted to 100 mL with distilled water.

Preparation of Standard Dextrose and Glucose Series

Standard dextrose: 200 mg dissolved in 100 mL of distilled water.

Glucose standard series: 200–2000 ppm prepared in increments of 200 ppm.

ADDITION TABLE

Group	Yeast Suspension (mL)	Saline (mL)	Standard Drug (mL)	Standard Glucose (mL)	Plant Extract (mL)
Yeast Blank	0.2	1.5	—	—	—
Drug Control	0.2	0.5	0.5	1	—
Negative Control	0.2	0.5	—	1	—
Sample Blank	—	1.2	—	—	0.5
Sample	0.2	—	—	1	0.5

After the addition the tubes were incubated at room temperature for the period of 5 minutes, 10 minutes and 15 minutes At the end of incubation, 0.5mL of supernatant from each of the tubes was removed and was added to 0.5mL of DNSA reagent. The tubes were then kept in a boiling water bath for 10 minutes, cooled. The volume was made up to 10mL with distilled water and colorimetric absorbance was measured at 530 nm.

RESULTS

Results of FRAP Assay (200 ppm - 2000 ppm standard) & Sample:

Concentration of Ascorbic acid standard in ppm	Absorbance at 530 nm	Concentration of Ascorbic acid standard in ppm	Absorbance at 530 nm
200	0.44	1400	0.88
400	0.49	1600	0.92
600	**0.58**	1800	0.96
800	0.66	2000	1.00
1000	0.75	**Sample**	**0.61**
1200	0.83	-	-
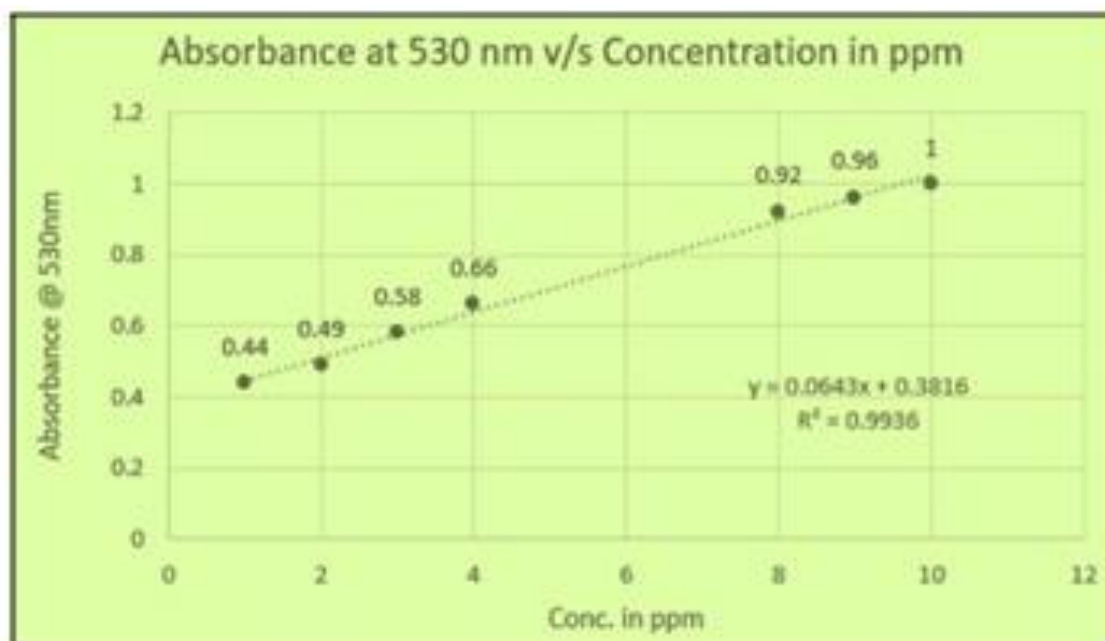
Graph 1: Calibration Curve of Absorbance at 530 nm vs. Concentration

The concentration of the unknown sample was determined using a single-point calibration method, based on the proportional relationship between absorbance and concentration. A 600 ppm standard solution exhibited an absorbance of 0.58, while the unknown sample recorded an absorbance of 0.61. The concentration of the unknown sample (X) was calculated using the equation:

$$x = 600 \text{ ppm} \times 0.61 / 0.58 = 631 \text{ ppm}$$

The calculated concentration (631 ppm) suggests that the Soxhlet extract of *Amaranthus cruentus* possesses antioxidant activity comparable to or greater than that of 600 ppm of standard ascorbic acid.

RESULT OF DPPH RADICAL SCAVENGING ASSAY BY HIGH PERFORMANCE THIN LAYER CHROMATOGRAPHY

The HPTLC plate was initially observed under 254 nm and 366 nm, revealing dark bluish bands and bright-red fluorescent bands, respectively. These bands are typically associated with polyphenols and flavonoids, which are bioactive compounds known for their antioxidant activity.

Decolourization at several bands indicated the presence of possible antioxidant compounds in the *Amaranthus cruentus* extract. These compounds reacted with the DPPH radical, reducing it and leading to a loss of colour.

Gallic acid, a well-known antioxidant, was used as a reference compound. When applied in increasing volumes, it exhibited a proportional increase in decolourization, confirming its antioxidant activity. The observation that gallic acid and the plant extract showed similar decolourization patterns reinforces the antioxidant potential of *A. cruentus*.

These results provide strong evidence that *A. cruentus* exhibits antioxidant properties. The use of gallic acid as a standard further validates the findings and highlights the potential health benefits of the plant extract.
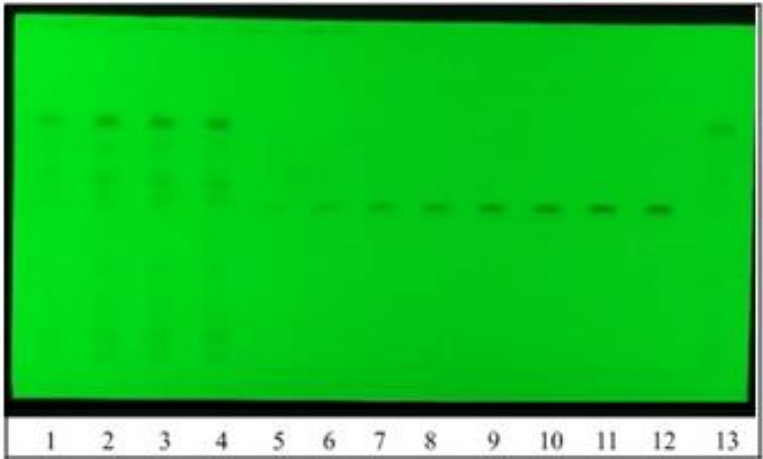
Figure 1: Plate image under 254 nm UV light.
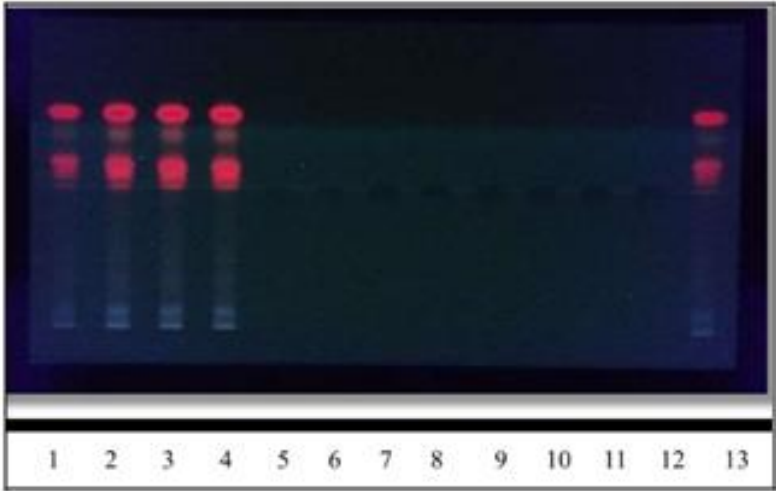
Figure 2: Plate image under 366 fluorescence.
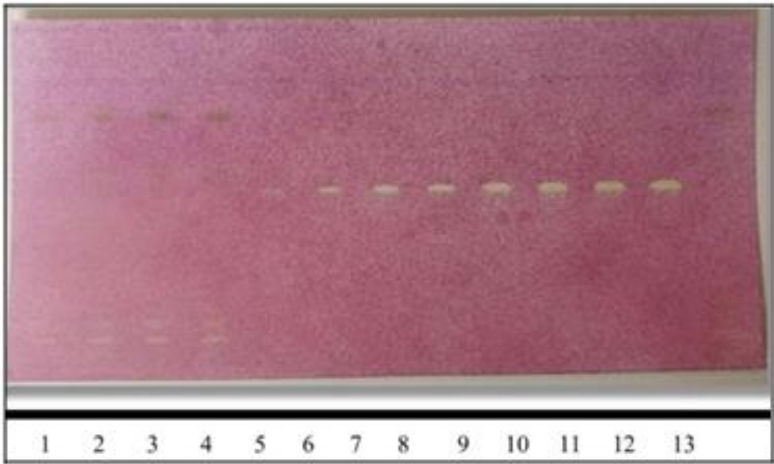
Figure 3: Plate image after derivatization with 0.4 % DPPH

SAMPLE APPLICATION POSITION WITH VOLUMES

Track no.	Volume and Sample	Track no.	Volume and Sample
1	2 μL gallic acid	8	4 μL gallic acid
2	4 μL gallic acid	9	5 μL gallic acid
3	4 μL gallic acid	10	6 μL gallic acid
4	4 μL gallic acid	11	7 μL gallic acid
5	1 μL gallic acid	12	8 μL gallic acid
6	2 μL gallic acid	13	2 μL gallic acid
7	3 μL gallic acid	-	-

RESULT OF IN-VITRO YEAST GLUCOSE UPTAKE ASSAY (200 PPM -2000 PPM):

Concentration of Ascorbic acid standard in ppm	Absorbance at 530 nm	Concentration of Ascorbic acid standard in ppm	Absorbance at 530 nm
200	0.15	1200	0.68
400	0.26	1400	0.77
600	0.38	1600	0.86
800	0.53	1800	0.92
1000	0.61	2000	0.98

Samples	5 min	10 min	15 min
Yeast Blank	0.07	0.06	0.06
Drug Control	0.26	0.24	0.20
Sample	0.32	0.21	0.19
Sample blank	0.18	0.15	0.17
Negative Control	0.80	0.79	0.87
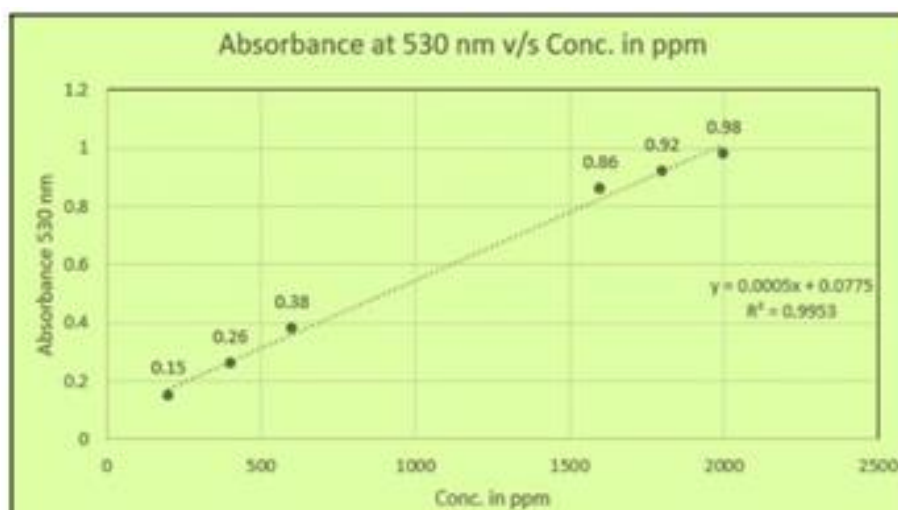
Graph 2: Calibration Curve of Absorbance at 530 nm vs. Concentration

A glucose standard series was used to establish a calibration curve for quantifying reducing sugars. The negative control sample served as a baseline, indicating maximum glucose uptake by yeast in the absence of an antidiabetic agent. The drug control sample, containing a known antidiabetic drug, exhibited a lower absorbance similar to the 400 ppm glucose standard, confirming its inhibitory effect on glucose uptake.

Initially (5 minutes), the extract showed higher absorbance than the drug control, suggesting a lower inhibitory effect. However, after 15 minutes of incubation, the extract's absorbance dropped below that of the drug control, indicating comparable antidiabetic potential. The absorbance was also close to the 200 ppm glucose standard, further supporting its inhibitory effect on reducing sugars. A more concentrated extract may enhance this activity.

The sample blank showed an absorbance similar to the sample extract, suggesting possible intrinsic reducing properties of the plant extract. The yeast blank showed negligible absorbance, confirming no significant interference from the medium.

These results provide strong evidence that *Amaranthus cruentus* extract may exhibit antidiabetic activity, effectively inhibiting glucose uptake by yeast.

CONCLUSION

Amaranthus cruentus is a widely recognized traditional herb with a rich history in folk medicine. Its versatility in both culinary and medicinal applications highlights its potential for further research and utilization.

The FRAP assay provided a reliable index of antioxidant activity, demonstrating that the Soxhlet extract exhibits a strong antioxidant potential (631 ppm), comparable to or exceeding 600 ppm of standard ascorbic acid.

This assay, based on the reduction of the ferric-tripyridyl triazine (Fe^{3+}-TPTZ) complex to its ferrous form, confirms the presence of bioactive antioxidants in the extract, as indicated by the observed color change from blue to bluish-green. Additionally, HPTLC analysis facilitated the development of a chromatographic fingerprint and showcasing radical scavenging activity, further validating the presence of antioxidant compounds.

In evaluating the antidiabetic potential of *A. cruentus*, the yeast cell model provided affirmative results, indicating its inhibitory effect on glucose uptake. These findings support the hypothesis that *A. cruentus* possesses bioactive compounds with potential therapeutic benefits in managing diabetes.

To fully establish its pharmacological relevance, In vivo studies on animal models, investigation of its molecular mechanisms of action, and isolation of active compounds are necessary. Future research should focus on extensive pharmacological and chemical characterization to elucidate the full potential of *A. cruentus* in mitigating diabetes and oxidative stress-related complications.

CONFLICT OF INTEREST

The authors hereby declare that they have no conflict of interest.

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CONVENIENT SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF BIMETALLIC SILVER NANOCOMPOSITES EMPLOYING POLYVINYL CHLORIDE

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ABSTRACT

Metal based nanocomposites have been in demand for the past few years due to their promising chemical and physical properties. In this present paper, we are reporting a very convenient and simple synthesis of bimetallic polymer nanocomposites. The polymer used is polyvinyl chloride and the metals used for this study include silver along with one of the metal from copper, cobalt, nickel, iron, manganese, cadmium. Silver is well-known for its broad-spectrum antimicrobial properties making it effective against some bacteria, fungi and some viruses. The combination of bimetals along with polyvinyl chloride results in enhanced characteristics, including antimicrobial properties, electrical conductivity and durability. The synthesized nanocomposites have been characterized by UV-Visible, FTIR, XRD, FESEM techniques to determine its morphology, composition and structure. The antimicrobial activity of these nanocomposites have been determined by Sterile Muller Hinton Agar.

Keywords: nanocomposites, polyvinyl chloride, antimicrobial, Sterile Muller Hinton Agar

INTRODUCTION

The field of nanotechnology has become apparent into great area of interest within the present scenario of research in material science. It is also a fast growing innovative technology for manipulating and creating the applications of nanomaterials. Being at the transition between bulk materials and atomic or molecular structures, these materials exhibit certain physical, chemical and biological properties that differ from their larger counterparts. Metal-based nanocomposites are of great interest due to their distinctive mechanical performances such as high tensile strength, good abrasion resistance, high thermal stability as well as electrical conductivity. Since nanocomposites are the materials that incorporate nanoparticles or other nanostructures into a larger matrix to enhance performance. Their combine properties enhance strength, conductivity and reactivity. Nanocomposites are a new class of materials in which the dimension of the dispersed particles occurred at the nanometre scale. Thus in polymer-metal nanocomposites, metal particles are dispersed in the polymer matrix at the nanometre scale (Rangareddy et al., n.d.). Inorganic metal impregnated nanocomposites have been known to have strong antimicrobial activity towards several bacteria, viruses, and eukaryotic microorganisms. Metals with inherent antimicrobial properties such as silver, copper, zinc at nanoscale constitute a special class of antimicrobials which have broad spectrum antimicrobial nature and pose minimum toxicity to humans. The new hybrid antimicrobial biomaterials would offer a potent antibacterial solution in the healthcare sector such as wound healing applications, tissue scaffolds, medical implants, surgical devices and instruments (Mamatha et al., 2021). Particularly optical properties arising from the particle surface plasma resonance (SPR) have been studied extensively. SPRs are observed for the so-called free electron metals and, in particular, for noble metal (Au, Ag, and Cu) NPs due to the interaction of surface electrons with the electromagnetic wave and the contribution from the inter-band transition of the d-shell electrons. Experimental and theoretical investigations of the extinction coefficient for small spherical clusters in a non-absorbing medium were carried out using the Mie theory. Based on this theory, the absorption peak is dependent on the type of metal, the surrounding medium, size and shape of the particles, the metal filling factor, as well as the inter-particle distance. Thus, considerable effort has been devoted to tuning the optical properties of nanocomposites by varying the size, shape, metal filling factor, and refractive index of the surrounding host. However, the effects are very small in the case of monometallic NPs such as Ag, Au, and Cu. Especially, Ag nanoparticles exhibit only a weak shift in the position of the plasma band as a result of the change in the size of the clusters due to the fact that the resonance frequency is located below the inter-band threshold (Beyene et al., 2012). In this research study, we have used silver as one of the metals along with polyvinyl chloride as the polymer. The precursor used for Ag is $AgNO_3$.

MATERIALS AND METHODS

Materials for fabrication of BNPs:

Silver nitrate ($AgNO_3$), Manganese (II) acetate ($Mn(CH_3COO)_2.4H_2O$), Copper (II) acetate ($Cu(CH_3COO)_2.H_2O$), Nickel (II) acetate ($Ni(CH_3COO)_2.4H_2O$), Cadmium (II) acetate ($Cd(CH_3COO)_2.2H_2O$),

Cobalt (II) nitrate $Co(NO_3)_2.6H_2O$, Ferrous ammonium sulphate $(NH_4)_2Fe(SO_4)_2.6H2O$, polyvinyl chloride (PVC), cyclohexanone and alcohol. All the chemicals used were of analytical grade with 99% purity and used as it is without further purification. All solutions were freshly prepared and all glass- wares used in the process, were washed with double distilled water and acetone and dried before use.

Materials for antimicrobial studies:
Microorganism culture (ATCC) cultures, test compounds (Probable antimicrobial agents), resazurin solution (0.01% w/v in sterile water), sterile 96-well microplates or sterile tubes, sterile pipettes and tips, sterile culture media (MS media), incubator.

Preparation of polymer matrix solution
The required polymer matrix was prepared by dissolving 1 gm of PVC in approximately 50 ml of cyclohexanone. The solution was slightly heated in order to ensure complete solubility of the polymer.

Preparation of Bimetallic Nanoparticles (BNP)
Bimetallic nanoparticles (BNP's) were prepared by using salts of six different transition metals individually, along with silver nitrate. The metals used along with silver were in +2 oxidation state each. The synthesis of $Ag-M^{2+}$ nanoparticles were carried out in approximately 10 ml of alcohol by adding 0.5 gm of $AgNO_3$. To this mixture, 0.5 gm of metal (II) acetate was added with constant stirring. This mixture was heated in a water bath for approximately 10 minutes at about 70-80℃ to ensure complete solubility of bimetallic salts in alcohol.

Preparation of Bimetallic Polymer Nanocomposites
To the solution of bimetallic nanoparticles (BNP's), the prepared solution of PVC was added dropwise with continuous stirring at room temperature. Within a few seconds, there was formation of solid nanocomposites with specific colour for each metal acetates used. The solid nanocomposites formed were filtered at room temperature and washed thoroughly with the mother liquor as well as alcohol. On complete filtration, the nanocomposite formed was dried in the oven at around 80℃ for 15 minutes and was stored in a labelled, clean and dry vial.

CHARACTERIZATION
The synthesised bimetallic polymer nanocomposites were subjected to various characterization techniques which gave us a clarity to understand its specific properties such as crystal structure, particle size distribution, functional group studies, elemental composition, crystallinity, optical properties and a variety of other basic features of nanoparticles. These techniques were useful to assist our method leading to a verified understanding of nanoscale properties and their interactions in advanced materials.

UV-VISIBLE SPECTRA
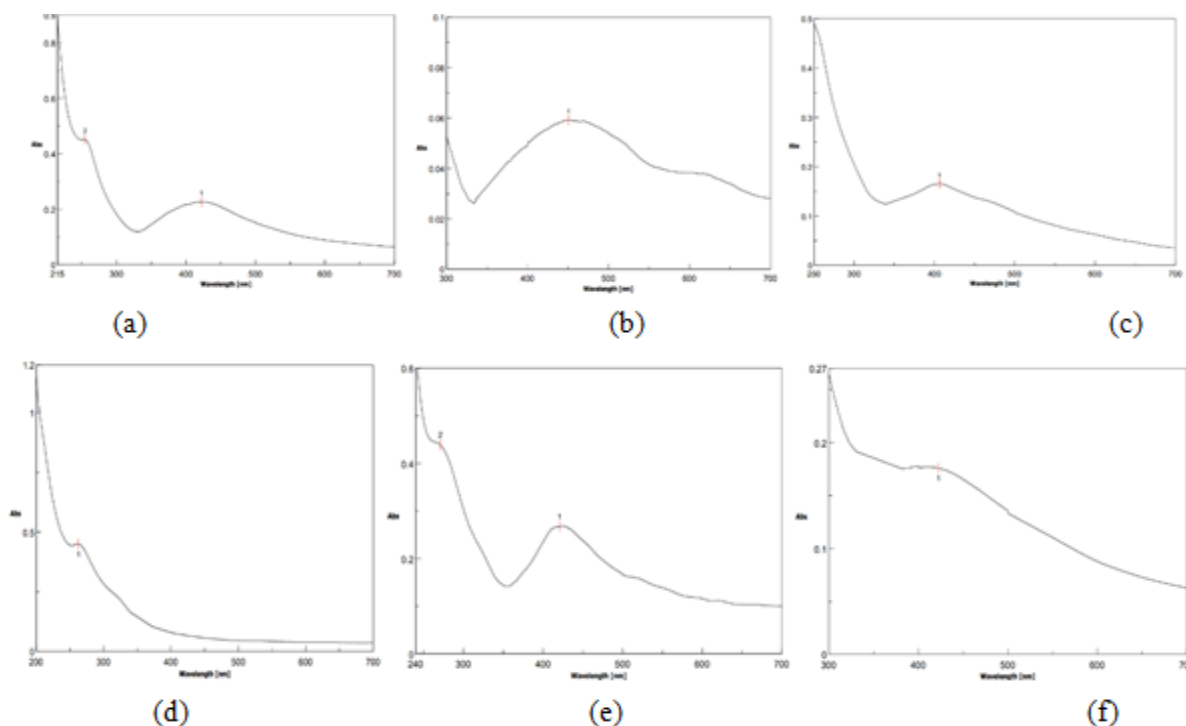
Fig.1. UV-Vis spectra of (a) Ag-Cd-PVC (b) Ag-Co-PVC (c) Ag-Cu-PVC (d) Ag-Fe-PVC (e) Ag-Mn-PVC (f) Ag-Ni-PVC

The property most immediately observed for metal nanoparticle dispersions of certain metals is their colour. Faraday's classical Au sol shows even now the clear ruby-red colour. Ruby glasses, with included Au nanoparticles, are very famous. Indeed, Au, Ag and Cu (Group 1B metal) nanoparticles all have characteristic colours related with their particle size. Thus, for these metals, observation of UV/VIS spectra can be a useful complement to other methods in characterizing metal particle (Toshima & Yonezawa, 1998).

The above graphs are of the UV-Visible spectra of synthesized, coloured bimetallic polymer nanocomposites. Graph **(a)** represents the UV-Visible spectra of off-white coloured Ag-Cd-PVC nanocomposite. Two peaks are observed at 422.2 nm as well as at 254.4 nm, in which, the earlier peak could be due to surface plasmon resonance of Ag-Cd NP's, confirming their presence in the polymer matrix (Beyene et al., 2012), while the later one, could be due to π-π* transitions in PVC. Graph **(b)** represents the spectrum for orangish-pink Ag-Co-PVC nanocomposite, in which a single peak is observed at 450.8 nm, indicating the presence of Ag-Co NP's which exhibit SPR. Graph **(c)** represents the UV-Visible spectra of bluish-green coloured Ag-Cu-PVC nanocomposite. It shows a broad peak at 406.2 nm, arising due to SPR of Ag-Cu NP's (Jacob et al., 2022; Mamatha et al., 2021). Graph **(d)** represents the UV-Visible spectra of brownish coloured Ag-Fe -PVC nanocomposite which shows a peak at 262.8 nm. The absence of a clear Ag SPR peak which lies approximately around 400-500 nm, suggests low Ag content or Ag nanoparticles being heavily influenced by Fe interactions (Padilla-Cruz et al., 2021). Graph **(e)** represents the UV-Visible spectra of black coloured Ag-Mn-PVC nanocomposite which shows two peaks at 420.8 nm as well as at 270.8 nm. The peak at 420.8 nm might be due to SPR of Ag NPs, but appear less intense as well as broader than expected for well-defined Ag-NPs. The second peak at 270.8 nm could be likely due to Mn^{2+} charge transfer along with the polymer, PVC. The broad peak shape, suggests that the presence of Mn might be affecting Ag NP formation, leading to certain shifts in absorbance behaviour. Graph **(f)** represents the UV-Visible spectra of yellowish-green coloured Ag-Ni -PVC nanocomposite which shows a peak at 422.4 nm. Here we can observe that the wavelength has blue-shifted to a shorter wavelength, which could be probably due to incorporation of Ni, influencing Ag NP size, electron density or suppressed SPR intensity. The peak broadening observed here can also be due to Ag-Ni alloy formation.

FT-IR SPECTRA
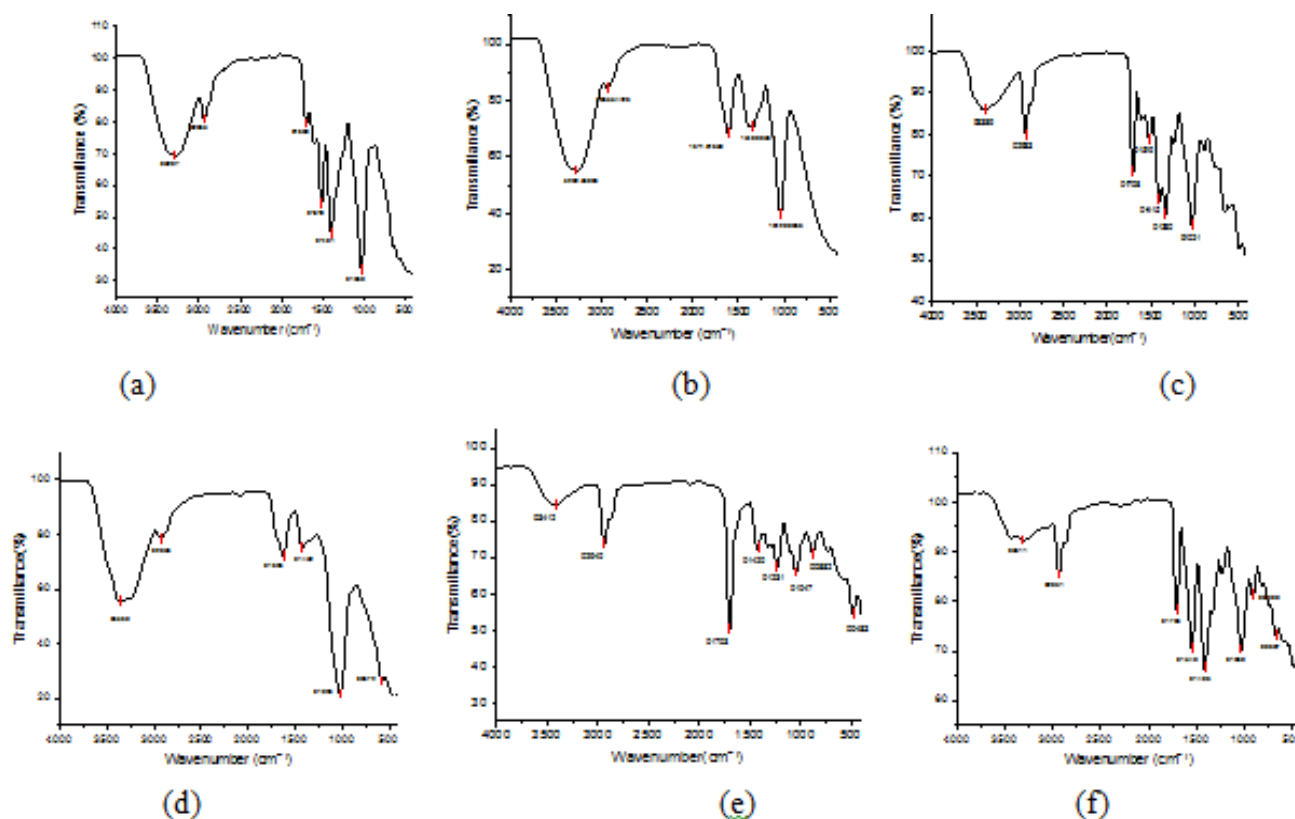
Fig.2. FT-IR spectra of (a) Ag-Cd-PVC (b) Ag-Co-PVC (c) Ag-Cu-PVC (d) Ag-Fe-PVC (e) Ag-Mn-PVC (f) Ag-Ni-PVC

All the above graphs, show some similarity in the range in which the peaks appear. The broader absorption peaks which appear in a range of 3500-3200 cm^{-1}, could be possible due to O-H stretching frequency, arising either due to moisture or hydroxyl groups.

Peaks around 2900cm^{-1} could be C-H stretching frequency from PVC backbone. The next set of peaks around 1600 cm^{-1}, is likely C=C stretching, resulting due to unsaturation from polymer, PVC. The peaks lying in a range of 1500-1400 cm^{-1}, might be due to C-H bending arising from PVC structure. Strong peaks observed around 1100-1000 cm^{-1}, is due to C-Cl stretching frequency, which is a characteristic of PVC. Lower-frequency bands around 600-500 cm^{-1}, could be due to bimetallic nanoparticle or metal-halogen interaction, confirming the presence of bimetallic nanoparticles in the polymer matrix.

XRD SPECTRA
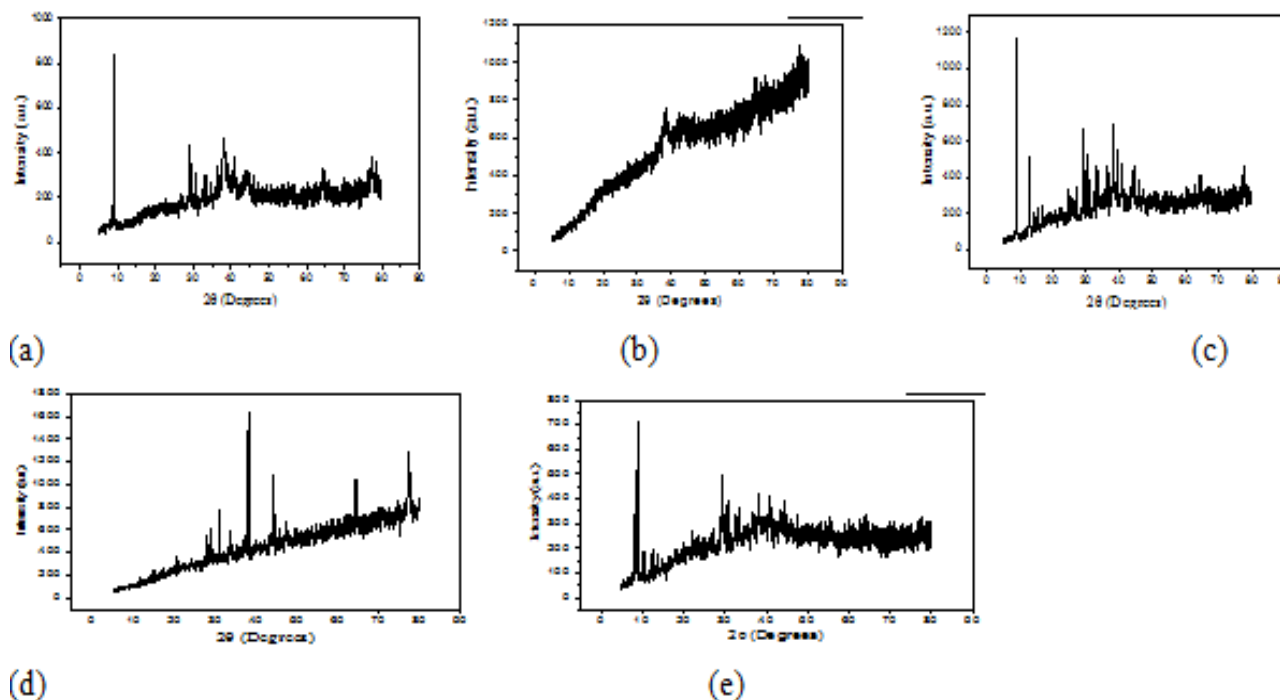
Fig.3. XRD spectra of (a) Ag-Cd-PVC (b) Ag-Co-PVC (c) Ag-Cu-PVC (d) Ag-Fe-PVC (e) Ag-Ni-PVC

From the five XRD graphs of the synthesized bimetallic polymer nanocomposites, graph **(b)** does not show distinct, sharp peaks and instead it shows broad and intense rise, which indicates the presence of an amorphous or semi-crystalline structure rather than a pure crystalline material (Toshima & Yonezawa, 1998).

Also, in the same graph, there is a steady increase from 0° to 80°, indicating that the NPs (Ag-Co) are highly dispersed in PVC matrix. The graphs **(a), (c), (d)** and **(e)**, show similar patterns having sharper peaks at lower angles (0° to 40°), indicating high crystallinity among the nanocomposites (Jang et al., 2020; Mamatha et al., 2021).

FESEM IMAGES
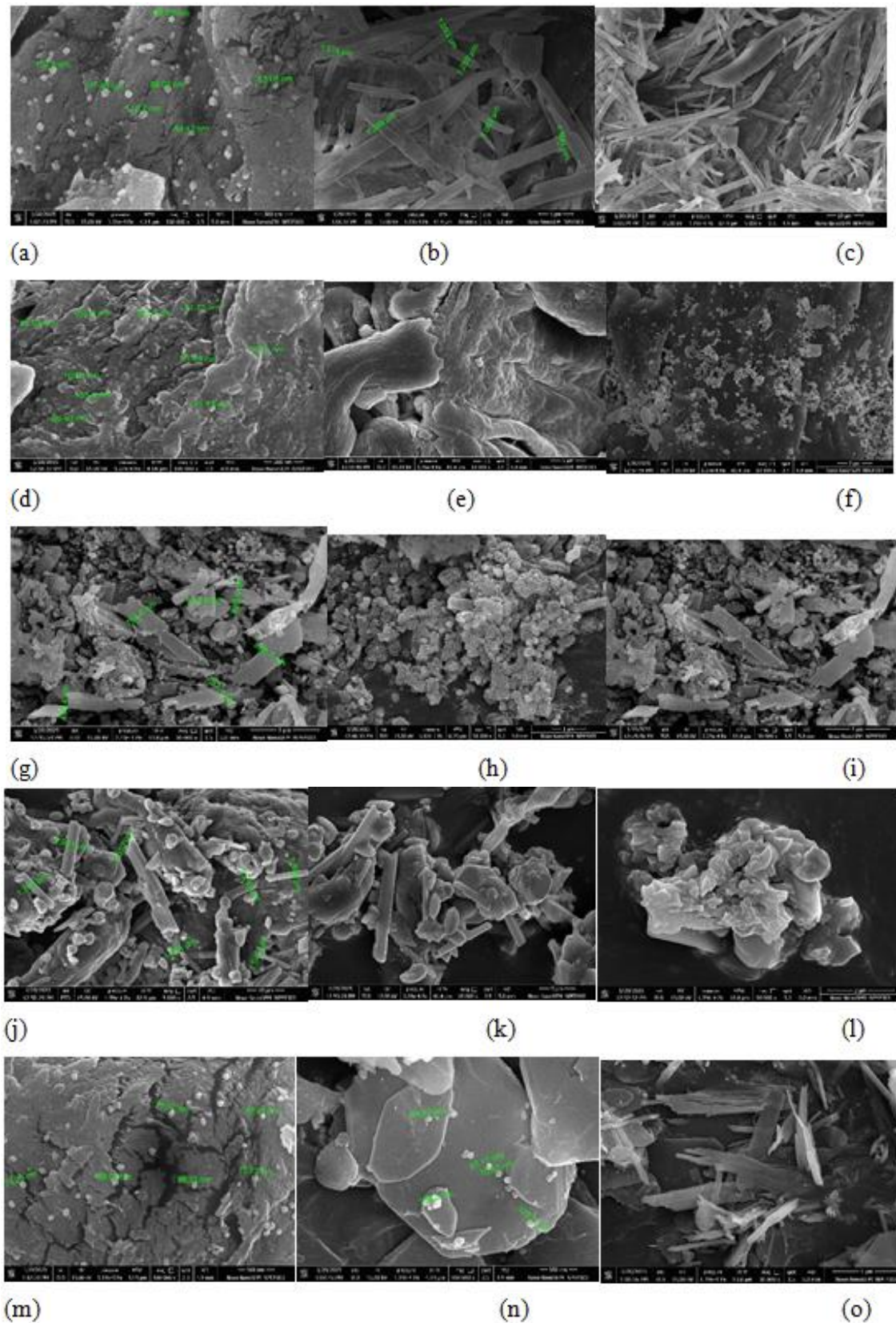
Fig.4. FESEM images of: **(a, b, c)** Ag-Cd-PVC **(d, e, f)** Ag-Co-PVC **(g, h, i)** Ag-Cu-PVC **(j, k, l)** Ag-Fe-PVC **(m, n, o)** Ag-Ni-PVC

The surface topology and elemental composition of bimetallic polymer nanocomposites were analysed by FESEM analysis and is shown in Fig. 4. From the surfaces morphology, it is clear that nanocomposites so formed, have an average size ranging from 83.68 to 118.7 nm for Ag-Cd-PVC NCs, 89.03 to 135 nm for Ag-

Co-PVC, 495.4 to 890.7 nm for Ag-Cu-PVC, 1.042 to 2.921 µm for Ag-Fe-PVC and 67.45 to 89.03 nm for Ag-Ni-PVC (Dlamini et al., 2023), (Oseni & Tessema Mola, 2019), (Pal et al., 2007), (Zhao et al., 2009).

ANTIMICROBIAL STUDIES

Medium: Sterile Muller Hinton Agar was used in this assay.

Use of standardized bacteria: Active cultures of bacterium *Staphylococcus aureus* (**ATCC 25932**) and *Escherichia coli* (**ATCC8739**) were used in this experiment.

Preparation of bacterial culture: Using aseptic techniques an isolated colony of bacteria was transferred into a 250 ml flask containing 100ml Muller-Hinton broth (2.1g of MH Himedia dissolved in 100ml distilled water digested and autoclaved at 15 psi for 20min), which was placed in the incubator overnight at $37°C$. Broth suspension of bacterial cultures of *Staphylococcus aureus and Escherichia coli* were ready after 24hrs of incubation. The optical density of the culture broth was adjusted to 0.5 McFarland Standard and recorded at 500 nm and the range obtained was between 0.5MFU (Cell density 1×10^8 CFU/mL) UV- Spectrophotometer (BioEra -2017). The final number of bacterial cells present on plate was adjusted to 1×10^5 CFU/mL.

Preparation of test compound and Dilutions: All the test compounds were crude.

Preparation of Microtiter Plates or Tubes:
- Dispense 100 µL of the microbial suspension into each well of the microtiter plate or sterile tubes.
- Add 100 µL of the test compound in the first well and serially dilute it to the last well.
- Include Growth and sterility control.

Inoculation of test organism: Add 100 µL of test organism as 0.5 MF Standard in all wells.

Incubation:
- Incubate the microtiter plate or tubes at the appropriate temperature for a specified duration of 18-24hrs, allowing the microbial growth and interaction with the test compounds.

Addition of Resazurin:
- After the desired incubation period, add 10 µL of resazurin solution to each well or tube.

Visual Observation:
- Incubate the microtiter plate or tubes again under suitable conditions for a defined period (usually 2-4 hours).
- Check for a color change in each well or tube. Reduction of resazurin by metabolically active microorganisms will result in a color change from blue to pink/purple.

   (a) **Escherichia coli (Gram Negative)**
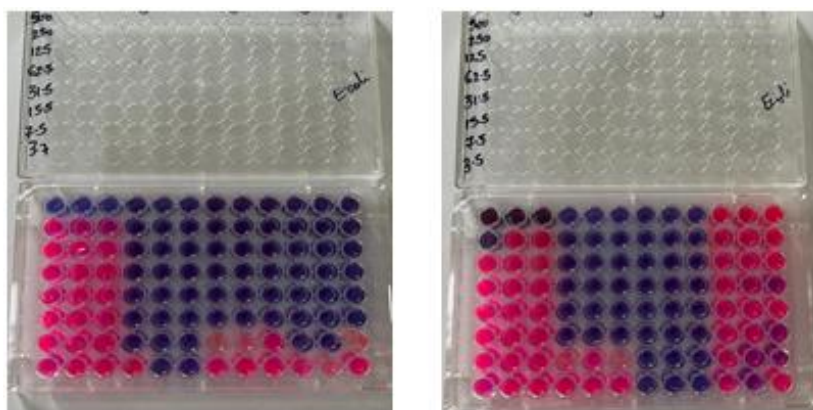
(b) Staphylococcus aureus (Gram Positive)
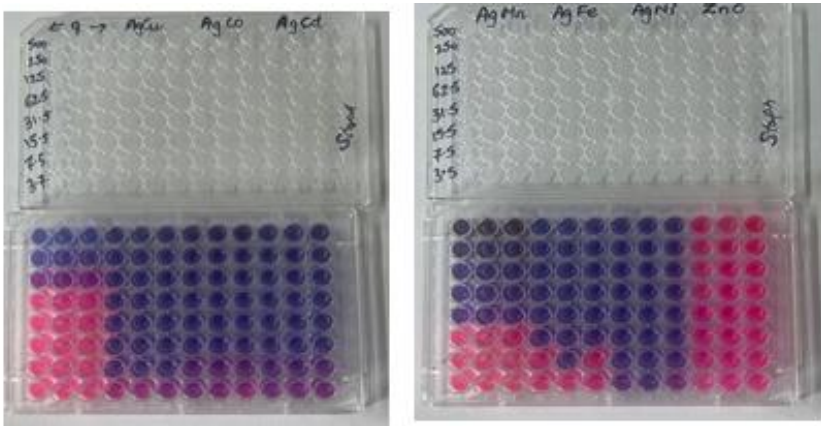
Fig.5. Images of antimicrobial studies against (a) Escherichia coli (b) Staphylococcus aureus

Table: 1. Antimicrobial activity against **Escherichia coli**

Concentration	Ag-Cd-PVC	Ag-Co-VC	Ag-Cu-PVC	Ag-Fe-PVC	Ag-Mn-PVC	Ag-Ni-PVC
500	Blue	Blue	Blue	Blue	Blue	Blue
250	Blue	Blue	Blue	Blue	Pink	Blue
125	Blue	Blue	Blue	Blue	Pink	Blue
62.5	Blue	Blue	Blue	Blue	Pink	Blue
31.5	Blue	Blue	Blue	Blue	Pink	Blue
15.5	Blue	Blue	Blue	Blue	Pink	Blue
7.5	Blue	Pink	Blue	Pink	Pink	Blue
3.7	Pink	Pink	Blue	Pink	Pink	Blue

Table: 2. Antimicrobial activity against **Staphylococcus aureus**

Concentration	Ag-Cd-PVC	Ag-Co-VC	Ag-Cu-PVC	Ag-Fe-PVC	Ag-Mn-PVC	Ag-Ni-PVC
500	Blue	Blue	Blue	Blue	Blue	Blue
250	Blue	Blue	Blue	Blue	Blue	Blue
125	Blue	Blue	Blue	Blue	Blue	Blue
62.5	Blue	Blue	Blue	Blue	Blue	Blue
31.5	Blue	Blue	Blue	Blue	Blue	Blue
15.5	Blue	Blue	Blue	Blue	Pink	Blue
7.5	Purple	Purple	Blue	Pink	Pink	Blue
3.7	Purple	Purple	Purple	Pink	Pink	Purple

RESULTS AND DISCUSSIONS

A resazurin-based test to evaluate the anti-microbial activity of nanocomposites were conducted against E-coli and Staphylococcus bacteria. From tables 1 and 2, it is observed that at higher concentrations, the top rows remain blue/purple, indicating that the nanocomposites effectively inhibit the growth of both Gram positive as well as Gram negative bacteria, while at lower concentrations (3.5 to 7.5 µg/mL), there is a transition from blue to pink, suggesting bacterial survival at lower concentration (Ranga Reddy et al., 2012), (Arora et al., 2020), (Jang et al., 2020), (Mamatha et al., 2021), (Sivaranjan et al., 2020), (Dlamini et al., 2023), (Padilla-Cruz et al., 2021).

CONCLUSIONS

Novel nanocomposites of polyvinyl chloride were successfully synthesized by adding the polymer solution to the prepared solution of bimetallic nanoparticles. Physicochemical characterization included XRD, FESEM, UV and FTIR spectroscopy. The nanocomposites were thoroughly characterized, and the obtained results hold a proof for the expected outcomes. The prepared nanocomposites also underwent a resazurin-based test to evaluate the anti-microbial activity of nanocomposites were conducted against E-coli and Staphylococcus bacteria. The results gave a clear indication that these nanocomposites inhibit the growth of bacteria, thereby proving to be great anti-microbial agents to be used for various complex biological applications.

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SYNTHESIS AND CHARACTERIZATIONS OF MNO$_2$ THICK FILMS BY SCREEN PRINTING METHOD

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ABSTRACT

Gas sensors play a pivotal role in various fields, ranging from industrial applications to environmental monitoring and healthcare. These devices are crucial for detecting and quantifying the presence of specific gases in the atmosphere or within controlled environments. The screen printing method is a simple and scalable technique for fabricating MnO$_2$ thick films with excellent adhesion and uniformity. In this work Manganese dioxide (MnO$_2$) nanoparticles are synthesized by co-precipitation method. MnO$_2$ thick films were prepared by using screen printing method. The structural, electrical and gas sensing properties of the prepared films were investigated using standard tools and techniques. XRD analysis confirmed the formation of crystalline MnO$_2$ nanoparticles, while FESEM revealed their surface morphology and nanoscale features. EDX analysis verified the existence of Mn and O elementals, ensuring the purity of the synthesized material. The prepared MnO$_2$ thick films were tested to oxidizing and reducing gases such as LPG, ethanol, H$_2$S, NO$_2$ and SO$_2$. Films shows maximum sensitivity to LPG at an operating temperature of 120°C among other targeted gases. Films also shows excellent selectivity and quick response and recovery time to LPG.

Keywords: Gas sensors, thick films, precipitation method, sensitivity, quick response.

1. INTRODUCTION

Air pollution is one of the most pressing environmental issues, caused by the release of harmful substances such as particulate matter (PM), carbon monoxide (CO), sulfur dioxide (SO$_2$), nitrogen oxides (NO$_x$), volatile organic compounds (VOCs), and greenhouse gases (GHGs) into the atmosphere. Major sources include industrial emissions, vehicle exhaust, burning of fossil fuels, agricultural activities, and natural processes like wildfires and volcanic eruptions [1, 2]. Air pollution has severe impacts on human health, leading to respiratory diseases, cardiovascular disorders, lung cancer, and neurological issues. Prolonged exposure to pollutants like fine particulate matter (PM$_{2.5}$ and PM$_{10}$) can cause chronic respiratory problems, while toxic gases such as carbon monoxide and nitrogen dioxide contribute to heart disease and reduced lung function. Additionally, air pollution has detrimental effects on the environment, causing acid rain, smog formation, depletion of the ozone layer, and climate change due to excessive greenhouse gas emissions [2, 3]. It also affects biodiversity, reducing agricultural productivity by damaging crops and soil fertility. Addressing air pollution requires stringent environmental regulations, adoption of cleaner energy sources, and the development of efficient air purification and gas sensing technologies to monitor and mitigate its impact on public health and ecosystems [3-5].

Nanoparticles have gained significant attention due to their unique physical and chemical properties, which differ from their bulk counterparts [6]. The need for nanoparticles arises in various fields, including electronics, catalysis, biomedical applications, and gas sensing. In the domain of gas sensors, nanoparticles offer enhanced surface area, high reactivity, and improved sensitivity, making them ideal candidates for detecting trace amounts of gases [5, 6]. Gas sensors play a crucial role in environmental monitoring, industrial safety, and healthcare by detecting toxic and flammable gases [7, 8]. Manganese dioxide (MnO$_2$) nanoparticles, in particular, have been widely explored for gas sensing applications due to their excellent redox properties, high surface-to-volume ratio, and catalytic efficiency in detecting gases like ammonia, hydrogen sulfide, and nitrogen oxides [9-11]. Several synthesis methods have been developed for MnO$_2$ nanoparticles, each offering distinct advantages in terms of morphology, crystallinity, and surface properties. The sol-gel method is a widely used technique that provides excellent control over particle size and porosity, making it suitable for various applications. The hydrothermal and solvothermal methods involve high-temperature and high-pressure reactions, allowing the growth of well-crystallized MnO$_2$ nanostructures with tunable shapes, such as nanorods, nanowires, and nanosheets. The co-precipitation method is a simple and cost-effective approach where manganese precursors, such as MnCl$_2$ or MnSO$_4$, react with an oxidizing agent like KMnO$_4$ to form MnO$_2$ nanoparticles, often followed by calcination to enhance crystallinity. The electrochemical deposition method enables the formation of MnO$_2$ films and nanostructures with high purity and controlled thickness, making it ideal for energy storage applications [11-13]. The microwave-assisted synthesis technique accelerates reaction rates, leading to highly uniform MnO$_2$ nanoparticles with improved phase purity.

Other methods, such as chemical vapor deposition (CVD) and ultrasonic-assisted synthesis, are also explored to achieve MnO_2 nanoparticles with specific characteristics for advanced applications [14, 15].

Screen printing is a cost-effective and scalable technique used for fabricating thick films of functional materials. It involves the deposition of ink or paste containing active nanoparticles onto a substrate through a patterned screen. This method is widely used in the fabrication of gas sensors, printed electronics, and biosensors due to its simplicity, reproducibility, and capability to produce uniform films with controlled thickness [16, 17]. The process consists of preparing the ink or paste, applying it onto a substrate using a squeegee, and subsequently curing or sintering the printed film to achieve the desired functional properties [17, 18].

In the present research work, MnO_2 nanoparticles synthesis by co-precipitation method. The thick films of MnO_2 nanoparticles were prepared by screen printing method. The structural, electrical and gas sensing properties of prepared MnO_2 thick films were investigated and reported.

2. EXPERIMENTAL WORK
All AR grade chemicals were used for the synthesis of MnO_2 nanoparticles. The co-precipitation method was used to synthesis of MnO_2 nanoparticles.

2.1 Synthesis of MnO_2 nanoparticles by co-precipitation method:
Manganese (II) sulphate was used as a source of Mn. The Manganese (II) sulphate 0.2M dissolved in 100 ml double distilled water with continuous stirring at constant temperature of 60°C using magnetic stirrer. During stirring, the NaOH solution was added dropwise in the prepared manganese sulphate solution. The stirring was continued for 60 minutes at a constant temperature of 60°C after added NaOH solution. After that, the brown precipitate formed was obtained. The obtained precipitate then washed with double distilled water and then calcinated at 400°C for 2 hours in the muffle furnace. Finally, the calcinated powder was crushed using molten and pestle for 3 hours and then used for further characterizations [19, 20].

2.2 Preparation of thick films by screen printing method:
The synthesized MnO_2 nanoparticles were used for the preparation of thick films. The thick films of MnO_2 nanoparticles were prepared on glass substrate by screen printing techniques. The process of thick films preparation is reveal in Fig. 1. The proper ration of organic and inorganic materials was used for the preparation of thick films. The 30% of organic and 70 % of inorganic materials was used. The organic material consist of ethyl cellulose (EC) and butyl carbitol acetate (BCA) as temporary binders. While inorganic part consist of synthesized MnO_2 nanoparticles [21, 22].
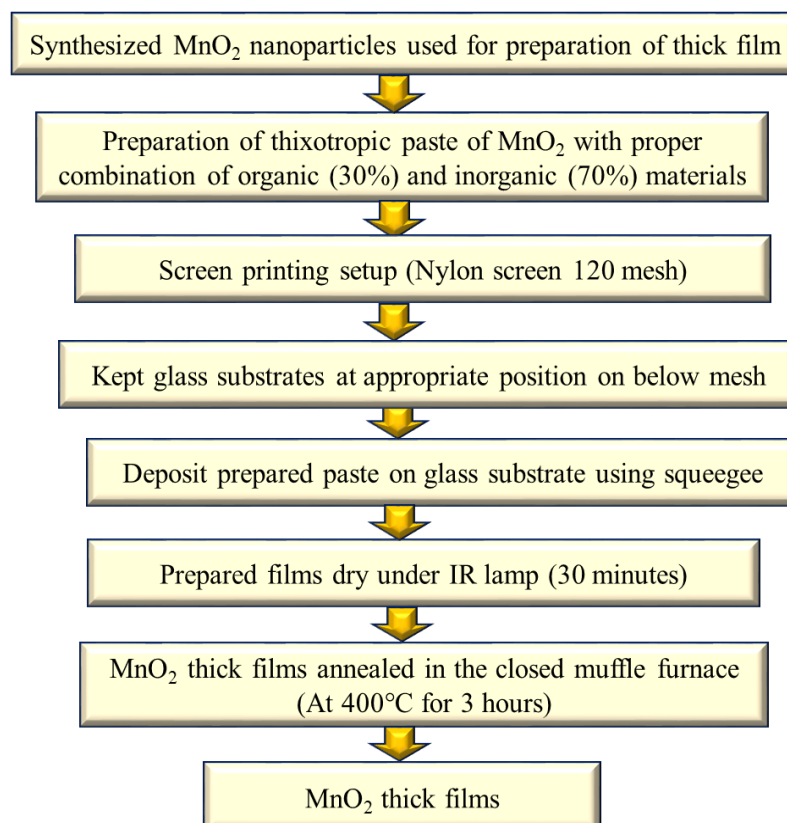
Figure 1: Process of MnO_2 thick films preparation

3. RESULT AND DISCUSSION

3.1 X-ray diffraction (XRD)

It is a widely used analytical technique for determining the crystalline structure, phase composition, and lattice parameters of materials. It is based on the constructive interference of X-rays with the atomic planes of a crystal, according to Bragg's Law. The obtained diffraction peaks are compared with standard reference data from the Joint Committee on Powder Diffraction Standards (JCPDS) to determine the material's phase composition.

Fig. 2 presents the X-ray diffraction (XRD) pattern of MnO_2 thick films, confirming their crystalline nature. The diffraction peak observed at 28.82° corresponds to the most intense reflection of the α-MnO_2 phase, as referenced in the Joint Committee on Powder Diffraction Standards (JCPDS) file 44-0141 [23, 24]. This indicates that α-MnO_2 is the predominant phase in the synthesized material. The presence of additional peaks suggests minor contributions from other phases or structural variations within the material. The crystallite size was estimated by using Debye Scherrer equation and it was found to be 39.32 nm.
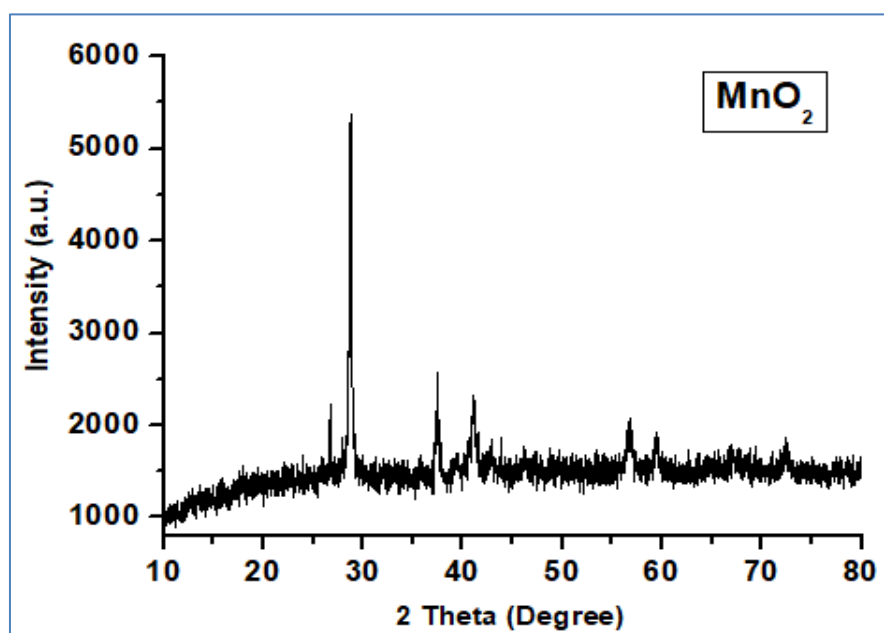
Figure 2: XRD pattern of MnO_2 thick films

3.2 Field Emission Scanning Electron Microscopy (FESEM)

Field Emission Scanning Electron Microscopy (FESEM) is an advanced imaging technique used to obtain high-resolution surface morphology and structural details of nanomaterials. Unlike conventional Scanning Electron Microscopy (SEM), FESEM utilizes a field emission gun (FEG) as an electron source, which provides a highly focused and coherent electron beam. This results in improved resolution (up to the nanometer scale), reduced sample charging, and enhanced depth of field, making it an essential tool for characterizing nanoparticles, thin films, and nanostructured materials. Fig. 3 presents the Field Emission Scanning Electron Microscopy (FESEM) image of MnO_2 thick films, revealing their surface morphology at a magnification of 100,000×. The FESEM image in Fig. 3 provides insights into the surface morphology of MnO_2 thick films, which are crucial for their application in LPG gas sensing. The observed porous and nanostructured morphology, with particle sizes ranging from 13.49 nm to 134.9 nm, enhances the material's surface-to-volume ratio, a key factor in gas sensing performance. The presence of nanosheets and nanorods increases the availability of active adsorption sites, facilitating effective gas diffusion and interaction with LPG molecules. Moreover, the porous nature of the MnO_2 structure allows for rapid gas penetration, leading to a quicker sensor response and recovery time [22, 23]. These structural features improve the sensitivity and selectivity of MnO_2-based sensors, making them highly efficient for LPG detection.
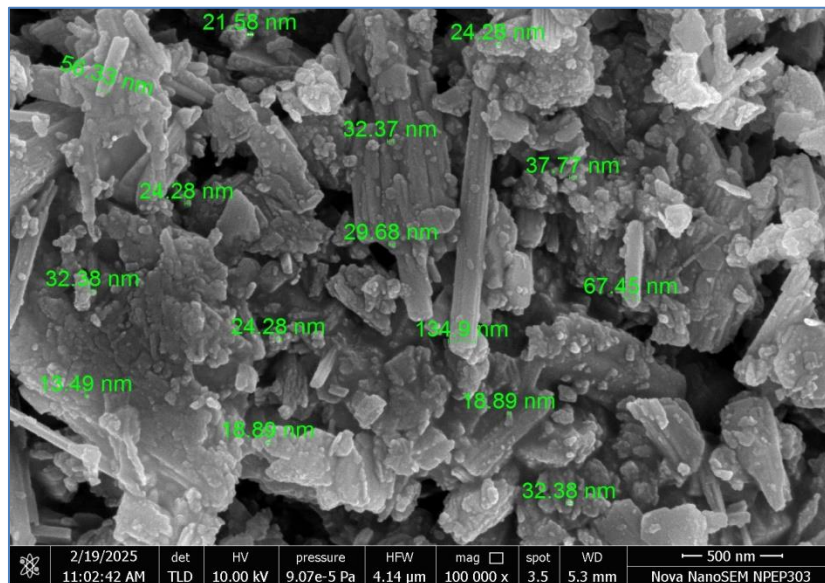
Figure 3: FESEM image of MnO_2 thick films

3.3 Energy-dispersive X-ray spectroscopy (EDX)

Energy-Dispersive X-ray Spectroscopy (EDX) coupled with EDX for elemental analysis, enabling the determination of the material's composition. Fig. 4 reveal the EDX spectra of MnO_2 thick films.
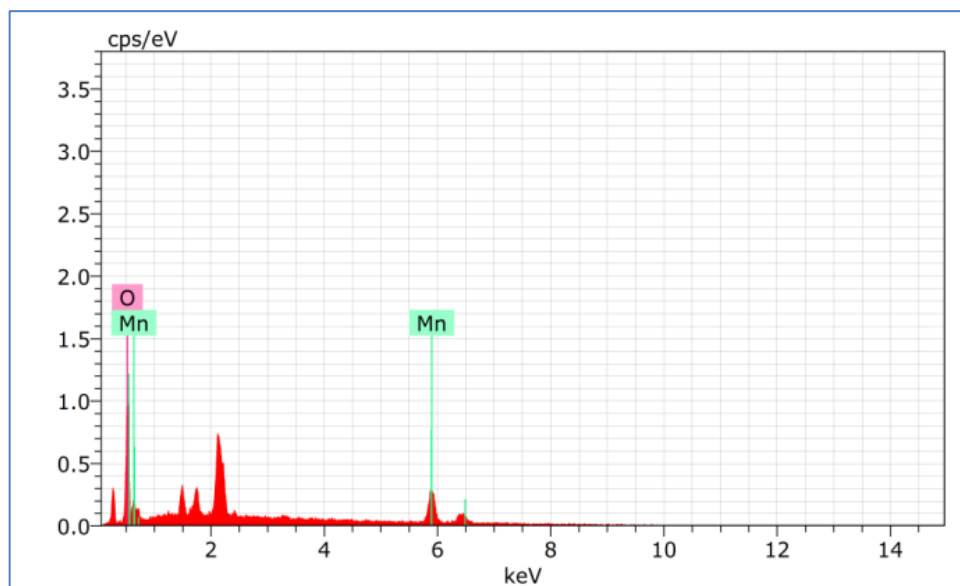
Figure 4: EDX spectra of MnO_2 thick films

The Energy Dispersive X-ray (EDX) spectrum of MnO_2 thick films, shown in Fig. 4, confirms the elemental composition of the synthesized material. The spectrum displays prominent peaks corresponding to manganese (Mn) and oxygen (O), validating the formation of MnO_2. The strong Mn peaks around 6 keV and the oxygen peak at ~0.5 keV indicate the presence of Mn in its oxidized state [22]. The absence of any significant impurities suggests the high purity of the synthesized MnO_2. This elemental confirmation is crucial for applications such as LPG gas sensing, where the interaction between MnO_2 and gas molecules depends on the material's composition and oxidation state, directly influencing the sensor's efficiency and response characteristics. The atomic percentage of Mn and O was found be 62.35% and 37.65 % respectively. While the weight percentage of Mn and O was found be 85.05% and 14.95 % respectively.

3.4 Electrical and gas sensing characterization:

The electrical and gas sensing characterizations MnO_2 thick films were carried out using static system and half bridge method [21]. The half-bridge method is a widely used electrical characterization technique for thick and thin film gas sensors, based on a resistive sensing mechanism. In this method, the MnO_2 film acts as a variable resistor in series with a known fixed resistor, forming a voltage divider circuit. A constant input voltage is applied across the circuit, and the voltage drop across the MnO_2 film is measured to determine its resistance. The method is particularly useful for gas sensing applications, where exposure to gases causes a change in

resistance due to interactions between gas molecules and the sensor surface. As observed in Fig. 5, the MnO_2 thick film exhibits a negative temperature coefficient of resistance (NTCR), confirming its semiconducting nature. The half-bridge method enables real-time monitoring of these resistance variations, making it a simple yet effective approach for evaluating the gas-sensing performance of metal oxide-based sensors [25, 26].

The temperature versus resistance (Rc) plot of MnO_2 thick films, shown in Fig. 5, demonstrates the material's semiconducting behavior. The electrical characterization was conducted using the half-bridge method, revealing a negative temperature coefficient of resistance (NTCR), which is characteristic of semiconductors. As the temperature increases from 300 K to 500 K, the resistance decreases significantly from approximately 1.8×10^9 Ω to 2.0×10^8 Ω, indicating enhanced charge carrier mobility at higher temperatures. This temperature-dependent electrical behavior is crucial for LPG gas sensing applications, as the interaction between gas molecules and MnO_2 alters its resistance, enabling effective detection based on conductivity variations [22, 25].
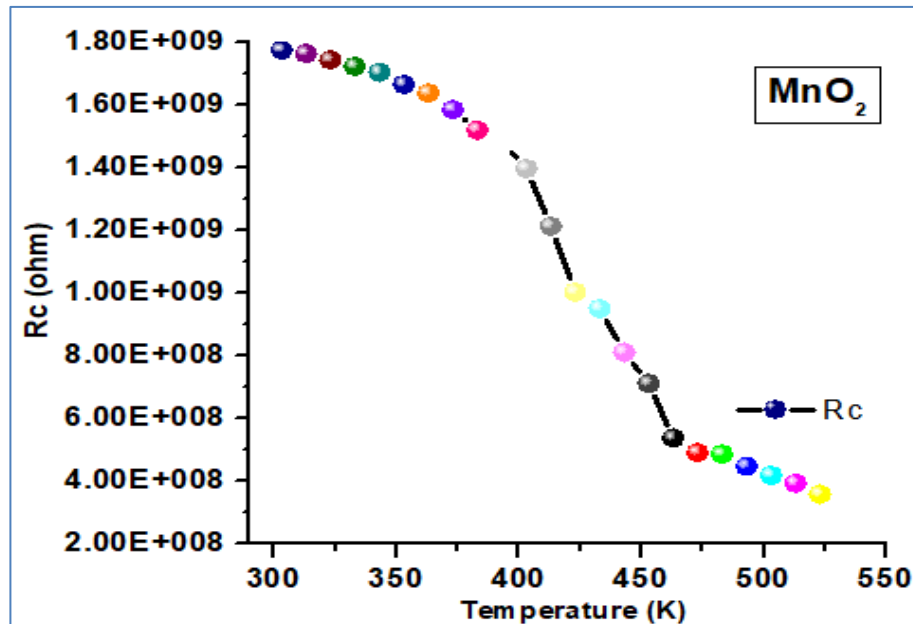
Figure 5: Temperature versus resistance plot of MnO_2 thick films

The resistivity, Temperature Coefficient of Resistance (TCR) and activation energy of MnO_2 thick films were calculated using equations 1, 2 and 3 respectively [21, 22].

$$\rho = \left(\frac{R \times b \times t}{l} \right) \Omega - m \qquad (1)$$

Where, ρ = Resistivity of prepared film, R = resistance at normal temperature, b = breadth of film, t = thickness of the film, L = length of the film.

$$TCR = \frac{1}{R_o} \left(\frac{\Delta R}{\Delta T} \right) \ /^o \ C \qquad (2)$$

Where, ΔR = change in resistance between temperature T_1 and T_2, ΔT = temperature difference between T_1 and T_2 and R_o = room temperature resistance of the film.

$$\Delta E = A e^{-Ea/kBT} \quad eV \qquad (3)$$

Where, ΔE = Activation energy, T = Temperature in Kelvin and A = Arrhenius prefactor.

The resistivity, TCR and activation energy of MnO_2 thick films were found to be 51495.7 ohm-m, -0.00576/°C, and 0.1502 eV respectively.

In the gas sensing characterizations, the sensitivity, selectivity and response and recovery time of MnO_2 thick films are investigated. The performance of a gas sensor is evaluated based on key parameters such as sensitivity, selectivity, and response and recovery time. Sensitivity refers to the sensor's ability to detect even small concentrations of a target gas and is typically expressed as the relative change in resistance or conductivity upon gas exposure. A highly sensitive sensor exhibits a significant electrical response even at low gas concentrations. Selectivity is the sensor's ability to distinguish the target gas from other interfering gases, ensuring accurate

detection in complex environments. It depends on factors such as surface modifications, doping, and operating temperature [25, 26]. Response time is the duration required for the sensor to reach 90% of its maximum signal change upon gas exposure, while recovery time is the time taken to return to its baseline resistance after gas removal. Faster response and recovery times indicate high efficiency and real-time applicability of the sensor. These characteristics are crucial for applications such as LPG gas sensing, where rapid and selective detection is essential for safety and industrial monitoring. The temperature versus sensitivity plot of MnO_2 thick films is reveal in Fig. 6.
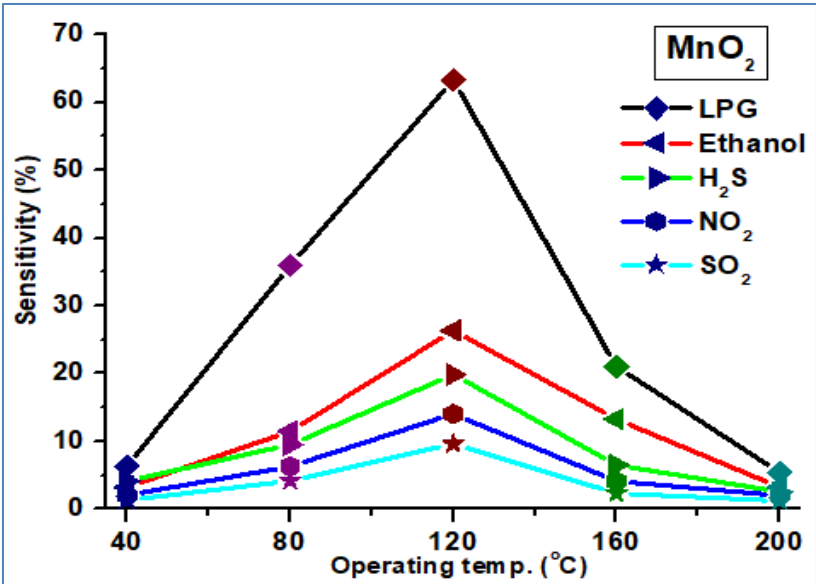
Figure 6: Temperature versus sensitivity plot of MnO_2 thick films

Fig. 6 illustrates the temperature-dependent sensitivity of MnO_2 thick films towards different gases, including LPG, ethanol, H_2S, NO_2, and SO_2. The plot reveals that the sensor exhibits the highest sensitivity to LPG at an optimal operating temperature of 120°C, with a peak sensitivity exceeding 63.29%, indicating strong interaction between MnO_2 and LPG molecules. In contrast, other gases such as ethanol, H_2S, NO_2, and SO_2 show lower sensitivity values, highlighting the selectivity of MnO_2 thick films towards LPG. The sensitivity decreases significantly beyond 120°C, which could be attributed to desorption of gas molecules at higher temperatures. This analysis confirms the potential of MnO_2 thick films as an effective LPG gas sensor, demonstrating an optimal balance of sensitivity and operating temperature for practical gas sensing applications [26, 27]. The sensitivity of the films was estimated using eq. 4.

$$Ra-Rg/Ra \times 100 \qquad (4)$$

Where, Ra- resistance of the film in air, and Rg- resistance of the film in presence of gas.
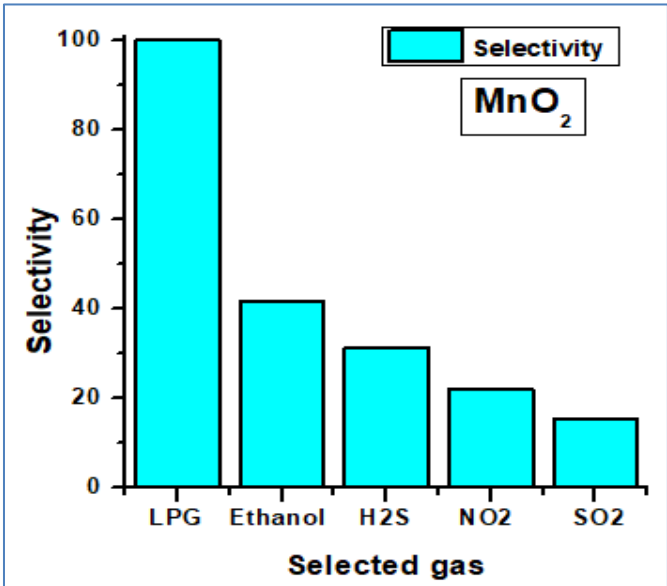
Figure 7: Selectivity histogram of MnO_2 thick films

Fig. 7 presents the selectivity of MnO_2 thick films towards different gases, including LPG, ethanol, H_2S, NO_2, and SO_2. The bar graph clearly shows that MnO_2 exhibits the highest selectivity for LPG, with a selectivity percentage nearing 100%, significantly surpassing that of other tested gases. Ethanol follows with moderate selectivity, while H_2S, NO_2, and SO_2 show relatively lower responses [28, 29]. The high selectivity for LPG suggests that MnO_2 thick films have a strong affinity for LPG molecules due to favorable adsorption-desorption dynamics, making them highly suitable for LPG gas sensing applications. The lower response to interfering gases ensures accurate detection and minimal cross-sensitivity, which is a crucial factor in gas sensor performance.

Fig. 8 illustrates the response and recovery characteristics of MnO_2 thick films when exposed to 1000 ppm of LPG gas. The response time refers to the duration required for the sensor to reach its peak sensitivity upon exposure to LPG, while the recovery time indicates how quickly the sensor regains its baseline state after gas removal [30]. As shown in the plot, the sensitivity increases sharply during the ON time (15 sec), reaching a maximum, and then decreases during the OFF time (54 Sec), signifying the desorption of gas molecules. The rapid response and recovery times demonstrate the sensor's efficiency in detecting LPG and returning to its initial state, making MnO_2 a promising material for real-time LPG sensing applications.
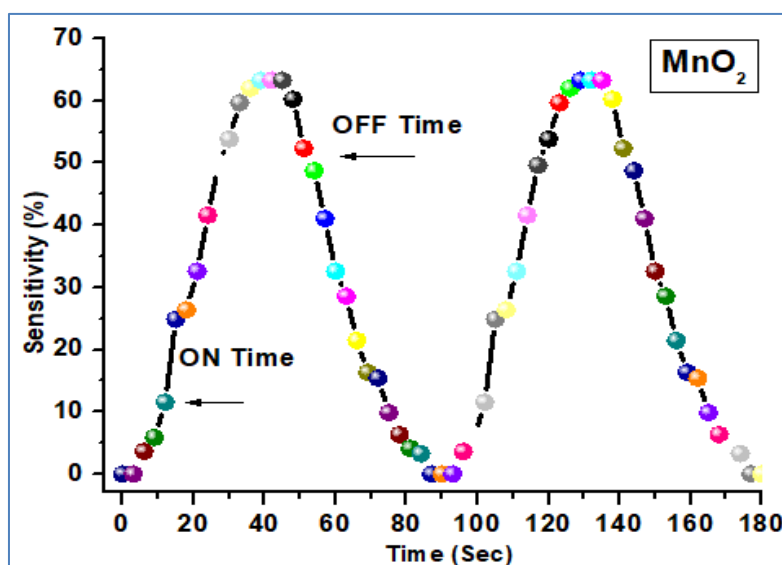
Figure 8: Response and recovery time to LPG

CONCLUSION AND FUTURE SCOPE

The comprehensive analysis of MnO_2 thick films for LPG gas sensing demonstrates their high sensitivity, selectivity, and fast response-recovery characteristics, making them a promising candidate for real-time gas detection. The FESEM and EDX analysis confirm the structural and elemental composition of the material, ensuring its suitability for gas sensing applications. The temperature-dependent resistance study indicates the semiconducting nature of MnO_2, which plays a crucial role in modulating the sensing response. The sensitivity plot highlights an optimum operating temperature (~120°C), where the highest sensitivity to LPG is observed. The selectivity study confirms of MnO_2 preference for LPG over other gases, ensuring minimal cross-interference. Furthermore, the response and recovery time analysis reveals a rapid detection capability, which is essential for real-time applications.

For future research, efforts can be directed towards enhancing the sensitivity and selectivity of MnO_2 sensors by doping with noble metals or forming composite structures with other metal oxides. The nanostructuring and surface modification techniques can be explored to improve gas adsorption and desorption rates, thereby reducing response-recovery times. Integration with wireless sensor networks and IoT platforms can further enable real-time monitoring of LPG leaks in industrial and domestic settings. Moreover, extending this study to other hazardous gases such as CO, NH_3, and CH_4 will broaden the application potential of MnO_2 based gas sensors, contributing to safer and more efficient gas detection systems.

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INTEGRATING THE IMPACT OF QUERCETIN AND CATECHIN ON LUNG CANCER USING COMPUTATIONAL METHODS

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ABSTRACT

Lung cancer is the most widespread disease leading to a number of deaths among people. In recent years, lung cancer has shown a significant increase amongst the health of people globally. Globocan has estimated that the immortality caused due to lung cancer is about 10.5% in the year 2024. K-ras (PDB ID : 4LUC) has always proved to be a therapeutic potential against the symptoms of lung cancer. In this study we investigate the efficiency of flavonoid compounds as K-ras inhibitors. The therapeutic potential of the selected flavonoids was analysed using computational methods. Molecular docking process was conducted to study the interaction of the selected flavonoids Quercetin and Catechin with active sites of 4LUC protein. The docking score of Quercetin and Catechin obtained is -8.9kcal/mol and -9.0kcal/mol respectively. These compounds were also compared with the standard reference drug Crizotinib to determine the efficacy of our selected compounds. These lead compounds were further tested for their pharmacokinetic properties using the ADMET predictions and visualised using Biovia Discovery Studio. As a result, both Quercetin and Catechin can be considered as the lead compounds effective in the lung cancer treatment.

Keywords: Lung cancer, natural product, computational methods, molecular docking, ADMET

1. INTRODUCTION

Lung Cancer (LC) is a type of cancer that initiates in lungs and gradually spreads to other body parts, further increasing the infection that sometime leads to death(Asaithamby et al., 2022; Devasia et al., 2023; Pillaiyar et al., 2020). It is the most widespread disease all over the globe. According to the statistics estimated by GLOBOCAN, it is observed that lung cancer is responsible for about 18% of deaths in 2020(Novaes et al., 2008; Siegel et al., 2024). In 2020 it was observed that an estimation of 2.2 million new cases were registered which was about 11.4% of all cancer cases(Travis et al., 2015). Likewise in 2022 an estimation of 2,480,675 new cases were observed(Bray et al., 2018; Spagnuolo et al., 2015). Recently it is said that more than 2,001,140 new cases were reported in 2024 causing an estimation of 611,720 deaths among people(Bizuayehu et al., 2024). All over India, it is observed that a total of 5.9% cancer cases are reported and 8.1% of cancer deaths have taken place till now. Among these, 80% of the cases were caused due to smoking history(Brown et al., 1996; Siegel et al., 2024).

Natural products have always proved to be the most efficient method to treat lung cancer(Jha et al., 2024). Natural products have always shown a therapeutic potential in the treatment process of lung cancer(Gilad et al., 2012; Jha et al., 2024; Ostios-Garcia et al., 2024). There are various treatment options of lung cancer such as chemotherapy, radiation therapy, immunotherapy, surgery, targeted drug therapy, etc(Brown et al., 1996). The drugs used for these treatment options are extracted and designed from the natural sources(Ostios-Garcia et al., 2024). Numerous natural products are approved by FDA (Food and Drug Administration) for the treatment of lung cancer such as Deguelin(Gao et al., 2020), Scopoletin(Highland et al., 2022), Rosmarinus Officialinus(Highland et al., 2022), Ribavirin(Paudel et al., 2024). These natural compounds enhance the intellectual developments but at the same time show less side effects and a long term toxicity. As a result, safer and traditional methods such as natural resources are used in the drug development and discovery(Paudel et al., 2024).

There are numerous natural products and sources that have shown a significant development in reducing the global extent of this disease(Jha et al., 2024). Among these natural products, flavonoid compounds have always shown a great therapeutic potential against the lung cancer symptoms. In addition to this, it has also shown anti-inflammatory, antioxidant and anti-microbial properties(Toigo et al., 2023). These extravagant properties of flavonoids has made them an effective and valuable source in the medications of lung cancer. However, it is difficult to explore each natural product in laboratory and also very expensive and time taking process(Eberhardt et al., 2021). Therefore to overcome all these difficulties, many new methods are being developed using computer aided drug design methods(Department of Biotechnology, Govind Ballabh Pant Engineering College, Pauri Garhwal-246194, Uttarakhand, India et al., 2015). Computational methods have shown a great help in drug discovery and development process by cutting the process of years into a number of

months(Alonso et al., 2006; Asaithamby et al., 2022; Department of Biotechnology, Govind Ballabh Pant Engineering College, Pauri Garhwal-246194, Uttarakhand, India et al., 2015; Haider et al., 2022; Sadybekov & Katritch, 2023). This study specifically focuses on filling the gap between natural products and computational methods by analysing the efficiency of several natural products in the lung cancer treatment. In this study we have used receptor K-ras (PDB ID : 4LUC) against the flavonoid compounds. The selected flavonoids for this study are Quercetin and Catechin. The computational methods used for this research are molecular docking and ADMET Study. The properties of the selected compounds are compared with the reference drug Crizotinib. The visualisation of the interactions were carried out using Chimera X and Biovia Discovery Studio. The computational methods are very useful by reducing the likelihood of unsuccessful clinical trials, labor costs and speeds up the process(Daoui et al., 2021; Schlessinger, 2002). This study offers a hope to people with their unmet medical needs.

2. MATERIALS AND METHODS

2.1 Preparation of Protein
The 3D structure of the protein molecule of K-Ras was downloaded using the Protein Data Bank (PDB ID : 4LUC) of Research Collaborators for Structural Bioinformatics (RCSB) database as shown in **Figure 1**. The structure of the protein molecule was prepared for docking process using Chimera software by separating all heteroatoms, non-protein molecules and all other chains. This prepared structure was then further edited with the help of AutoDock Tools by removing the water molecules, addition of polar hydrogens, kollmann charges, etc. This edited structure was further saved in the PDBQT format.
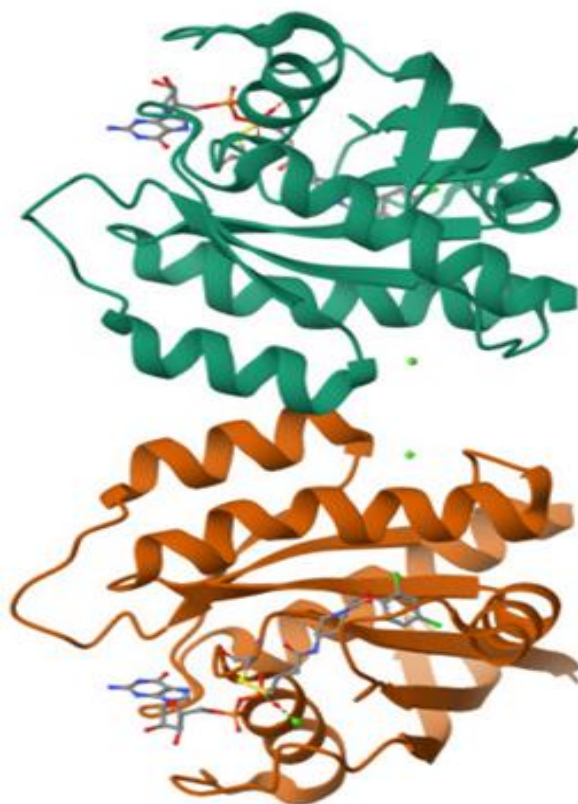
Figure 1 – The three dimensional structure of K-RAS (PDB ID: 4LUC)

2.2 Preparation of Ligands
The 3D conformer of the selected flavonoid molecules were downloaded from PubChem database, Quercetin (CID: 5280343) and Catechin (CID: 73160). The 2D structures of the ligand molecules are shown in **Figure 2.** These structures were later downloaded in SDF format from PubChem. The geometry optimization process was carried out using Avogadro software. Later, using the AutoDock Tools software the process of addition of Gasteiger charges and were saved in PDBQT format. The reference drug Crizotinib was also downloaded using the PubChem database.
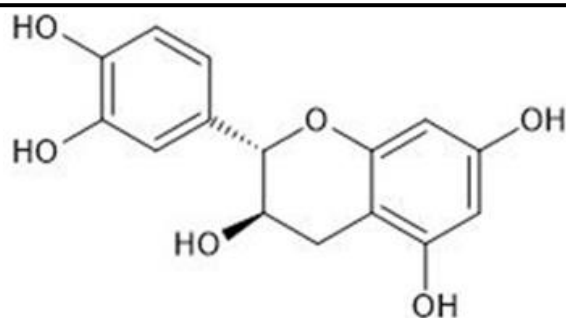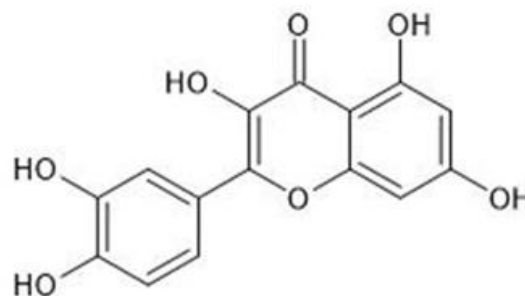
(a) Catechin   (b) Quercetin

Figure 2 – The molecular structure of selected flavonoid compounds

2.3 Molecular Docking

Molecular Docking is process that helps to predict the interactions between the small molecules and large biomolecules(Anwar et al., 2021). It is the common and most useful tool of computer aided drug design because it helps to predict the stability and structure of protein-ligand complex. For this molecular docking process we have used AutoDock Vina software to determine the interactions between K-Ras (PDB ID: 4LUC) and flavonoid compounds (Catechin and Quercetin) along with the binding energies and type of interactions. These formed complexes were later on compared with the reference drug Crizotinib.

2.4 ADME-Tox Predictions

The selected lead compounds were further tested for drug-likeness and pharmacokinetic profile by analysing the parameters that are absorption, distribution, metabolism, excretion and toxicity(Eberhardt et al., 2021). The ADME study was conducted using SwissADME database. Using this database we determined molecular weight, H-bond acceptor, H-bond donor, lipophilicity, water solubility, bioavailability score, synthetic accessibility, druglikeness and pharmacokinetic properties. The toxicity analysis was carried out using ProTox database. The toxicity analysis was carried out for the prediction of parameters such as hepatotoxicity, carcinogenicity, cytotoxicity, immunotoxicity, mutagenicity, LD_{50} and toxicity level.

3. RESULTS AND DISCUSSION

3.1 Molecular Docking

The protein-ligand complex interactions were determined by carrying out the docking process in order to obtain the best interaction with highest binding energy. This molecular docking process is carried out using AutoDock Vina software. The docking analysis report is mentioned in **Table 1**. This table represents the molecular docking results of the selected flavonoid compounds with K-Ras (PDB ID: 4LUC). The docking interactions of these compounds were compared with the reference drug Crizotinib. The binding energy of reference drug crizotinib was found to be -9.1 kcal/mol. The selected flavonoid compounds, Quercetin and Catechin indicated favourable binding energy of -8.9 kcal/mol and -9.0 kcal/mol respectively. **Table 1** consists of the binding energies obtained and type of interaction involved in the binding of 4LUC with Quercetin, Catechin and reference drug Crizotinib.

The visualisation of the protein-ligand interactions was carried out using Biovia Discovery Studio. The 2D ligand interactions were also visualised using Biovia Discovery Studio. The 3D binding site was visualised using the software Chimera X. The visualisation of the interactions by Chimera X is mentioned in **Figure 3** while the visualisation by Biovia Discovery Studio is shown in **Figure 4.**

Table 1 – Molecular Docking Analysis

Natural Product	Binding Energy (kcal/mol)	Type of Interactions
Crizotinib	-9.1 kcal/mol	Van der Waals, Conventional hydrogen bond, Pi-Pi T-shaped, Pi-Alkyl
Catechin	-9.0 kcal/mol	Van der Waals, Pi-lone pair, Pi-Alkyl
Quercetin	-8.9 kcal/mol	Van der Waals, Pi-Anion, Pi-Donor, Hydrogen bond, conventional hydrogen bond, Pi-lone pair
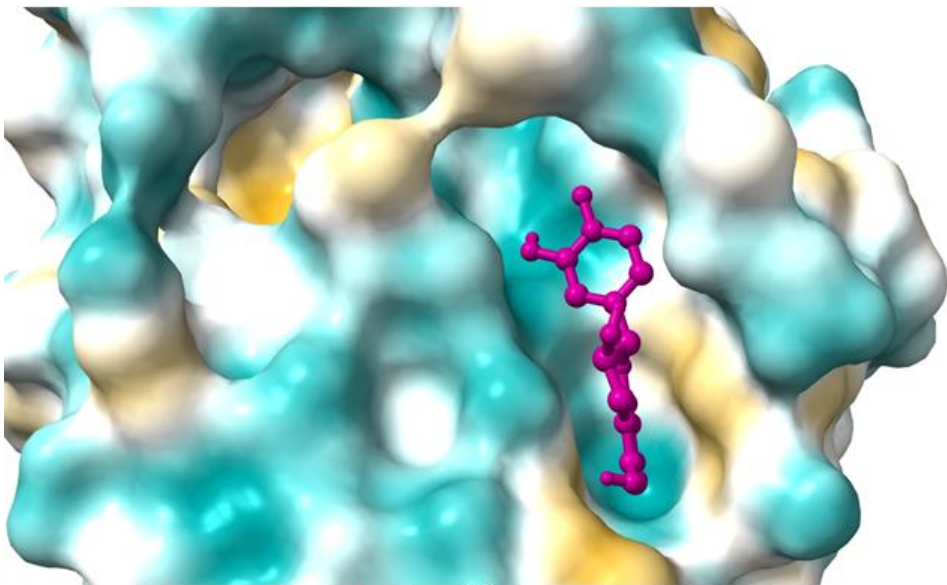
(a)
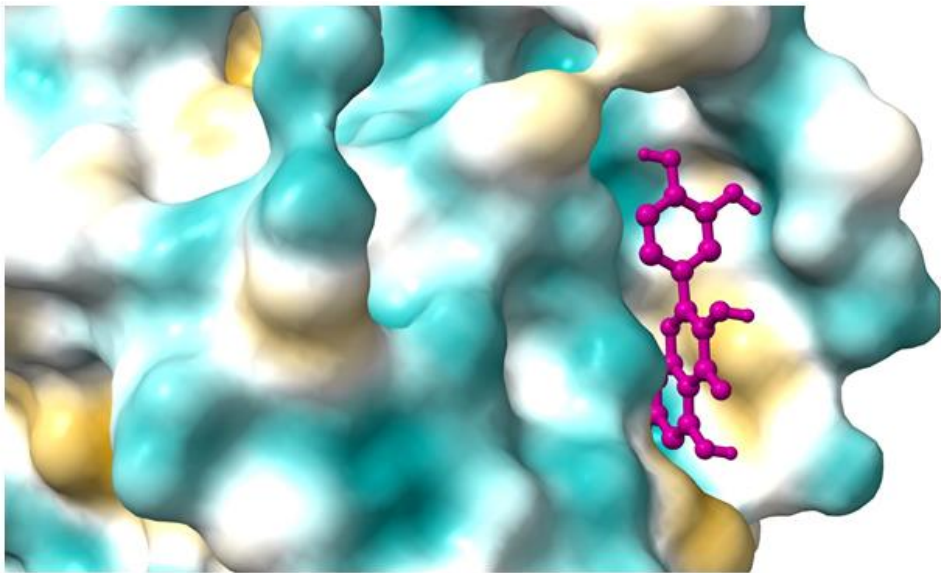
(b)

Figure 3 – 3D interactions of (a) Catechin with 4LUC (b)Quercetin with 4LUC

(a)

(b)
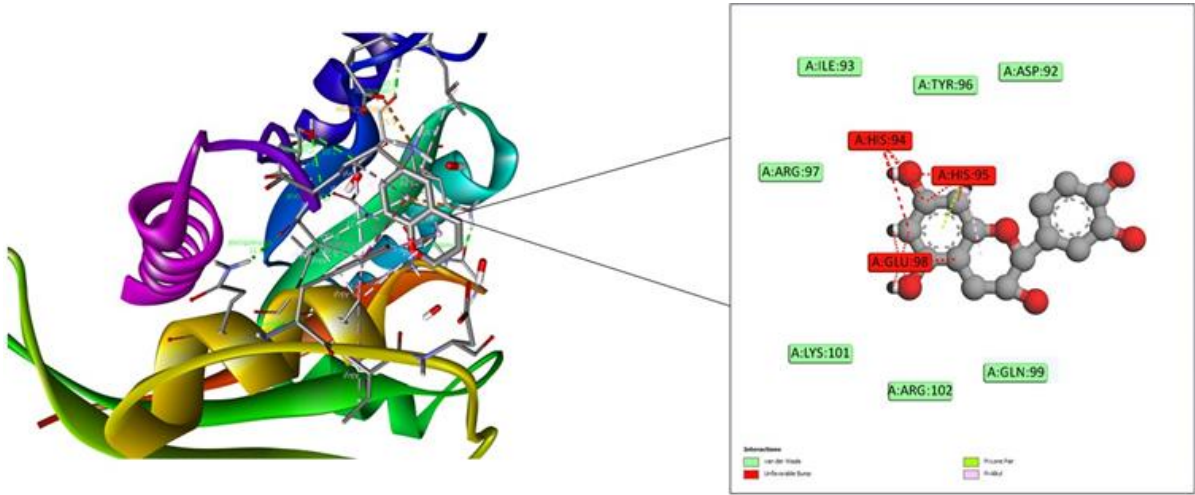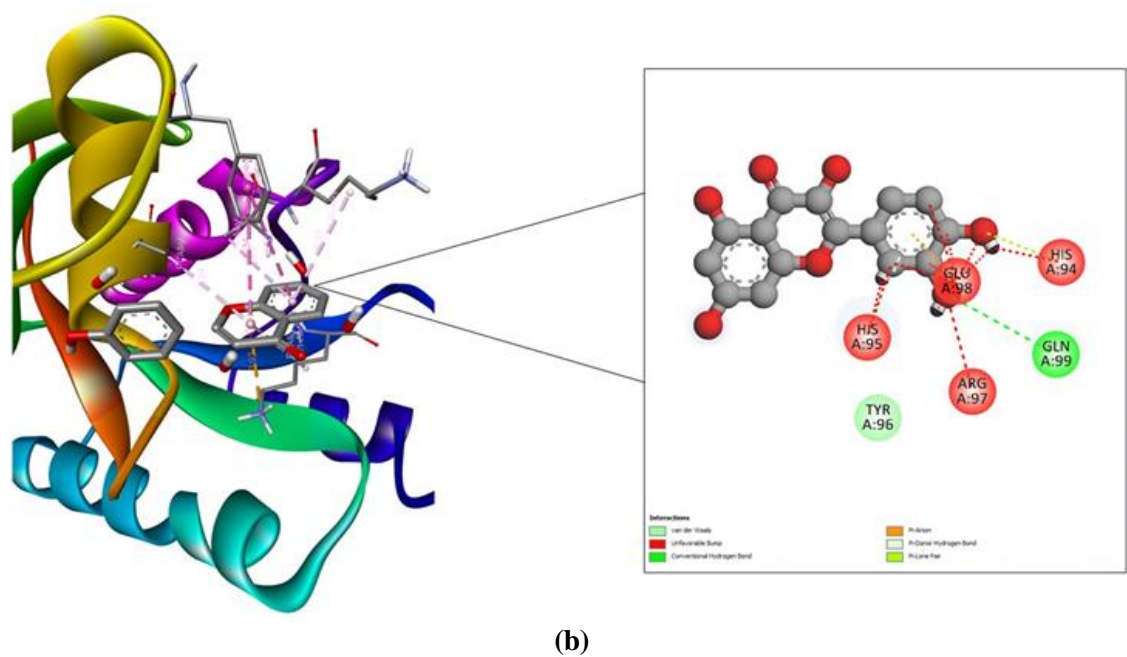
Figure 4 – 2D interactions of (a) Catechin with 4LUC (b) Quercetin with 4LUC

3.2 ADMET Study

It is the most important factor for drug discovery process. It includes testing the absorption, distribution, metabolism, excretion and toxicity (ADMET) analysis. The toxicity prediction of all selected compounds was carried out using Pro Tox 3.0. Parameters of toxicity that were analysed like hepatotoxicity, carcinogenicity, immunotoxicity, mutagenicity, cytotoxicity, LD_{50} and toxicity level as shown in **Table 2**. As a result, the selected compounds shown the toxicity range from 3 to 6. This indicates that Catechin is comparatively less toxic than that of Quercetin as well as the reference drug Crizotinib. Likewise, these drugs were also tested through SwissADME database. The parameters essential for an efficient drug are molecular weight ranged as <500Da, hydrogen bond donors <5, hydrogen bond acceptors <10, lipophilicity <5, solubility <6, minimum bioavailability score of 0.55 and synthetic accessibility ranged from 1(easy synthesis) to 10 (hard synthesis). The results of SwissADME are shown in **Table 3.** According to the efficient drug requirement drug should not be BBB permeant but should be high in gastrointestinal tract absorption. As a result, both catechin and quercetin have shown a great potential for lung cancer treatment but comparatively Catechin has shown the best effect and satisfied all the drug criteria of potential candidates for lung cancer treatment.

Table 2 – Toxicity Predictions

Natural Product	Hepatotoxicity	Carcinogenicity	Immunotoxicity	Mutagenicity	Cytotoxicity	LD50	Toxicity
Crizotinib	Inactive	Active	Active	Inactive	Inactive	1000 mg/kg	4
Catechin	Inactive	Inactive	Inactive	Inactive	Inactive	10000 mg/kg	6
Quercetin	Inactive	Active	Inactive	Active	Inactive	159 mg/kg	3

Table 3 – ADMET Analysis

NATURAL PRODUCT	M.W (g/mol)	H-ACCEPTOR	H-DONOR	LOG P	LOG S	GI	BBB	LIPINSKI	BIOAVAILABILITY SCORE	SYNTHETIC ACCESSIBILITY
Crizotinib (Reference)	450.34 g/mol	5	2	3.86	-5.05	High	No	Yes; 0 violation	0.55	3.77
Catechin	290.27 g/mol	6	5	0.83	-2.22	High	No	Yes; 0 violation	0.55	3.50
Querctin	302.24 g/mol	7	5	1.23	-3.16	High	No	Yes; 0 violation	0.55	3.23

Figure 5 exhibits the bioavailability radar plot and boiled egg diagram of the compounds Quercetin and Catechin. The pink area in the radar plot defines the specific physicochemical space for oral bioavailability. In Quercetin it is clearly visible that the compound fits well in the pink region except for insaturation parameter whereas in Catechin it is clearly visible that it fits well in the pink region which means it provides a potential bioavailability. The radar plot defines different parameters that are lipophilicity, size, flexibility, polarity, insaturation, insolubility. Figure 5 also includes the boiled egg model of both compounds. The white region of the model specifies the gastrointestinal absorption whereas the yellow region predicts the brain permeability.

(a)

(b)
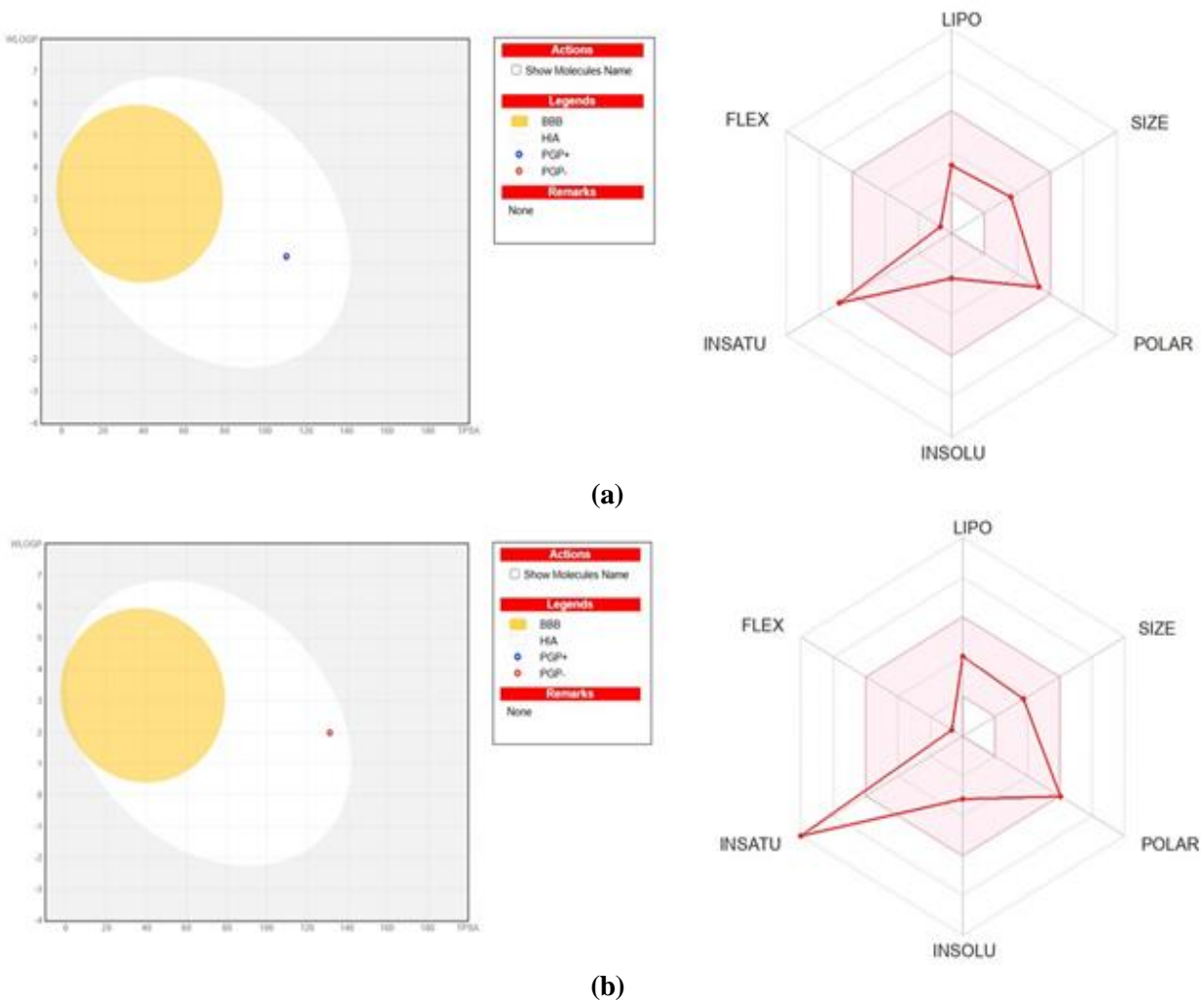
Figure 5 – Boiled Egg Model and Bioavailability Radar Plot of (a) Catechin (b)Quercetin. Data retrieved from swissadme.

4. CONCLUSION

The study examines the K-Ras inhibitor activity of the selected flavonoid compounds in the treatment of lung cancer. Among these compounds Catechin showed the most effective therapeutic potential against the K-Ras

receptor. The docking analysis suggests that Catechin can be the lead component against lung cancer symptoms showing effective and strong interactions with the active sites of K-Ras with the docking score of -9.0 kcal/mol. Further, from the ADME study and toxicity predictions Catechin has served the best drug-likeness and pharmacokinetic properties with low toxicity. As a result, this study suggests that Catechin is a potential candidate in the treatment of lung cancer.

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SYNTHESIS OF GRAPHENE OXIDE AND IT'S USE IN REMEDIATION OF METRIBUZIN AND ATRAZINE

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ABSTRACT

The production of graphene oxide (GO) and its use in the remediation of two commonly used triazine herbicides—metribuzin and atrazine is investigated in this work High-quality GO with increased adsorption capabilities was synthesized and investigated using modified Hummers' approach under FTIR, XRD, SEM, and BET surface area analysis. Under several conditions—including pH (3–9), contact time (5–180 min), initial pollutant concentration (1–50 mg/L), and temperature (15–45°C)—batch adsorption studies assessed the removal efficiency. Under optimal conditions (pH 7.0, contact period 120 min, adsorbent dosage 0.8 g/L, 25°C), GO shown outstanding removal efficiency of 97.3% for metribuzin and 94.8% for atrazine. While this matched with the Langmuir model, implying monolayer adsorption with maximal capacities of 487.6 mg/g for metribuzin and 421.3 mg/g for atrazine, adsorption kinetics followed pseudo-second-order models. Thermodynamic investigation found the adsorption mechanism to be exothermic and spontaneous. Therefore verifying its possible use in sustainable water treatment.

Keywords: Graphene Oxide, Metribuzin, Atrazine, Adsorption, Water Remediation, Herbicide Removal

1. INTRODUCTION

The usage of herbicides in agriculture has resulted in their broad presence in water supplies, therefore posing major environmental and health issues on a worldwide basis. Among these herbicides, metribuzin (4-amino-6-tert-butyl-3-methylthio-1,2,4-triazin-5(4H)-one) and atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazin-5) have attracted especially interest because of their persistence, great mobility in soil, and possible toxicity to non-target organisms and humans. Widely used for control of broadleaf weeds and grasses in crops like soybeans, potatoes, and tomatoes, metribuzin has been found in surface and groundwaters at levels above recommended limits in agricultural areas. Likewise, one of the most widely used herbicides globally for the production of corn and sorghum, atrazine, has been often identified in drinking water sources and raises questions about its endocrine-disruption ability and possible carcinogenicity.

Removing these stubborn herbicides from water has proved difficult using the traditional water treatment techniques—chlorine, ozonation, and activated carbon filtration. As such, the development of more sustainable and effective remedial methods is quite urgently needed. Because of their special characteristics like high surface area, adjustable surface chemistry, and increased reactivity, nanomaterials have become more interesting options for the elimination of pollutants in recent years. Of them, graphene-based materials—especially graphene oxide (GO)—have shown extraordinary promise for uses in environmental remediation.

An oxidized variation of graphene, graphene oxide has many oxygen-containing functional groups (hydroxyl, carboxyl, and epoxy) on its basal planes and edges, so offering many active sites for contaminant adsorption via several processes, including π-π interactions, hydrogen bonding, and electrostatic attraction. Although GO has a high specific surface area and is therefore a good option for aqueous phase cleanup, its hydrophilic and dispersible character in water is due in part to these functional groups. Furthermore, the easy synthesis of GO from cheap graphite and its amenability to further functionalization presents chances to improve its selectivity and adsorption capability toward particular pollutants.

Though GO-based adsorbents are becoming more and more popular, thorough studies looking at their efficacy for simultaneous removal of several types of herbicides, such metribuzin and atrazine, are still rare. Developing sensible and reasonably priced water treatment solutions depends on an awareness of the adsorption behavior, processes, and regeneration capability of GO for these herbicides. Furthermore, the influence of environmental conditions like pH, temperature, and the presence of competing ions on the adsorption performance has to be completely investigated to determine the application of GO in real water matrix.

This work attempts to close these information gaps by methodically synthesizing GO utilizing modified Hummers' approach and assessing its possibilities for the remedial treatment of metribuzin and atrazine from environment.

The results of this work are predicted to be very important for the domains of environmental nanotechnology and water treatment since they provide viable answers for the rising problem of herbicide contamination of

water supplies. Moreover, the information acquired by this work could direct the design and optimization of GO-based adsorbents for a wider spectrum of organic pollutants, thereby promoting sustainable water management techniques all around.

2. OBJECTIVES

1. To synthesize graphene oxide using modified Hummers' method and characterize its physicochemical properties using FTIR, XRD, SEM, TEM, and BET surface area analysis.

2. To evaluate the adsorption performance of graphene oxide for metribuzin and atrazine removal from aqueous solutions under various experimental conditions (pH, contact time, initial concentration, adsorbent dose, and temperature).

3. To elucidate the adsorption mechanisms, kinetics, isotherms, and thermodynamics governing the interaction between graphene oxide and the selected herbicides, and assess the regeneration potential of graphene oxide for sustainable water treatment applications.

3. SCOPE

This work consists in a thorough investigation of graphene oxide as an adsorbent for the atrazine and metribuzin removal from water. The scope covers the production and thorough characterization of graphene oxide employing several analytical approaches to establish structural-property correlations. The vast spectrum of experimental circumstances covered by the adsorption research helps to identify ideal parameters for maximum removal effectiveness, so offering useful information for use in daily life. Providing basic knowledge of the adsorption processes, the research spans mechanical studies using kinetic, isotherm, and thermodynamic analyses. Although concentrated on two particular herbicides, the approaches and results of this work can provide a basis for investigating the efficacy of graphene oxide against other organic pollutants of similar chemical structures, so extending its use in environmental remedial technologies.

4. BACKGROUND

4.1 Structural and Chemical Properties of Graphene Oxide

Derived from controlled oxidation of graphite, graphene oxide is a two-dimensional carbon nanomaterial with special structural and chemical characteristics that make it especially appropriate for uses in environmental remediation. Unlike pure graphene, which consists of a perfectly arranged hexagonal lattice of sp2-hybridized carbon atoms, GO has a disrupted structure with both sp2- and sp³-hybridized domains resulting from the introduction of many oxygen-containing functional groups during the oxidation process.

Originally suggested by Lerf-Klinowski and subsequently improved by many researchers, the structural model of GO shows a sheet-like structure with basal planes containing hydroxyl and epoxy (1,2-ether) groups whereas the sheet margins are mostly adorned with carboxyl and carbonyl functionalities. This heterogeneous distribution of functional groups produces a material with amphiphilic properties, in which hydrophobic portions (pristine graphene-like domains) coexist with hydrophilic parts (oxygen-rich domains), therefore facilitating interactions with many pollutants via several channels.

The electronic characteristics of GO are considerably changed by the oxygen functions as compared to graphene. Due to its wide π-conjugated system, graphene shows remarkable electrical conductivity; yet, the sp³ hybridization in GO disturbs this conjugation and produces semiconducting or insulating behaviour depending on the degree of oxidation. But because the oxygen groups act as active sites for further functionalization and contaminant binding, this electrical change brings new chemical reactivity.

The ionizable functional groups—mostly carboxylic acids (pKa $\approx$ 4-5) and phenolic hydroxyls (pKa $\approx$ 8-10)—govern the acid-base characteristics of GO. GO's surface charge thus changes from somewhat positive in very acidic conditions to progressively negative as pH increases, so affecting its electrostatic interactions with charged impurities. Given changes in solution chemistry, this pH-dependent behaviour offers chances for regulated release and selective adsorption.

Go's increased reactivity and adsorption capacity are a result of the structural flaws brought forth by oxidation—that is, vacancies, holes, and edge sites. Particularly those able to create coordinative interactions with under-coordinated carbon atoms, these flaws sometimes act as high-energy binding sites for toxins. Furthermore, the folded and wrinkled form of GO sheets in solution generates a hierarchical structure with micropores, mesopores, and macropores, therefore enabling mass transfer and offering adsorption sites with different binding energies.

4.2 Chemistry of Metribuzin and Atrazine

Triazine-based herbicides extensively used in agriculture for pre-emergence and post-emergence weed control are metribuzin (4-amino-6-tert-butyl-3-methylthio-1,2, 4-triazin-5(4H)-one) and atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine). Developing appropriate cleanup plans requires a knowledge of their molecular structures, physicochemical characteristics, and environmental behaviour.

Together with a carbonyl group, metribuzin comprises a 1,2,4-triazine ring with amino, methylthio, and tert-butyl substituents. This chemical configuration produces a log Kow (octanol-water partition coefficient) of 1.65 and a modest water solubility (1050 mg/L at 20°C), therefore showing balanced hydrophilic-hydrophobic properties. The amino nitrogen (conjugate acid pKa = 0.99) causes the chemical to have weak basic characteristics; it also exists mostly in its neutral state at pH values significant for the environment. Deprotonation of the amide nitrogen (pKa = 12.8) may occur in very alkaline conditions (pH > 11), therefore introducing negative charges that may affect adsorption behavior.

Compared to metribuzin, atrazine has a 1,3,5-triazine ring containing chloro, ethylamino, and isopropylamino substituents that lowers water solubility (33 mg/L at 25°C) and increases hydrophobicity (log Kow = 2.61). Atrazine's secondary amino groups can protonate at an acidic pH (conjugate acid pKa = 1.7), therefore making the molecule positively charged and maybe improving its interaction with negatively charged adsorbent surfaces. Furthermore, whilst the triazine ring offers opportunities for π-π interactions with sp2-hybridized carbon structures, these amino groups can engage in hydrogen bonding as both donors and acceptors.

With rates quite depending on pH, temperature, and the presence of photosensitizers, both herbicides show photolytic and hydrolytic breakdown in aquatic environments. Under acidic circumstances, atrazine degradation accelerates mostly by hydrolysis of the C-Cl bond; metribuzin is more sensitive to base-catalyzed hydrolysis and undergoes methylthio group oxidation. The adsorption behavior and environmental durability of chemicals can be much changed by these transformation mechanisms.

Sorption-desorption dynamics in soil-water systems affect the environmental mobility of certain herbicides. While metribuzin shows reduced affinity (Koc = 40–60 mL/g), studies have indicated that atrazine exhibits modest sorption to soil organic matter (Koc = 100–200 mL/g), hence increasing leaching potential. This diverse behavior emphasizes the need of creating adsorbents with customized surface qualities to efficiently remove various pollutants from water.

4.3 Adsorption Mechanisms on Graphene Oxide

Operating either concurrently or sequentially depending on the molecular properties of the adsorbate and the solution conditions, the adsorption of organic pollutants on GO entails several interaction processes. Several possible mechanisms have been suggested for triazine herbicides such as metribuzin and atrazine depending on computational analyses and experimental data.

The main process by which aromatic molecules adsorber onto GO is π-π interactions. Especially in areas with low oxygen functionalization, the triazine rings in metribuzin and atrazine can interact in π-π stacking with the remaining sp²-hybridized domains on GO sheets. Usually stronger for compounds with electron-withdrawing substituents (like the chloro group in atrazine), these interactions improve the π-electron deficiency of the aromatic system and strengthen the contact with the electron-rich areas of GO. Wang et al. (2016) computed binding energies of 20–35 kJ/mol for atrazine-GO π-π interactions, therefore stressing their relevance in the whole adsorption process.

Another important mechanism is hydrogen bonding, especially in light of GO's plethora of oxygen functions and the hydrogen bond donor/acceptor groups in the herbicides. Whereas the carbonyl and ether functions of GO can interact with the hydrogen atoms of amino groups, the hydroxyl and carboxyl groups on GO can create hydrogen bonds with the amino groups of atrazine and metribuzin. Li et al. (2017) conducted molecular dynamics simulations showing that, depending on the particular functional groups involved, a single atrazine molecule could make up to 3-4 hydrogen bonds with GO surfaces using binding energies ranging from 10 to 25 kJ/mol.

Particularly at pH values where either the adsorbent or adsorbate bears a net charge, electrostatic interactions are rather important. Protonation of amino groups under acidic conditions (pH < 2) produces positive charges for atrazine that may interact with negatively charged carboxylate groups on GO. Analogously, deprotonated functional groups on GO can reject negatively charged herbicide species at very alkaline pH. The extent of these electrostatic contributions changes with ionic strength since large salt concentrations can screen charges and reduce long-range electrostatic forces.

Particularly those with strong non-polar components like the tert-butyl group in metribuzin and the isopropyl group in atrazine, hydrophobic interactions significantly help organic pollutants to be adsorbed. The inclination of hydrophobic moieties to reduce contact with water, seeking connection with the hydrophobic areas (sp2 domains) on GO surfaces drives these interactions. Usually matching the octanol-water partition coefficient (Kow), the strength of hydrophobic contacts indicates perhaps stronger effects for atrazine than for metribuzin.

Lewis acid-base interactions can develop between electron-rich spots on the molecule (nitrogen atoms, carbonyl oxygen) and electron-deficient areas on GO (such as carbocations at defect sites or metal contaminants). Although these interactions are highly confined and selective, they can greatly affect the total binding energy especially in compounds with strong nucleophilic cores.

The proportionate contribution of every mechanism depends on several elements, among which are:

1. Higher oxidation brings more oxygen functions, hence improving hydrogen bonding potential and lowering accessible sp2 domains for π-π interactions.

2. Solution pH modulates electrostatic interactions and hydrogen bonding capacity, therefore affecting the ionization state of both GO and herbicides.

3. Higher temperatures usually promote hydrophobic contacts while weakening hydrogen bonds and π-π interactions, therefore affecting the thermodynamics of adsorption.

4. Ionic strength: shields electrostatic interactions and can change the shape of GO sheets, therefore influencing the access to adsorption sites.

Knowing these mechanisms helps one to maximize GO-based adsorbents by means of focused changes improving particular interactions with the target pollutants of interest.

5. RESEARCH METHODOLOGY

The aim of the research approach used in this work was to methodically explore the adsorption capacity of graphene oxide (GO) for the elimination from aqueous solutions metribuzin and atrazine. The experimental methodologies, analytical approaches, and data processing tools applied are described in this part.

5.1 Materials and Reagents

Using a modified Hummers' approach as reported by Marcano et al. (2010), high-purity graphene oxide was synthesised. Graphite powder was oxidized under controlled temperatures in a mixture of sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) using potassium permanganate ($KMnO_4$). To get single or few-layer GO sheets, the resulting material was exfoliated and refined through several washing cycles.
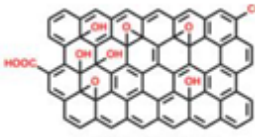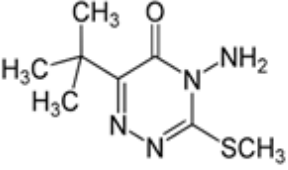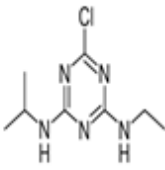
Purchased from a reliable chemical supplier were analytical grade metrizin (4-amino-6-tert-butyl-3-methylthio-1,2,4-triazin-5(4H)-one, >99% purity) and atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazin-5(4H)). To stop photodegradation, stock solutions of each herbicide—1000 mg/L—were made in deionized water and kept at 4°C in amber glass bottles.

5.2 Characterization of Graphene Oxide

The synthesized GO was characterized using multiple analytical techniques to confirm its structural and chemical properties:

1. **X-ray Diffraction (XRD)** was performed to determine the interlayer spacing and crystalline structure using a diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å) in the 2θ range of 5-60° at a scan rate of 2°/min.

2. **Fourier Transform Infrared Spectroscopy (FTIR)** was conducted to identify functional groups present on GO surfaces. Spectra were recorded in the range of 4000-400 cm^{-1} with 32 scans at a resolution of 4 cm^{-1}.

3. **Scanning Electron Microscopy (SEM)** and **Transmission Electron Microscopy (TEM)** were utilized to visualize the morphology and layered structure of GO sheets.

4. **Brunauer-Emmett-Teller (BET)** analysis was performed to determine the specific surface area and pore size distribution using nitrogen adsorption-desorption isotherms at 77 K.

5. **X-ray Photoelectron Spectroscopy (XPS)** was employed to analyze the elemental composition and chemical states of carbon and oxygen in GO.

6. **Zeta Potential** measurements were conducted across a pH range of 2-12 to determine the surface charge characteristics of GO.

Table 1: Physicochemical Properties of Graphene Oxide and Target Herbicides

Property	Graphene Oxide	Metribuzin	Atrazine
Structure	Graphene oxide Sourcehttps://www.graphene-info.com/reduced-graphene-oxide-introduction	Source: https://en.wikipedia.org/wiki/Metribuzin	Source: https://en.wikipedia.org/wiki/Atrazine
Surface Area (m^2/g)	486	-	-
Zeta Potential (pH 7, mV)	-38.5	-	-
Water Solubility (mg/L)	Highly dispersible	1050 (20°C)	33 (25°C)
Log Kow	-	1.65	2.61
pKa	4.3 (carboxyl), 9.8 (phenol)	0.99, 12.8	1.7
Molecular Weight (g/mol)	-	214.3	215.7

a

Characteristics	Average Value
Hydrodynamic Radius	511 ± 37 nm
Zeta Potential	$-36,9 \pm 9,6$ mV
Thickness	$0,78 \pm 0,03$ nm
C/O atomic ratio	$1,9 \pm 0,1$
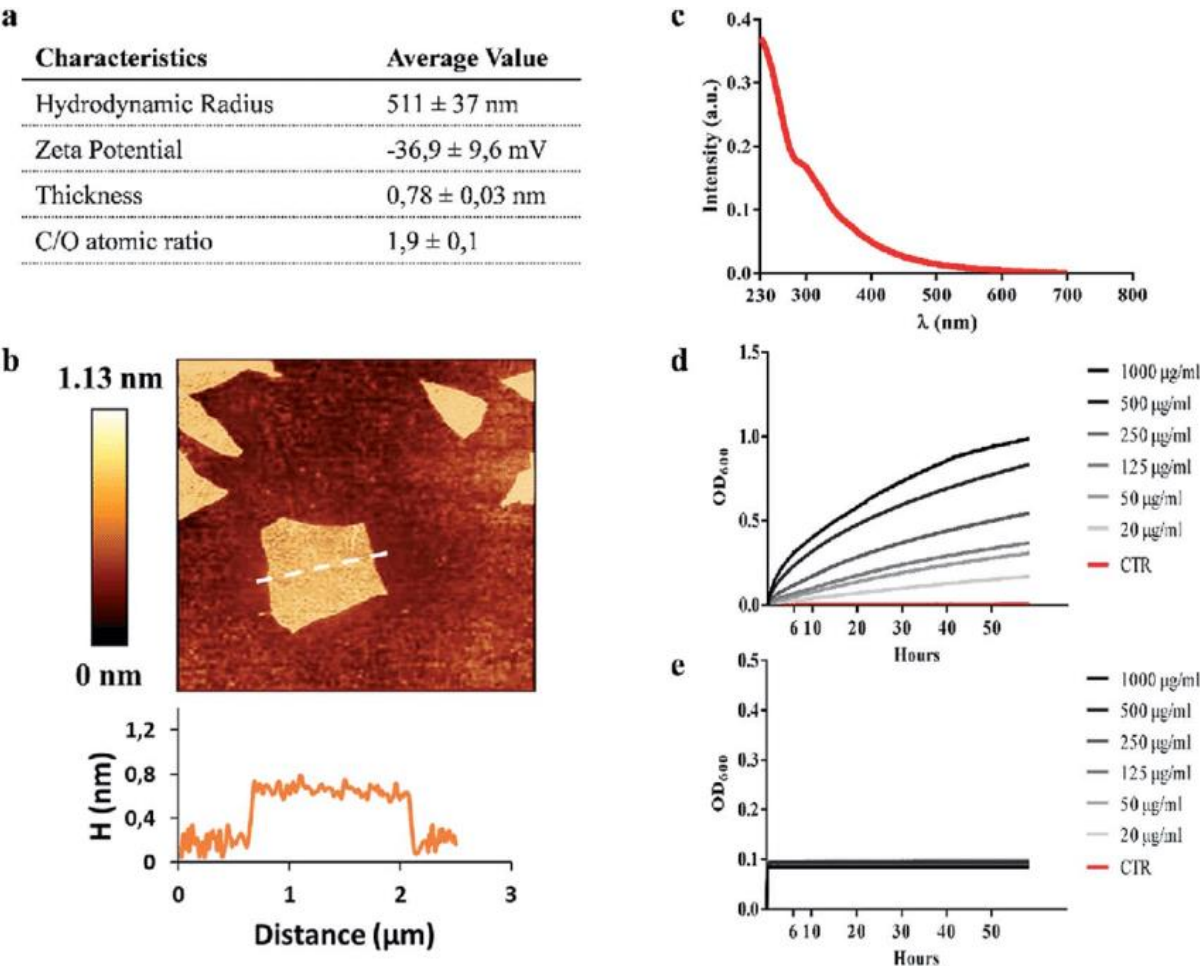
Figure 1: Characterization of Graphene Oxide

5.3 Batch Adsorption Experiments

Under several settings, batch adsorption studies were conducted to assess metribuzin and atrazine removal efficacy by GO. A standard experiment would have a predefined GO (10–500 mg/L) addition to herbicide solutions (1–50 mg/L) in 250 mL Erlenmeyer flasks. On an orbital shaker set at 150 rpm, the mixes were stirred and kept under controlled temperatures (15–45°C).

The following parameters were systematically investigated:

1. **Effect of Contact Time**: Samples were collected at predetermined intervals (5, 15, 30, 60, 120, 240, 360, and 480 minutes) to establish the kinetics of adsorption.

2. **Effect of Initial pH**: The solution pH was adjusted from 2 to 11 using 0.1 M HCl or 0.1 M NaOH to determine the optimal pH for herbicide removal.

3. **Effect of Adsorbent Dosage**: GO concentrations ranging from 10 to 500 mg/L were tested to identify the optimal dosage for maximum removal efficiency.

4. **Effect of Initial Herbicide Concentration**: Adsorption isotherms were constructed using herbicide concentrations from 1 to 50 mg/L at the optimal pH and adsorbent dosage.

5. **Effect of Temperature**: Experiments were conducted at 15, 25, 35, and 45°C to determine thermodynamic parameters.

After reaching equilibrium, samples were filtered through 0.45 µm membrane filters to separate the adsorbent, and the filtrate was analyzed for residual herbicide concentration.

5.4 Analytical Methods

High-performance liquid chromatography (HPLC) fitted with a UV-Vis detector helped to ascertain the amounts of metribuzin and atrazine. Using a C18 reverse-phase column (150 mm × 4.6 mm, 5 µm), the chromatographic separation was carried out under a flow rate of 1 mL/min using a mobile phase comprising acetonitrile and water (60:40, v/v). For metribuzin, the detection wavelengths were assigned 294 nm; for atrazine, they were 225 nm. For both the herbicides, the limit of detection (LOD) was 0.05 µg/L.

5.6 Data Analysis

The adsorption capacity at equilibrium, q_e (mg/g), was calculated using the following equation:

$$q_e = (C_0 - C_e) \times V / m$$

where C_0 and C_e are the initial and equilibrium concentrations of the herbicide (mg/L), respectively, V is the volume of the solution (L), and m is the mass of GO adsorbent (g).

The removal efficiency (%) was calculated as:
Removal efficiency (%) = $[(C_0 - C_e) / C_0] \times 100$

Pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were applied to investigate the rate-controlling processes in adsorption kinetics. The maximum adsorption capacity and adsorption intensity were determined by fitting equilibrium data to Langmuir, Freundlich, and BET isotherm models.

The experimental results were validated by statistical analysis conducted under analysis of variance (ANOVA) with a significance threshold of 0.05. Every experiment was carried out in triplicate; the findings were presented as mean values with standard deviations.

6. DISCUSSION

6.1 Structural and Surface Properties of Graphene Oxide
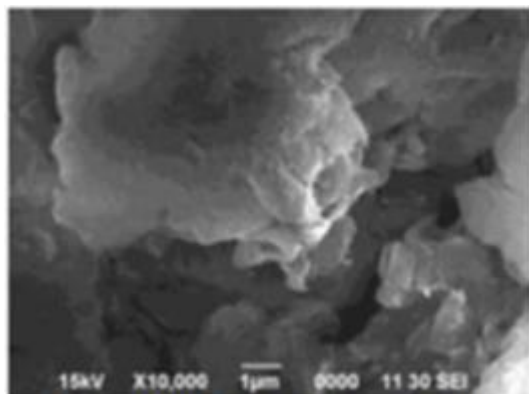
Figure 2: SEM at 10K magnification
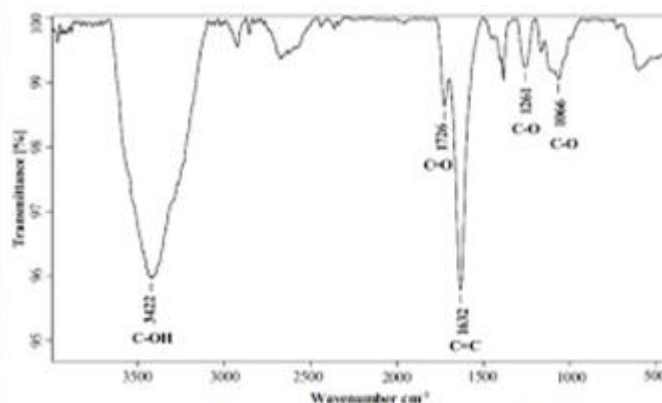
Figure 3: FTIR spectra of GO

The thorough characterizing of the produced GO validated its successful preparation and exposed important characteristics directly affecting its adsorption capacity for herbicides. With an interlayer spacing of roughly 0.82 nm, XRD investigation revealed a distinctive peak at $2\theta = 10.8°$, significantly higher than that of graphite (0.34 nm). This enlarged distance helps water molecules and herbicide chemicals to be intercalated between GO layers, hence improving access to adsorption sites.

Various oxygen-containing functional groups—hydroxyl (3422 cm⁻¹), carbonyl (1726 cm⁻¹), epoxy (1261 cm⁻¹), and C=C aromatic domains (1632 cm⁻¹)—were verified by FTIR spectra on GO surfaces. As the literature review describes, the plethora of these functional groups offers several binding sites for herbicide molecules via hydrogen bonding, π-π interactions, and electrostatic attraction.

Under SEM and TEM, the morphological study revealed that GO comprised of folded and wrinkled sheets with lateral dimensions ranging from 0.5 to 5 μm, producing a hierarchical structure with micro, meso, and macropores. BET analysis found a specific surface area of 486 m²/g. XPS research revealed a C/O atomic ratio of about 2.1, implying a significant degree of oxidation. This high surface area combined with the varied pore structure promotes fast mass transfer and affords several adsorption sites for the target herbicides. With relative abundances of 41.3%, 35.7%, 14.8%, and 8.2%, respectively, deconvolution of the C1s peak exposed contributions from C-C/C=C (284.6 eV), C-O (286.7 eV), C=O (287.9 eV), and O-C=O (289.1 eV). This dispersion of carbon-oxygen functions supports the suggested adsorption mechanisms including several kinds of interactions and confirms the FTIR results.

6.2 Adsorption Performance for Metribuzin and Atrazine
The batch adsorption experiments demonstrated that GO exhibits excellent removal capabilities for both herbicides, albeit with different affinities and mechanisms.

6.2.1 Effect of Solution pH
The adsorption of both herbicides was strongly pH-dependent, with maximum removal efficiencies observed at pH 3-4 for atrazine (94.7%) and pH 5-6 for metribuzin (89.3%). This differential behaviour can be explained by considering the molecular structures and ionization states of the herbicides in relation to the surface charge of GO.
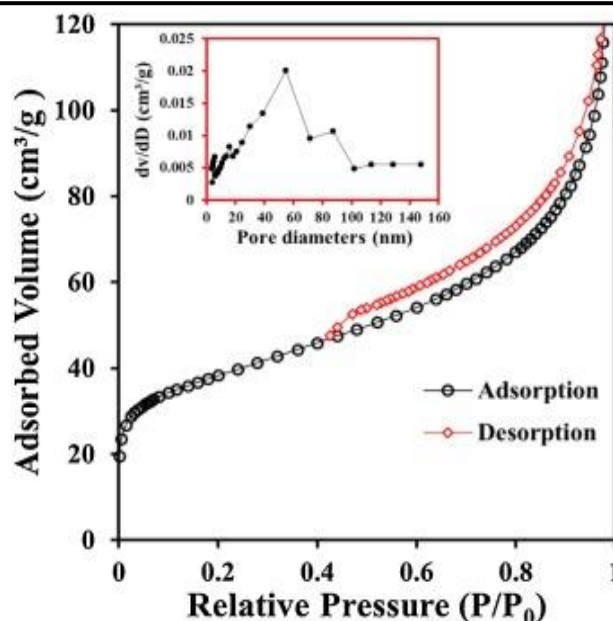
Figure 4: Adsorption Isotherms for nitrogen on GO (BET Analysis for GO)

Whereas atrazine lives mostly in its neutral form, GO's surface becomes less negative at low pH values (2-4) when carboxyl groups are protonated (pKa approximates 4-5). Under these conditions, with minimum electrostatic repulsion, hydrogen bonding and π-π interactions predominate the adsorption process. The increased negative charge on GO surfaces (from deprotonation of carboxyl and phenolic groups) generates electrostatic repulsion with any partially negative areas on atrazine molecules as pH rises beyond 7, therefore lowering the adsorption effectiveness.

For metribuzin, the ideal pH range (5–6) corresponds to situations whereby GO surfaces exhibit moderate negative charge while metribuzin stays neutral. Whereas the triazine ring interacts π-π with graphene domains, the carbonyl and amino groups in metribuzin can establish strong hydrogen bonds with hydroxyl groups on GO.

6.2.2 Adsorption Kinetics
The kinetic experiments showed fast initial adsorption rates for both herbicides; around 70% of equilibrium capacity was reached in the first 60 minutes, then the approach to equilibrium slowed over 4–6 hours. This biphasic pattern points to first adsorption on easily accessible surface locations then slower diffusion into porous materials or less accessible areas between stacked GO sheets.

The pseudo-second-order model (R^2 > 0.995) best fit the kinetic data, suggesting that either rate-limiting chemisorption mechanisms involving electron sharing or exchange between adsorbent and adsorbate may be present. The computed rate constants (k_2) for atrazine were 4.82×10^{-1} g/mg·min and for metribuzin were 3.67×10^{-1} g/mg·min, implying rather faster adsorption kinetics for atrazine. This variation could be ascribed to atrazine's increased hydrophobicity (log Kow = 2.61 vs. 1.65 for metribuzin), therefore improving its affinity for the hydrophobic regions of GO.

6.2.3 Adsorption Isotherms
Different isotherm models were investigated in the equilibrium adsorption data to grasp the adsorption processes and capacity. With R^2 > 0.992, the Langmuir model suggested monolayer adsorption on energetically homogenous locations for both herbicides. Derived from the Langmuir equation, the maximum adsorption capacities (q_{max}) for atrazine were 35.7 mg/g; for metribuzin at 25°C and ideal pH levels were 29.4 mg/g.

There are various reasons why atrazine's higher adsorption capability than metribuzin can be justified:
1. The triazine ring's π-electron shortage is enhanced by the chloro substituent in atrazine, therefore increasing π-π interactions with GO's sp2 domains.

2. Stronger connection with the hydrophobic areas of GO sheets is promoted by atrazine's greater hydrophobicity.

3. The ethylamino and isopropylamino groups in atrazine offer several locations for hydrogen bonding with oxygen functions on GO.

Both herbicides showed favorable adsorption (1 < n < 10) with the Freundlich constant (n) values of 2.37 for atrazine and 2.05 for metribuzin. The somewhat higher n value for atrazine points to a more heterogeneous adsorption process maybe including several contact mechanisms with different intensities.

6. LIMITATION

- The research mostly concentrates on synthetic aqueous solutions including individual herbicides (metribuzin and atrazine) under controlled laboratory conditions, which may not fully reflect the complexity of real environmental water matrix including multiple contaminants, dissolved organic matter, and various competing ions that could influence the adsorption performance of graphene oxide.

- Although batch adsorption studies offer important new perspectives on adsorption behavior, they do not consider the dynamic flow circumstances experienced in continuous treatment systems.

- Important issues for sustainable implementation are long-term stability, potential leaching of adsorbed herbicides, or the environmental fate of spent graphene oxide, are not a part of this research addresses.

7. CONCLUSION

With maximal adsorption capacities of 35.7 mg/g and 29.4 mg/g respectively, this work shows that graphene oxide is a quite efficient adsorbent for removing metribuzin and atrazine from aqueous solutions. Multiple factors control the adsorption process: π-π interactions, hydrogen bonding, and hydrophobic effects; relative contributions depend on solution chemistry. For atrazine, the ideal pH range for best elimination effectiveness is 3–4; for metribuzin, it is 5–6. Although competing ions and natural organic matter lower adsorption efficacy, GO shows great removal capacity under environmentally relevant settings, therefore highlighting its possible use in actual water treatment systems.

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SYNTHESIS AND CHARACTERIZATION OF 2-(4-BROMO-2-FLUOROPHENYL)-3-CHLORO-4H-1-BENZOPYRAN-4-ONE DERIVATIVES BY NON-CONVENTIONAL METHOD

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ABSTRACT

4-Bromo-2-fluorobenzaldehyde when treated with substituted hydroxyacetophenones yields chalcones 3. These chalcones were cyclized under microwave irradiation using DMSO/ CuCl$_2$ gave the compound 2-(4-Bromo-2-fluorophenyl)-3-chloro-4H-1-benzopyran-4-one 4. The structures of compounds have been established on the basis of spectral data. These compounds were screened for their antimicrobial activities.

Keywords: Chromones, Microwave, Eco-friendly

INTRODUCTION

Chromones and their derivatives are broadly available in nature. Chromones coming from synthesis or natural products, plays an important role in life science[1]. The activities are associated with chromone moieties are antitumor, antioxidant, antiallergic, anti-inflammatory and antibacterial.[2] Chromones molecules having heterocyclic substituents at 2-position have been reported to shows antibacterial, antifungal, antitumor, activities. Some chromones also possess potential HIV integrase inhibition activity.[3-5]

The introduction of fluorine and /or perfluoroalkyl groups strategically in heterocyclic systems, may drastically modifies the chemical properties, and biological activities also for the synthesized molecules [6-10]

The chromones with halogen at C-3 position has great significance in terms of their anti-microbial activities and medicinal values. The well-known method is halogenation of C-3 substituted Chromones by using variety of halogenating agents [11-14]. The syntheses of 3-Chlorochromones by using DMSO/ CuCl$_2$ as a catalyst is the interesting route to introduce chlorine at C-3 position in chromone.

Activities associated with these nuclei and advantages of microwave in organic synthesis prompted us to synthesize new chromones by microwave methods.

RESULTS AND DISCUSSION

2- Hydroxy acetophenones (substituted) **1** on treatment with fluorinated aldehydes **2** afforded compound **3** chalcones. Chalcone showed IR absorption bands at 3530 cm^{-1} due to –OH functionality. ^{1}HNMR shows peak at 11.90 δ due to –OH protons. The structure of compounds was also confirmed by Mass spectrum.

Compound **3** on treatment with DMSO/ CuCl$_2$ under microwave irradiation yields compound **4** named chlorochromones. Chlorochromones are confirmed by IR frequencies like 1665 cm^{-1} for C=O and 1115 cm^{-1} for Ar-Cl. This structure is also confirmed by ^{1}HNMR and Mass spectrum.

ANTIMICROBIAL ACTIVITY

Synthesized chlorochromones were screened for their antibacterial activities against the bacteria *B. Subtilis, E-coli* and *A. Niger* using standard antibiotic drug Streptomycin. The biological activities associated with these compounds have been evaluated by turbidity method using DMSO as a solvent. MIC was determined after 48 hr or 72 hr incubation. Incubation zone were measured in mm and results obtained are shown in Table **2.** Most of the compound showed moderate and few compounds showed good antibacterial activity against *E-coli & B. Subtilis.*

EXPERIMENTAL

The melting points were determined in open capillary tubes are uncorrected. IR spectra were recorded on a Perkin-Elmer FT spectrophotometer in a KBr disc. ^{1}H NMR spectra were recorded on a Bruker Avance II 400 MHz spectrophotometer DMSO-d6 as a solvent and TMS as an internal standard (chemical shift in δ values). Mass spectra were obtained on a Finnigan mass spectrometer. Purity of the compounds was checked by TLC on silica gel G plates.

SCHEME
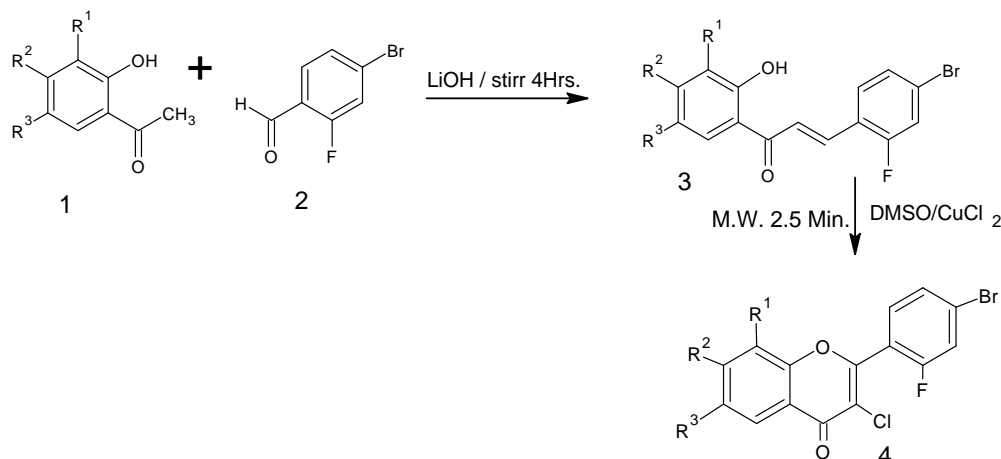
General procedure for Synthesis of 2-(4-Bromo-2-fluorophenyl)-3-chloro-4*H*-1-benzopyran-4-one Derivatives by microwave irradiation:

(2E)-3-(4-bromo-2-fluorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one (1) (0.001mol) and DMSO (10 ml) and excess of $CuCl_2$ (2 gms.) were taken in 50 ml beaker. It was then exposed to microwave irradiation at an output of 300W for 2-3 minutes. After completion of reaction (checked by TLC) contents were cooled to room temperature and poured over crushed ice, solid thus obtained was separated by filtration, washed with water, followed by HCl solution and again with water. Product was crystallized with alcohol.

This typical experimental procedure was used for the preparation of all the compounds listed in **Table 1**. The structures of synthesized compounds have been confirmed by IR, NMR and mass spectral studies.
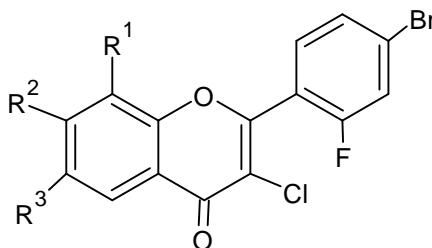
Table 1 - Characterization data of the 3-chlorochromones.

Compd. No.	R_1	R	R_3	Yield (%)	Microwave Time (min)	M.P. (^{0}C)
4a	H	H	Cl	82	2.5	198
4b	H	H	Me	85	2.5	205
4c	H	H	Br	76	2.5	188
4d	H	Me	H	78	2.5	176
4e	H	H	H	76	2.5	180

IR SPECTRA

IR spectra of representative compounds in this series were scanned on Perkin-Elmer FT spectrophotometer. IR spectrum (KBr disc) of **4a** showed following characteristic absorption bands.
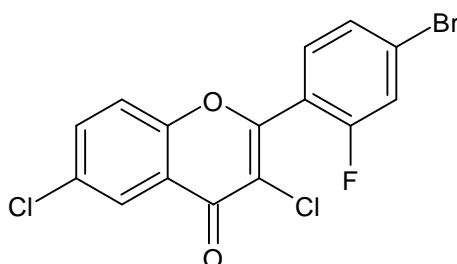
4a 3068cm^{-1} (Ar C-H), 1665cm$^-$ (C=O stretch), 1614 & 1512 cm^{-1} (aromatic ring), 1047 cm^{-1} (C-Br stretch), 1115 cm^{-1}(C-Cl stretch), 1135 cm^{-1}(C-F stretch)

NMR SPECTRA
The ^{1}H NMR of a few compounds were scanned on Brucker 300 MHz FT spectrometer using *DMSO+CDCl$_3$* as a solvent and TMS as an internal standard.

The ^{1}H NMR spectra of **2a** showed following characteristic signals.

7.51 δ to 8.16 δ multiplet 6H aromatic

MASS SPECTRA
The mass spectra of **4a** showed following peaks in its spectrum.

(m/e) =388 (M$^+$, 100%).

Table 2: Antibacterial activity of compounds

Compd.	E. coli	B. Subtilis	A. Niger
4a	9	10	8
4b	10	9	8
4c	9	9	9
4d	8	8	8
4e	9	9	10
Streptomycin	8	9	11

CONCLUSION
The synthesized chlorochromones were screened for their antibacterial activities against the bacteria *B. Subtilis, E-coli* and *A. Niger* using standard antibiotic drug Streptomycin. Most of the compound showed moderate and few compounds showed good antibacterial activity against *E-coli & B. Subtilis.*

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SYNTHESIS AND ANTI-MICROBIAL ACTIVITY OF 2-SUBSTITUTED BENZIMIDAZOLE DERIVATIVES BY USING LEMON JUICE AS AN EFFICIENT BIO-CATALYST

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ABSTRACT

The 2-substituted benzimidazole derivatives were prepared from the condensation reaction between o-Phenylenediamine and various carbonyl compounds using lemon juice as an efficient bio-catalyst. The yield of all benzimidazole derivatives were found to be in the range of 60-80%. The purity of the compounds was ascertained by melting point and TLC. The characterization of synthesized benzimidazole derivatives were carried out by using IR, ^{1}H NMR, ^{13}C NMR and Mass spectroscopy. The benzimidazole derivatives were screened against Gram Positive bacteria Staphylococcus aureus, Gram Negative bacteria Salmonella typhi and fungal culture of Candida albicans using tube dilution method.

Keywords: Benzimidazole, o-Phenylenediamine, lemon juice, anti-microbial, bio-catalyst.

1. INTRODUCTION

Green Techniques are closely aligned with the 12 principles of Green Chemistry, which focus on sustainability, energy efficiency, reduced toxicity of reagents, intermediates, and final products, minimizing harm to the environment and human health, lowering the risk of global warming, and promoting the more efficient use of natural resources and agricultural waste.
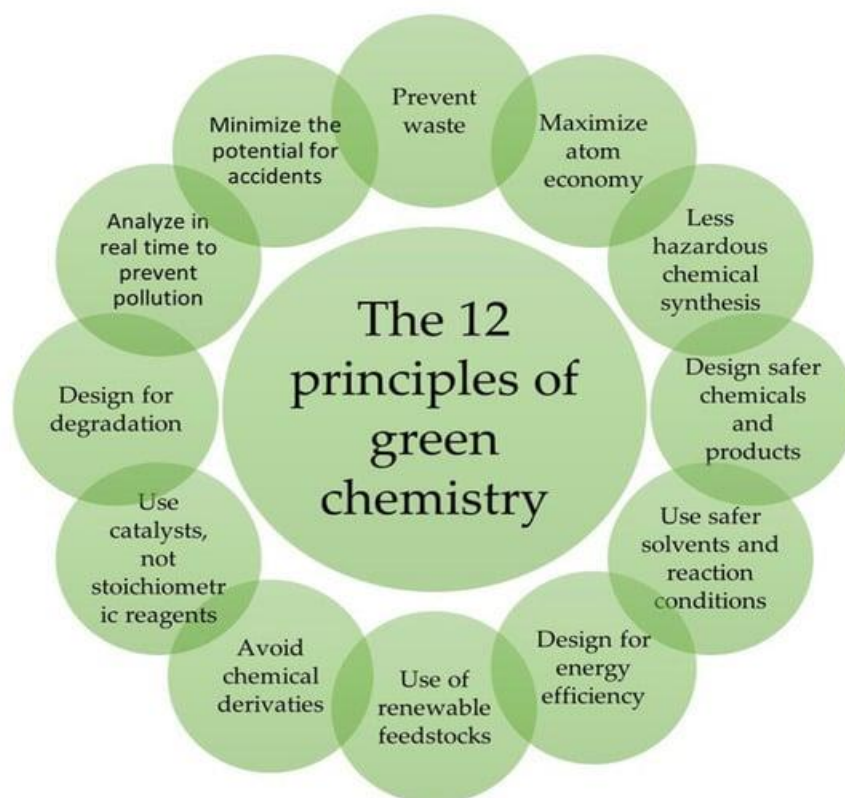
Figure 1. 12 principles of Green Chemistry [1]

Benzimidazole was traditionally synthesized through methods that were time- and energy-intensive, produced byproducts, had low atomic efficiency, and required hazardous solvents. To address these drawbacks, modern green techniques have been developed, including the use of water extracts from agricultural waste as catalysts [2], solvent-free methods [3], ionic liquids [4], and lemon juice as a potent catalyst [5], among others.

Benzimidazole is a crucial pharmacophore and a favoured structure in medicinal chemistry, exhibiting a wide range of therapeutic properties such as antiulcer, antihypertensive, analgesic, antiviral, antifungal, antibacterial, anticancer, and antihistaminic activities [6].
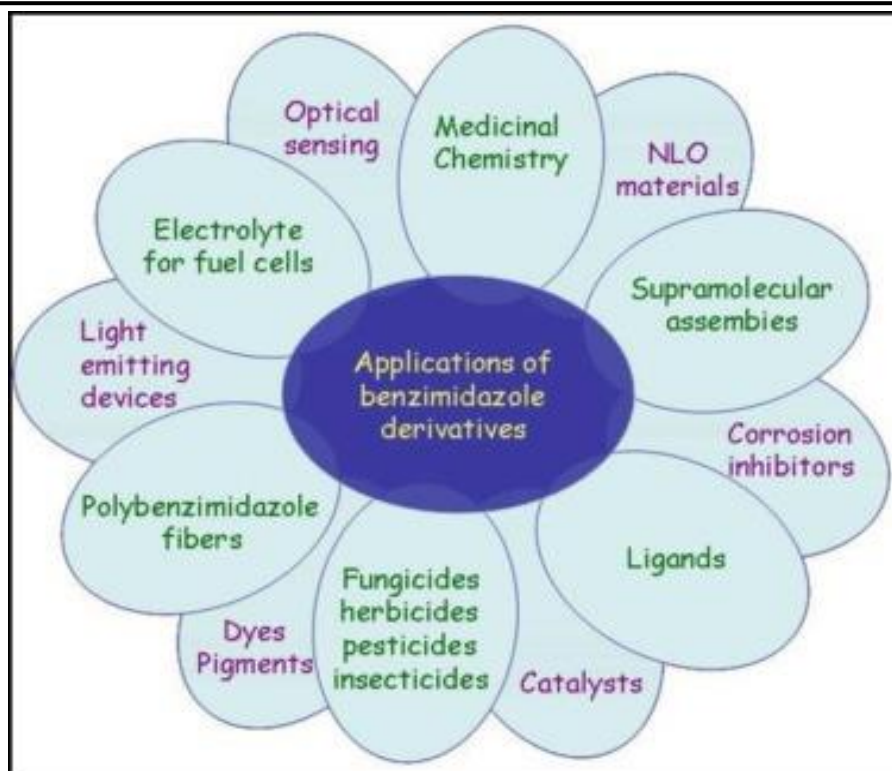
Figure 2. Applications of Benzimidazole [7]

In this study, we present the synthesis of 2-substituted benzimidazole derivatives through the condensation of ortho-phenylenediamine with different aldehydes, using lemon juice as an oxidative biocatalyst.
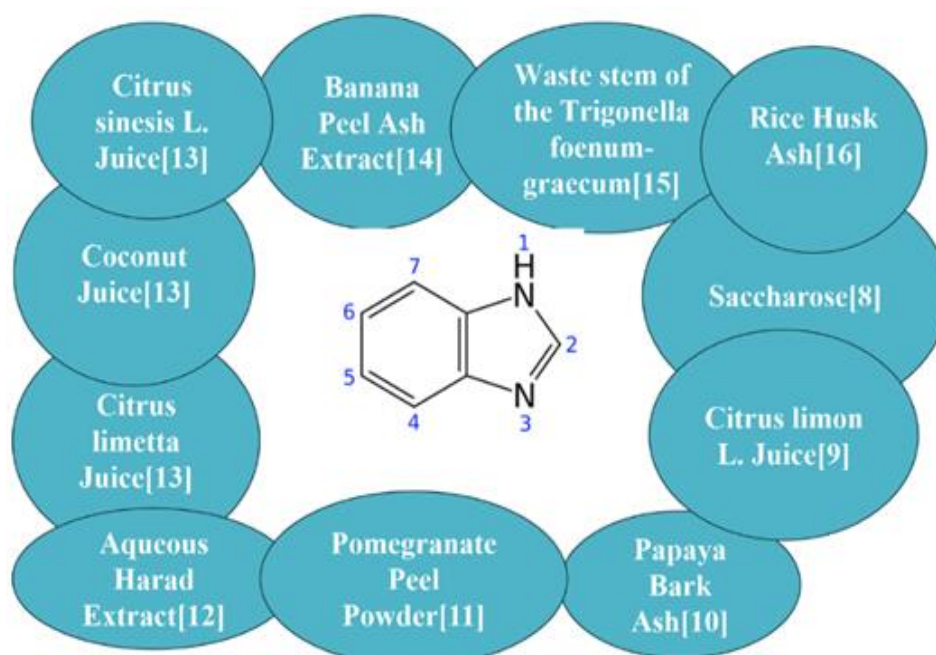
Figure 3. Use of Plant based Bio-Catalyst for synthesis of 2-Aryl Benzimidazole Derivatives

2. MATERIALS AND METHODS

Solvents and reagents were commercially sourced from local suppliers and used as received without further purification. Melting points of all synthesized compounds were determined in open capillary tubes and were uncorrected. The purity of the compounds was checked by TLC on pre-coated silica gel G plates and visualized with iodine vapour. The IR spectra were recorded on PerkinElmer Frontier FT-IR spectrophotometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on Bruker Ultra shield, Avance II model NMR spectrometer. Chemical shifts values of ^{1}H and ^{13}C NMR are reported in ppm relative to tetramethyl silane (TMS) as an internal reference in CDCl$_3$/DMSO-d6 as a solvent. Mass spectra were recorded on AB SCIEX QTRAP 3200 model LC–MS spectrophotometer.

3. EXPERIMENTAL

3.1 General Procedure for Extraction of Citrus Limon:

Fresh lemons were bought from the market, cut in half, and the juice was extracted using a lemon squeezer at room temperature. The extracted juice was then filtered through a household sieve to remove any solid particles. The resulting clear juice was used as a biocatalyst.

3.2 Method for synthesis of 2-aryl benzimidazoles:

A mixture of o-phenylenediamine (1 mmol), arylaldehyde (1 mmol), and lemon juice (8-10 ml) was mechanically stirred in a round-bottom flask for 15-20 minutes at room temperature. The reaction progress was monitored by TLC. Once the reaction was complete, the mixture was poured into ice-cold water, and the crude product was filtered and recrystallized from ethanol.
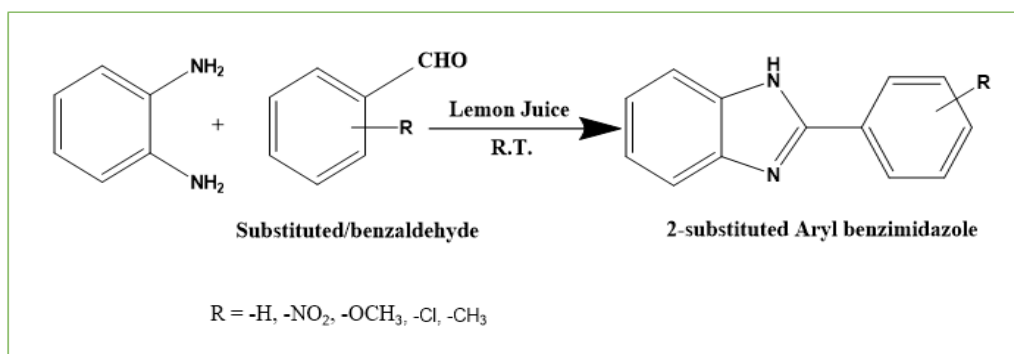
Scheme I: Method for synthesis of 2-aryl benzimidazole

Table No. 1: Physical Data of Synthesized compounds.

Sr. No.	OPDA	Aldehyde	Product	Colour	Yield (%)	M.P. (^{0}C) Observed	M.P. (^{0}C) Reported
1.				Pale Yellow	80	290-293	289[17]
2				White	78	285-288	290[18]
3				White	75	232-235	234[18]
4				Dark Yellow	70	323-328	325[19]
5				Dark Yellow	80	262-266	265-265[10]
6				Brown	78	205-210	204-206[10]
7				White	76	230-233	232[20]
8				Brown	69	155-159	156-158[17]
9				Yellow	73	222-226	224[17]
10				Yellow	78	195-200	199-200[19]
11				Orange	69	270-275	272-274[20]

3.3 Spectral Analysis of selected compounds:

2-Phenyl-1H-benzimidazole (Sr. No. 1):

IR (νmax, cm^{-1},KBr): 3047, 2920, 1623, 1450

^{1}H NMR (400 MHz,DMSO-d6): δ 7.2 (d, 1H, Ar), 7.38-7.46 (m, 3H, Ar), 7.51-7.53(m, 4H, Ar), 7.6-7.63 (m, 4H, Ar), 7.91-7.93 (m, 1H, Ar), 9.94(bs, 1H, NH)

^{13}C NMR (100 MHz, DMSO-d6): δ 124.5, 126.1,127.5, 128, 132.5, 133, 134.5, 135, 136.1, 138

MS (m/z): 195.09(M+) (cal: 194.23)

2-(2-Nitrophenyl)-1H-benzimidazole (Sr. No. 5):

IR(νmax, cm^{-1}, KBr): 3275, 3127, 1645, 1453;

^{1}H NMR (300 MHz,DMSO-d6): δ 7.37-7.41 (m, 2H, Ar), 7.55-7.68 (m, 4H, Ar),7.91-7.93 (d, 1H, Ar), 8.31-8.32 (d, 1H, Ar), 12.46 (bs, 1H, NH)

^{13}C NMR (100 MHz, DMSO-d6): δ 116.7, 12.2, 123.3, 123.6,124.4, 125.7, 129.6, 134.6, 135.8, 138.1, 139.9, 146.3, 150.4

MS (m/z): 240 (M+) (cal: 239.23)

2-(4-Methylphenyl)-1H-benzimidazole (Sr. No. 9):

IR (νmax, cm^{-1}, KBr): 3279, 3022, 1634, 1471

^{1}H NMR (400 MHz, DMSO-d6): δ 1.23 (s, 3H, CH3), 7.20-7.38 (m, 3H, Ar), 7.51-7.65 (m, 2H, Ar), 8.05-8.07 (d, 2H, Ar), 8.30 (s, 1H, Ar), 12.87 (bs, 1H, NH)

^{13}C NMR (100 MHz, DMSO-d6): δ 21.22, 111.3, 118.9, 121.5, 126.8, 127.8, 127.7, 129.9, 134.9, 139.9,143.9, 151.6

MS (m/z): 209.10 (M+) (cal: 208.26)

2-(4-Hydroxyphenyl)-1H-benzimidazole (Sr. No. 11):

IR (νmax, cm^{-1}, KBr): 3467, 3358, 3054, 1643, 1461

^{1}H NMR(400 MHz, DMSO-d6): δ 6.96-6.99 (d, 2H, Ar), 7.31-7.33 (m,2H, Ar), 7.66-7.68 (d, 2H, Ar), 7.62-7.68 (m, 2H, Ar), 8.59 (s,1H, OH), 12.29 (bs, 1H, NH)

^{13}C NMR (100 MHz, DMSO-d6):δ 115.9, 116.1, 116.9, 122.2, 124.2, 125.1, 126.7, 136.2, 138.3,150.2, 160.3.

MS (m/z): 211 (M+) (cal: 210.23)

4. ANTI-MICROBIAL ACTIVITY

The in vitro testing of synthesized compounds were carried out against Gram Positive Bacteria *Staphylococcus aureus*, Gram Negative Bacteria *Salmonella typhi* and against fungal culture of *Candida albicans*.

Method: Tube Dilution Method [21]

Bacterial Culture Medium: Mueller-Hinton (M.H.) broth as a culture medium.

Fungal Culture Medium: Sabouraud's Agar Slants as a culture medium.

Standard Control: Ampicillin (M.I.C = 0.01 μg/mL) against Gram Positive Bacteria *Staphylococcus aureus*.

Trimethoprim (M.I.C = 1 μg/mL) against Gram Negative Bacteria *Salmonella typhi*.

Miconazole (M.I.C = 0.625 μg/mL) against *Candida albicans*.

Preperation of Drug Solution: 0.01 gm (10 mg) of drug sample dissolved in 10 mL dimethyl sulfoxide (D.M.S.O) to give stock solution of 1000 μg/mL

Table No. 2: Serial Dilutions of drug samples.

Drug stock solution in (mL)	M.H. broth/Sabouraud's broth in (mL)	Concentration (µg/mL)
2 mL	8 mL	200 µg/mL
1 mL	9 mL	100 µg/mL
0.5 mL	9.5 mL	50 µg/mL
0.4 mL	9.6 mL	40 µg/mL
0.2 mL	9.8 mL	20 µg/mL
0.1 mL	9.9 mL	10 µg/mL

Table No. 3: Result of Anti-Microbial Activity.(N.A.: Not Active at/below 200 µg/mL)

Sr. No.	Name of the Product	S. aureus (µg/mL)	S. typhi (µg/mL)	C. albicans (µg/mL)
1	2-Phenyl-1H-benzimidazole	N.A.	N.A.	N.A.
2	2-(4-Chlorophenyl)-1H-benzimidazole	100	200	200
3	2-(2-Chlorophenyl)-1H-benzimidazole	100	200	200
4	2-(4-Nitrophenyl)-1H-benzimidazole	50	100	200
5	2-(2-Nitrophenyl)-1H-benzimidazole	100	200	200
6	2-(3-Nitrophenyl)-1H-benzimidazole	50	200	200
7	2-(4-Methoxyphenyl)-1H-benzimidazole	50	100	100
8	2-(2-Methoxyphenyl)-1H-benzimidazole	100	100	200
9	2-(4-Methylphenyl)-1H-benzimidazole	200	200	N.A.
10	2-(2-Methylphenyl)-1H-benzimidazole	N.A.	N.A.	N.A.
11	2-(4-hydroxyphenyl)-1H-benzimidazole	50	100	100

5. RESULT AND DISCUSSION

2-Substituted aryl benzimidazoles are synthesized in an eco-friendly manner using lemon juice as an effective biocatalyst at room temperature through mechanical stirring. This method is simple to perform, requires no complex setup, is energy-efficient, and cost-effective. In contrast, the manual grinding method using a mortar and pestle is time-consuming and demands significant physical effort.

The antimicrobial activity results are moderate. The antimicrobial screening could have been enhanced if substituted OPDA had been used. Additionally, aldehydes with stronger electron-withdrawing groups might have yielded better antimicrobial results.

6. CONCLUSION

The synthesis of benzimidazole through the green techniques outlined here achieved a good yield of around 70% to 80%. Employing a sonicator or microwave-assisted synthesis with lemon juice as an efficient biocatalyst might have further shortened the reaction time.

By all above discussion it is concluded that biological activity enhanced by or dependent on:

1. Electron withdrawing functional groups

2. Highly substituted OPDA

3. Biologically active substitutions

4. Hyperconjugation.

7. CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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GRAFTING POTATO STARCH WITH MONOMER METHACRYLAMIDE, USING POTASSIUM PERSULPHATE AS AN INITIATOR

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ABSTRACT

Synthesis of graft copolymers made from potato starch and methacrylamide was done by initiator potassium persulphate (PPS). Optimum conditions for the reaction were systematically examined by studying the effects of various factors like, the variation in concentration of the initiator, the variation in the concentration of the monomer, the polymerization time, the temperature of the reaction, the material-to-solvent ratio, the inclusion of alcohol in the medium, and the stirring speed. Formation of graft copolymers was further confirmed by Gravimetric analysis like grafting percentage, grafting efficiency, and % Add on.

Keywords: *Graft copolymers, Methacrylamide, Potassium persulphate (PPS), Potato starch, Optimization, Gravimetric estimation, Grafting parameters.*

1. INTRODUCTION

Starch, a naturally abundant and sustainable polysaccharide, is a promising material for diverse applications due to its biocompatibility, biodegradability, and low cost. However, its limitations, like poor water solubility and thermal instability, makes it necessary to have chemical modifications to enhance its performance[1]. Graft copolymerization, particularly with vinyl monomers, have proved to be a potential technique, effectively merging the desirable attributes of starch with synthetic polymers. Grafting of vinyl monomers onto starch backbones introduces functional groups, enhancing properties such as metal ion binding and extending shelf-life. The resultant semi-synthetic polymers offer alternatives to petroleum-based materials, addressing environmental concerns. Methacrylamide (MAM) is a vinyl monomer that can be grafted onto starch to improve its properties, such as water absorbency, film-forming ability, and mechanical strength[2]. Graft copolymers of starch and MAM have potential applications in various fields, such as superabsorbents[3], flocculants[4], and drug delivery systems[5].

Potassium persulfate ($K_2S_2O_8$) is a commonly used initiator for graft copolymerization due to its high efficiency and low cost. It can generate free radicals that initiate the polymerization of vinyl monomers and grafting onto the starch backbone[11].

In this study, we investigated the graft copolymerization of MAM onto potato starch using $K_2S_2O_8$ as an initiator. The effects of various reaction conditions on the grafting process were studied to optimize the reaction conditions. The graft copolymers were characterized by gravimetric analysis to determine the grafting efficiency and grafting parameters.

2. EXPERIMENTAL SETUP

2.1 Materials used:

Pure potato starch, LR grade (Loba Chemie Pvt. Ltd, India) was dried in an air oven at 110 ^{0}C for about 10 hrs to remove moisture. Experimentally, it has been found that 10 hours is sufficient time for drying starch to make it moisture free. Potassium persulphate (PPS)[(AR), (Loba Chemie Pvt. Ltd, India) used as supplied. A 0.1 mol/L solution of PPS was prepared in distilled water. Methacrylamide (MAM) (LR) (Otto Chemika Biochemika Reagents, Germany) was used as supplied.

2.2 Graft Copolymerization

2g of pure dried potato starch was taken in a beaker and 70 ml of distilled water was added to make a homogenous starch slurry. The beaker was kept in a water bath at a constant temperature for further reaction. A predetermined amount of PPS was added to the slurry and allowed to react for ten minutes to produce free radicals on the starch backbone. Then a known amount of monomer was added, and a total volume was made up to 100 mL by adding distilled water. This was carried out with constant stirring of 300 rpm. The reaction was carried out for a duration of 180 minutes. The synthesized graft copolymer was filtered using Whatman filter paper no. 41. The homopolymer of MAM (PMAM) formed in reaction mixture is highly soluble in water. Consequently, it was subjected to multiple washings with warm water to ensure the complete elimination of PMAM. It was further dried for 24 hours at 70^{0}C in a vacuum oven and was weighed. [11, 14] Control reactions were also conducted under same conditions and as per above process except addition of monomer. [16]

2.3 Parameters for Grafting

The percentage of graft efficiency (%GE), percentage of grafting (%G), and percentage of add-on (%Add-on) were calculated using the following formulas:[6]

$$\%GE = 100\ (W_2 - W_1)\ /\ W_3$$

$$\%G = 100\ (W_2 - W_1)\ /\ W_1$$

$$\%Add\text{-}on = 100\ (W_2 - W_1)\ /\ W_2$$

Where W_1 is the weight of pure starch, W_2 is the weight of the graft copolymer, and W_3 is the weight of the monomer.

2.4 Gravimetric estimation

A successful grafting was determined through precise gravimetric analysis. The initial mass of the starch substrate (W_1), the final mass of the resulting graft copolymer (W_2), and the quantity of monomer introduced (W_3) were recorded systematically. An increase in the mass of the reaction product relative to a control sample was an indicator of successful grafting. This increase in the residual mass was used to determine the grafting parameters like, percentage grafting efficiency (%GE), percentage grafting (%G) and % Add-on. [16,17].

3. RESULTS AND OBSERVATIONS

Potato starch was chosen for grafting because it's abundant, renewable, biodegradable, and readily accessible. The main purpose of this research was to attach methacrylamide (MAM) molecules to the potato starch chains through a chemical process called graft copolymerization.

This technique allows us to create starch-based materials with tailored properties. [7]

3.1 Physical appearance

The shade of the grafted copolymer was white in colour and were crystalline in nature.

3.2 Evidence for grafting

The water-soluble homopolymer, poly(methacrylamide) (PMAM), was effectively removed through washing with warm water. Even after this removal, a consistent increase in the weight of the reaction residue was observed in all graft copolymerization reactions compared to the control. This weight gain is evidence of successful monomer grafting onto the starch backbone[8].

To quantify the extent of grafting, we calculated the percentage grafting efficiency (%GE), percentage grafting (%G), and percentage add-on. These calculations were based on the measured weight increase[9,10]. Notably, control experiments revealed a consistent loss of 0.126 g of starch per 2 g of initial starch. Therefore, starch loss from the control was considered into the grafting residue weight measurements, ensuring accurate determination of the grafting parameters.

3.3 Effect of varying initiator concentration:

The changes in grafting parameters with change in concentration of PPS, can be observed from Table 1. and figure 1. The effect of initiator concentration on the grafting parameters were studied by varying the concentration of PPS from 2 ml to 10 ml, while keeping other reaction parameters constant. Initially grafting increased till 10 ml and after that started declining.

Table 1: Impact of the concentration of the initiator on grafting

Sr. No.	PPS mL	%GE	%G	%Add-on
1	2	6.60	6.60	6.19
2	4	8.50	8.50	7.83
3	6	10.47	10.47	9.47
4	8	10.75	10.75	9.71
5	10	14.30	14.30	12.51
6	12	10.73	10.73	9.69
7	14	9.4	9.45	8.63

(**Reaction conditions:** Starch 2 gm; [MAM] = 2 gm; Total volume=100 mL; Temperature=30°C; Polymerization time=180 min; Stirring rate=300 rpm)
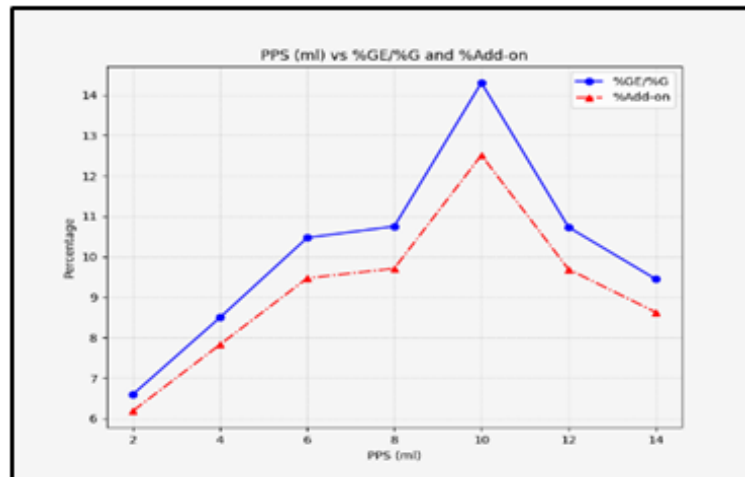
Figure 1- Grafting Parameters versus concentration of PPS in mol/l

This could be due to the increase in the number of free radicals generated with increasing initiator concentration, which leads to more grafting sites on the starch backbone.[11] However, at higher initiator concentrations, the rate of homopolymerization of MAM increases, which reduces the grafting efficiency.

3.4 Effect of varying monomer concentration:

It is observed from Table 2 and figure 2, the effect of monomer concentration on the grafting parameters was studied by varying the concentration of MAM from 2 to 12 g while keeping other reaction parameters constant. The results showed that the grafting efficiency was high at 2gm after which it decreased with increasing monomer concentration up to 12 g, while %G and %Add-on increases with monomer concentration.

Table 2: Impact of monomer concentration on grafting efficiency

Sr. No.	MAM gm	%GE	%G	%Add-on
1	2	14.63	14.63	12.77
2	4	6.42	12.83	11.37
3	6	5.30	15.90	13.72
4	8	5.12	20.47	16.99
5	10	4.12	20.60	17.08
6	12	3.97	23.83	19.25

(**Reaction conditions:** Starch = 2gm; [PPS] = 10 ml; Total volume: 100mL; Temperature = $30^{o}C$; Polymerization time: 180 min; stirring rate = 300 rpm Solvent =Distilled.H_2O)
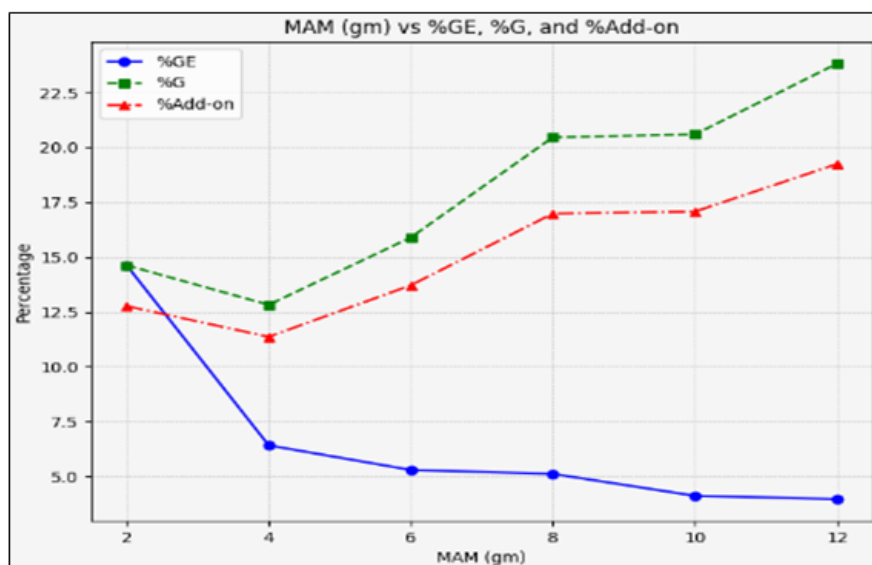
Figure 2- Grafting Parameters versus concentration of MAM in gram

This could be due to the increase in the availability of MAM molecules for grafting with increasing monomer concentration. However, at higher MAM concentrations, the rate of homopolymerization of MAM (PMAM), increases, which increases the viscosity of the reaction medium and reduces the grafting efficiency[12].

3.5 Effect of varying polymerization time:

The effect of polymerization time on the grafting parameters was studied by varying the reaction time from 30 to 240 minutes while keeping other reaction conditions constant. Table 3 and figure 3, indicates that the values of grafting parameters increases with an increase in polymerization time till 180 mins. After 180 mins it is steady. It is evident that an induction period is necessary for grafting. The optimum duration for the polymerization of MAM on potato starch is established at 180 minutes.

Table 3: Impact of polymerization duration on the grafting process

Sr. No.	Time (min)	%GE	% G	% Add-on
1	30	3.83	3.83	3.69
2	60	7.33	7.33	6.83
3	90	10.58	10.58	9.57
4	120	11.35	11.35	10.19
5	150	12.51	12.51	11.12
6	180	13.81	13.81	12.13
7	210	13.88	13.88	12.19
8	240	13.88	13.88	12.19

(**Reaction conditions:** Starch = 2g; [PPS] = 10 ml, [MAM] = 2gm; Total volume: 100mL; Temperature = 30°C; stirring rate =300 rpm)
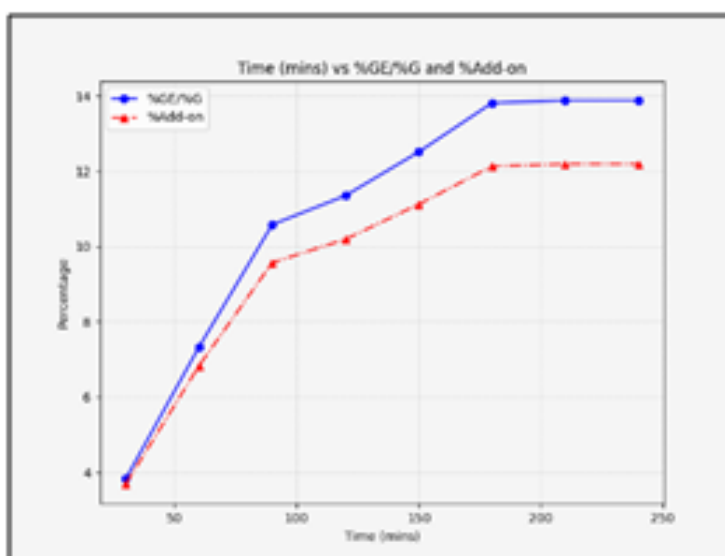
Figure 3- Grafting Parameter   versus. polymerization time in mins

The consumption of monomers leads to a decrease in the availability for grafting, resulting in a decline in the grafting parameters as the polymerization time extends. The depletion of monomers or active sites may be the cause of the grafting parameters leveling out over prolonged polymerization times[13].

3.6 Effect of varying Material-to-liquor ratio:

The ratio of material to liquor was modified by changing the quantity of water added to the reaction medium. The effect of material-to-liquor ratio on the grafting parameters was studied by varying Material-to-liquor ratio from 1:25 to 1:05 i.e reducing water from 100 ml to 20 ml, while keeping other reaction conditions constant. The information presented in Table 4 and graphically shown in and figure 4. indicates that an initial decrease in grafting parameters takes place when the water volume falls from 100 mL to 80 ml.

Table 4: Impact of material-to-liquor ratio on the grafting process

Sr. No.	Material-to-liquor ratio	% GE	% G	% Add-on
1	01:25	13.18	13.18	11.65
2	1:22.5	13.15	13.15	11.62
3	01:20	15.18	15.18	13.18
4	1:17.5	14.65	14.65	12.78
5	01:15	13.78	13.78	12.11
6	1:12.5	13.25	13.25	11.70
7	01:10	12.83	12.83	11.37
8	1:7.5	12.71	12.71	11.28
9	1:05	12.43	12.43	11.06

(**Reaction conditions:** Starch= 2gm; [PPS]=10 ml; [MAM]= 2gm; Temperature= 30°C; Polymerization time: 180 min, stirring rate=300rpm)
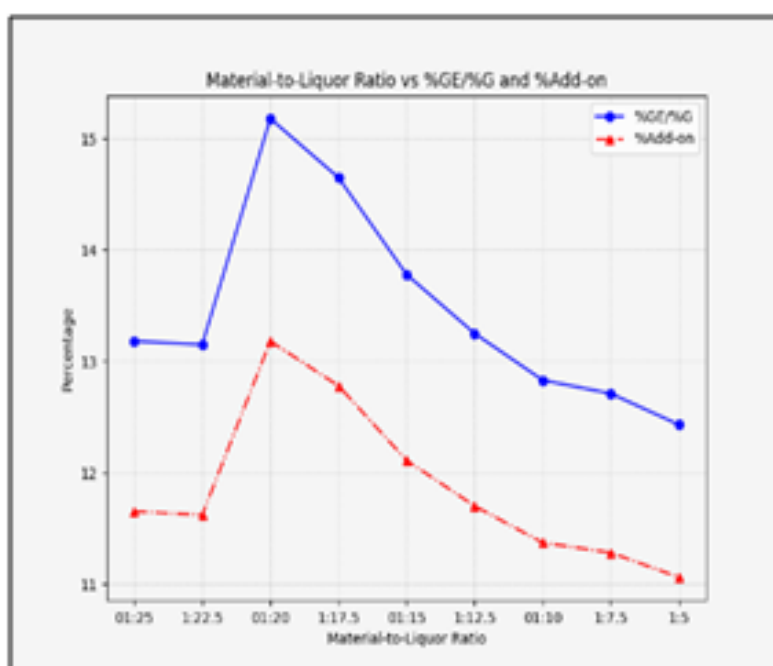
Figure 4- Grafting Parameters versus material-to-liquor ratio

Initial decrease can be reasoned on the basis of no better orientation of monomers in the reaction medium, resulting in lesser kinetic probability of collision between them.

After the Material-to-liquor ratio of 80 mL (1:20) there is decrease in grafting parameters. Due to low water volumes, there is restricted mobility between reactants [14], hence monomers are unable to access the free radical sites that have developed on the backbone of the starch. Therefore, the ideal material-to-liquor ratio for the graft copolymerization of MAM on potato starch was found to be 1:20, or 80 ml of water.

3.7 Effect of different reaction temperatures:
The effect of reaction temperature on the grafting parameters was studied by varying the reaction temperature from 25 to 50°C while keeping other reaction parameters constant. Table 5 and figure 5, indicates that the optimal temperature for graft copolymerization is elevated to 35°C. Grafting parameters decrease as the reaction temperature rises more.

Table 5: Impact of reaction temperature on grafting

Sr. No.	Temp. (°C)	%GE	%G	%Add-on
1	25	8.65	8.65	7.96
2	30	10.32	10.32	9.35
3	35	14.7	14.7	12.82
4	40	10.5	10.5	9.50
5	45	9.68	9.68	8.83
6	50	8.83	8.83	7.96

(**Reaction conditions:** Starch = 2g; [PPS] = 10 ml; [MAM] = 2gm; Total volume: 100 mL; Polymerization time: 180 min; stirring rate = 300 rpm, Solvent = H_2O)
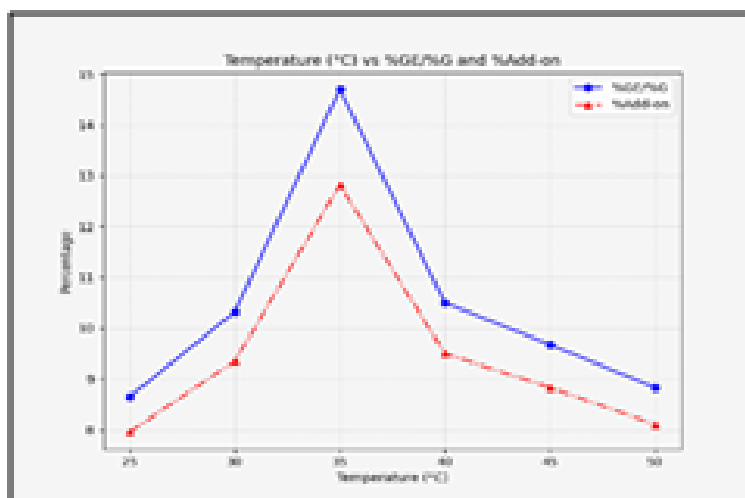
Figure 5- Grafting Parameters versus Temperature of reaction medium

As with increasing reaction temperature, there is an increase in the rate of free radical generation and thus the rate of homopolymerization of MAM increases, which reduces the grafting efficiency. This can be also explained by morphological changes in starch at high temperature which makes it resistant to MAM grafting [16,19]. Thus, the ideal temperature for graft copolymerisation is 35°C.

3.8 Effect of varying Solvent:

The effect of the presence of various alcohols in our solvent water was studied. The alcohol to water ratio 1:4 was maintained, keeping overall reaction volume 100 ml. It was observed from table 6. and figure 6, that presence of alcohol resulted in decrease in grafting parameters values. This decrease was proportional to the polarity and chain length of alcohol.

Table 6: Impact of solvent presence on grafting

Sr. No.	Solvent	%GE	%G	%Add-on
1	water	14.6	14.6	12.74
2	water + methanol[4:1]	9.4	9.4	8.56
3	water + ethanol[4:1]	6.2	6.2	5.81
4	water + propanol[4:1]	4.8	4.8	4.58

(**Reaction conditions:** Starch = 2g; [PPS] = 10 ml; [MAM]= 2gm. Total volume =100 mL; Temperature = 35°C; Polymerization time = 180 min Alcohol= 20 mL, stirring rate = 300 rpm)
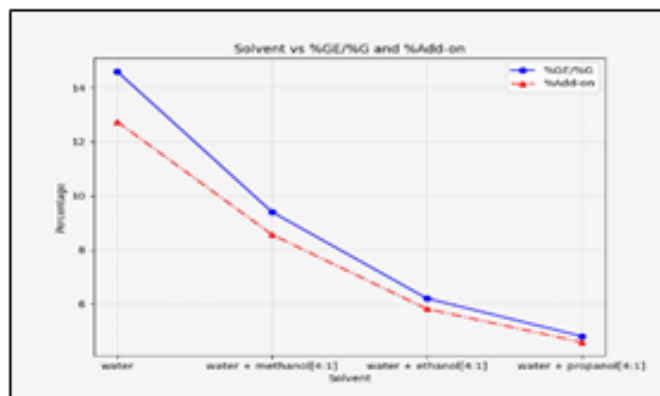
Figure 6- Grafting Parameters versus solvent used for reaction medium.

Table 7: Dielectric constant of solvent

Solvent	Dielectric constant
Water	81
Methanol	32.7
Ethanol	24.5
Propanol	17.9

The results showed that the grafting efficiency and grafting parameters were higher when water was used as a solvent compared to a mixture of water and alcohol. This could be due to the better solubility of starch and MAM in water, which leads to more grafting sites on the starch backbone[14,20].

3.9 Effect of varying Stirring rate:
The effect of stirring rate on the grafting parameters was studied by varying the stirring rate from

100 to 500 rpm while keeping other reaction parameters constant.

Table 7: Effect of stirring rate on the grafting

Sr. No.	Stirring rate in rpm	%GE	%G	%Add-on
1	100	11.85	11.85	10.59
2	200	12.36	12.36	11.00
3	300	13.01	13.01	11.51
4	400	13.23	13.23	11.68
5	500	13.2	13.2	11.66

(**Reaction conditions:** Starch = 2g; [PPS] = 10 ml; [MAM]= 2gm. Total volume =100 mL; Temperature = 35^0C; Polymerization time = 180 mins)

Figure 7- Grafting Parameters versus stirring speed in rpm.

The results showed that the grafting efficiency and grafting parameters increased with increasing stirring rate up to 400 rpm and steady at 500 rpm. This could be due to the better mixing of the reaction mixture at higher stirring rates, which leads to more contact between the reactants and better and even grafting. Optimum stirring rate is 400 rpm.

4. CONCLUSION

Graft copolymerization of methacrylamide onto potato starch was successfully carried out using potassium per sulphate as an initiator. The optimum conditions for grafting were found to be:

- Initiator Concentration of 10 ml (0.01 Mol/L),

- Monomer Concentration of 2 gm,

- Polymerization Time of 180 minutes,

- Reaction Temperature of 35°c,

- Material-To-Liquor ratio of 1:20, and

- Stirring Rate of 400 rpm.

The graft copolymers were characterized by gravimetric analysis, which confirmed the grafting of methacrylamide onto the starch backbone. The grafting efficiency and grafting parameters were influenced by various reaction parameters, including initiator concentration, monomer concentration, polymerization time, reaction temperature, material-to-liquor ratio, solvent, and stirring rate.

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EXTRACT`ION OF DYES FROM VARIOUS FLOWERS AND IT'S APPLICATIONS

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I. Abstract
Over the past few decades, researchers worldwide have been motivated to explore alternative renewable bio-based materials for colouring purposes, aiming to minimize the negative environmental impact associated with the use of synthetic dyes. Natural dyes extracted from flower crops have gained increasing attention in recent years due to their potential as a sustainable alternative to synthetic dyes, which have negative environmental impacts. A variety of exquisite shades, ranging from delicate pastels to vibrant and striking tones, can be derived by extracting pigments found in numerous flowers. Unlike synthetic dyes, natural dyes are renewable, biodegradable, and non-toxic. Moreover, natural colourants offer diverse practical finishing characteristics, such as insect repellent, deodorizing, anti-feedant, antimicrobial, fluorescence, and UV protection properties

In this study, dyes were extracted from the various flowers by aqueous extract on method which is the most important use of the flowers. Cotton fabric is used as a substrate was dyed from natural dyes. dye on the fabric. These findings reveal the different shades from the floral dye. These can be useful for coloration of fabrics with different shades using same flowers. Also, these dyes were used for the preparation of the natural lip balm which is the important cosmetic product for lips as it adds glamours touch and shine to the beauty as current cosmetic lip products are based on use of toxic chemical ingredients with various adverse effects. That's why it leads to study natural ingredients used to product on of natural lip balm from certain flowers.

Keywords: Natural dyes, Red and Pink Rose flower, yellow and orange marigold flower, Blue-butterfly Pea flower, Aster flower, Cotton fabric, Mordant, Dye potential, Lip balm, Cosmetic, Lip dryness, Plant-based dyes, Eco-friendly dyes.

II. Introduction
In our daily lives, colour is significant since it serves as a vital visual sign when it changes. Throughout the beginning of time, the vibrant and calming colours of nature have mesmerised humans[1] . Both pigments and dyes are included in these colorants. The coloured substances known as dyes have a strong affinity for textile fibres and fabrics through various physical and chemical interactions[2].

India is rich in biodiversity not only rich with only 2.4% of world's land area, account for 7-8% of all recorded species, including plant and animal species. There are about 15000 species of flowering plants which is 6% of world's total. Nature has abundance of colours. The leaves of plant have various shades of green, flowers have variety of hues of red, yellow, blue, violet etc.

Since, ancient time natural dyes have been used for colouring and printing fabrics. As natural dyes are more environmentally friendly because they degrade faster. They are non-toxic, non-allergic, readily available and renewable. This research was performed with extracting natural dye from the petal of different flowers using water as solvent and to investigate its dyeing effect on cotton fabric sample. The effect of mordant on the stability of the dye as well as on colour shade were also analysed. Characterisation of the natural dyes were done by FT-IR analysis. Light fastness and wash fastness were also evaluated for fabric samples.

Cosmetics also have demand since historical time. These days people prefer naturally derived cosmetic products. As cosmetic plays important role in today's lifestyle. Along all cosmetic products, natural lip balm preparations are most widely used to increase the beauty of lips and add glamour touch and shine to the beauty. Lip balms provide a natural way to promote healthy and moisturised lip. Current cosmetic lip products are based on the use of toxic chemical ingredients with various adverse effect. This work also involved the production of a lip balm by formulated with natural materials. Natural lip balms preparations applied on the lips to avoid and protect against adverse environmental pollutant. Natural lip balm helps to maintain and promote health lips.

III. Experimental Method

I. Materials

- **Source**

Fresh flowers of Red Rose (Rosa indica), Pink Rose (Rosa meldomonac), Orange Marigold (Tagetes erecta), Yellow Marigold (Tagetes erecta), Pink Kaner (Nerium Indicum), Red Kaner (Nerium oleander), Aster Flower (Aster amellus) and Blue Butterfly Pea Flower (Clitoria ternatea).

- **Substrate**

Pure soft cotton fabric.

- **Chemicals**

Chemicals such as 5% NaOH solu on, 10% K2Cr2O7, bees wax, petroleum jelly, honey.

II. Extraction Of Dyes

Different types of the flowers were collected from the flower market of Dada-West Mumbai, Maharashtra. Floral petals are segregated, washed and air died to remove impurities. Several batches of 10-15 grams of fresh petals are kept for oven dry in hot air oven. Only the pigmented parts of the floral parts is used for the study.

The petals are kept for 40 minutes at 1000C to remove the water content present in them. The dried petals are finely grinded into the powder. Same procedure is used for other seven different floral petals. Distilled water is used for the extraction of the dye. Dried petals were boiled for 30-35 minutes until the dye released. Mixture is allowed to cool and filtered using whatman filter paper to remove impurities. All the samples are then mixed with arabic gum powder to increase the intensity and adhesiveness of the dye.

The dye extracted by aqueous extraction method were further characterised by FT-IR spectra. By performing an infrared absorption spectrum, Fourier Transform Infrared Spectroscopy (FT IR) helps in determining chemical bonds in molecule. This analysis is essential in characterising the samples and identifying the functional group on the surface of the floral extract dye.

III. Preparation of mordant and dyeing procedure

Potassium dichromate is used as mordant. 10gms of K2Cr2O7 is dissolved in 100ml of distilled water. Cloth used for dyeing is dissolved in 5% Sodium hydroxide solution and refluxed for 10mins to remove starch and other dirt particles from it. The treated cloth is then simmered in mordant solution for 20mins and then it is taken out. The dye is applied to fabric by two methods:

- **Without Mordant:** Fabric treated with 5% NaOH solu on is directly dip in the dye and the fabric is boiled gently for half an hour for allowing the dye to enter in the cloth properly. The cloth is then taken out and dried for further studies.

- **With Mordant:** The mordanted cloth is then dip in the dye for half an hour for allowing dye to enter in the cloth. Aer that cloth is taken out and dried.

Dried material was washed with cold water and dried in the sunlight for testing washing fastness and light fastness.

IV. PREPARATION OF NATURAL LIP BALM

The raw material were weighed on a balance accurately. The preparation method involved heating of aloe vera gel, petroleum jelly, floral extract and honey on the water bath till the homogenous mixture is formed. The mixture is then poured in the container and solidifies in the refrigerator and a er used for the itching test by applying it on the hand.

V. PICTORIAL PROCEDURE

VI. CHARACTERISATION OF THE DYES (FT-IR ANALYSIS)

a. FT-IR for Red Rose sample

The FT-IR spectra of a rose can reveal the presence of various func onal groups such as hydroxyl groups, carbonyl groups and aromatic rings.In the FT-IR spectrum of a rose sharp band was observed. These bands on the area near 3500 cm^{-1} shows the stretching vibration of the hydroxyl groups and the nearby band at 1600 cm^{-1} atributed to the bending vibrations of the various functional groups in the rose, including the aromatic rings in the essential oils.
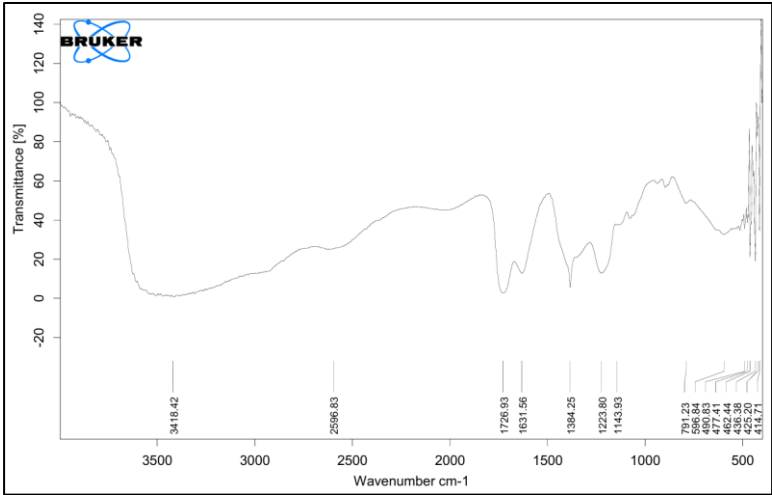
Sample detail

File Name	Creation Date	X-axis Start Value	X-axis End Value	X-axis Unit	Y-axis Unit
Indian Red Rose	06-06-2024 01:10:05 PM	3500	500	Wavenumber cm^{-1}	Transmittance

Peak Table

Peak number	1	2	3	4	5	6
X(cm^{-1})	2596.83	1726.93	1631.56	1384.25	1143.93	791.23
Y(%)	22	0.5	14	10	38	42

b. FT-IR for Orange Marigold sample

Marigold, also known as Calendula officinalis, is popular medicinal herb with various biological activities. The region around 500 cm^{-1} shows small but intense peak which shows C-X strech. The peak at 790 cm^{-1} indicates the presence of C-H stretching vibration. The sharp and intense peaks at 1385 cm^{-1} indicates C-H stretching. The region around 2500 cm^{-1} to 2950 cm^{-1} shows small peak which indicates N=C=O and CH stretching.
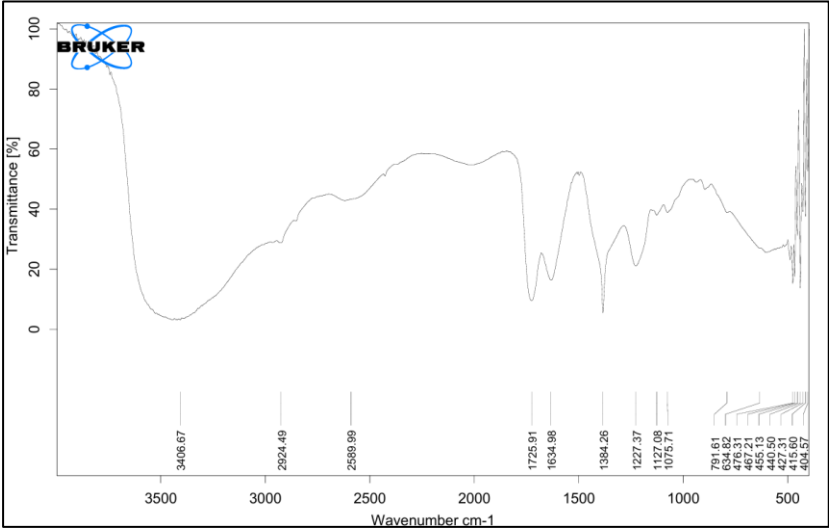
Sample detail

File Name	Creation Date	X-axis Start Value	X-axis End Value	X-axis Unit	Y-axis Unit
Orange Marigold	06-06-2024 01:15:12 PM	3500	500	Wavenumber cm^{-1}	Transmittance

Peak Table

Peak number	1	2	3	4	5	6
X(cm^{-1})	3406.67	2924.49	2589.99	1634.98	1227.37	634.82
Y(%)	05	23	42	15	19.5	35.2

c. FT-IR for Blue Butterfly Pea sample

FT-IR spectral analysis of blue butterfly pea dye reveals distinct peaks for following chemical characterisation:

The broad peak near 3400 cm^{-1} indicates the presence of -NH stretch. The C=O stretching vibration could be assigned to the band that appeared at 1730 cm^{-1}. At 2600 cm^{-1} absorption is due to C≡C stretching and at 1635 cm^{-1} due to C=O.
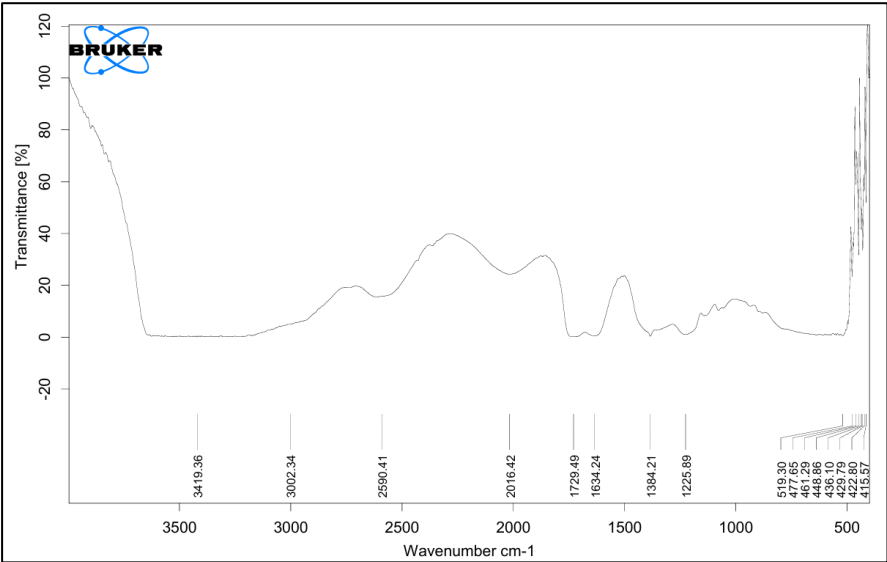
Sample detail

File Name	Creation Date	X-axis Start Value	X-axis End Value	X-axis Unit	Y-axis Unit
Blue Butterfly Pea	06-06-2024 01:20:12 PM	3500	500	Wavenumber cm^{-1}	Transmittance

Peak Table

Peak number	1	2	3	4	5
X(cm^{-1})	3002.34	2590.41	2016.42	448.86	415.57
Y(%)	7.2	11.2	20.9	40	93

d. FT-IR for Yellow Marigold sample

Marigold belongs to Asteraceae family and commonly used as ornamental flowers. It has biological activities including an inflammatory, an oxidant and anmicrobial properties.

The region around 500 cm^{-1} shows small intense peak of C-X bonding. The peak in range of 3584 cm^{-1} to 3700 cm^{-1} corresponds to multiple peaks of OH out of plane deformation in benzene ring. Peak at 1400 cm^{-1} shows -CH group in aromatic ring.
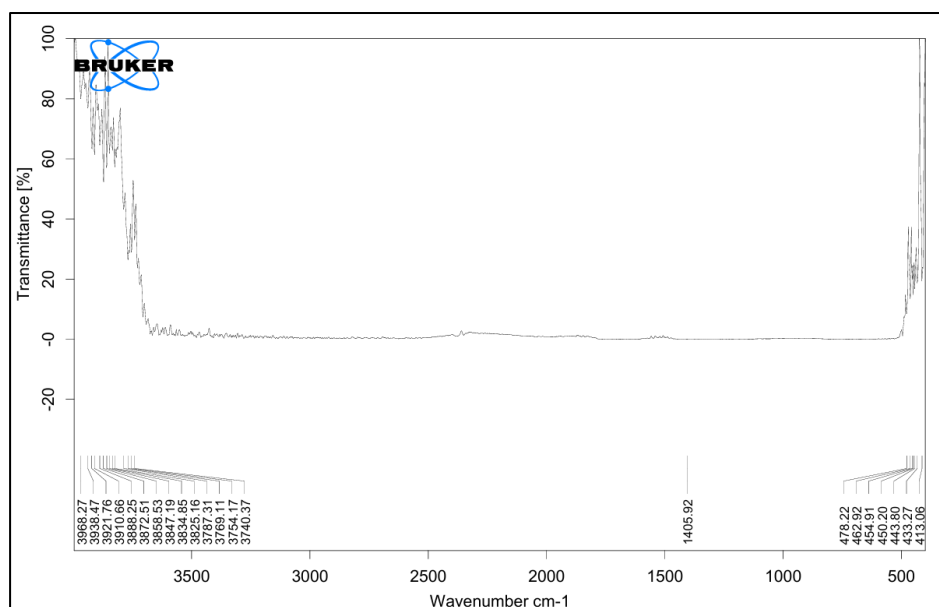
Sample detail

File Name	Creation Date	X-axis Start Value	X-axis End Value	X-axis Unit	Y-axis Unit
Yellow Marigold	06-06-2024 01:30:02 PM	3500	500	Wavenumber cm^{-1}	Transmittance

Peak Table

Peak number	1	2	3	4	5
X(cm^{-1})	3968.27	3938.47	3921.76	3872.51	433.27
Y(%)	80	78	62	57	22

e. FT-IR for Pink Rose sample

In FT-IR spectrum of pink rose broad and sharp band of 3227.99 cm^{-1} indicates O-H stretch of alcohol and phenol group. Range from 660 cm^{-1} to 910 cm^{-1} indicates the stretching of NH bend (Amine group).
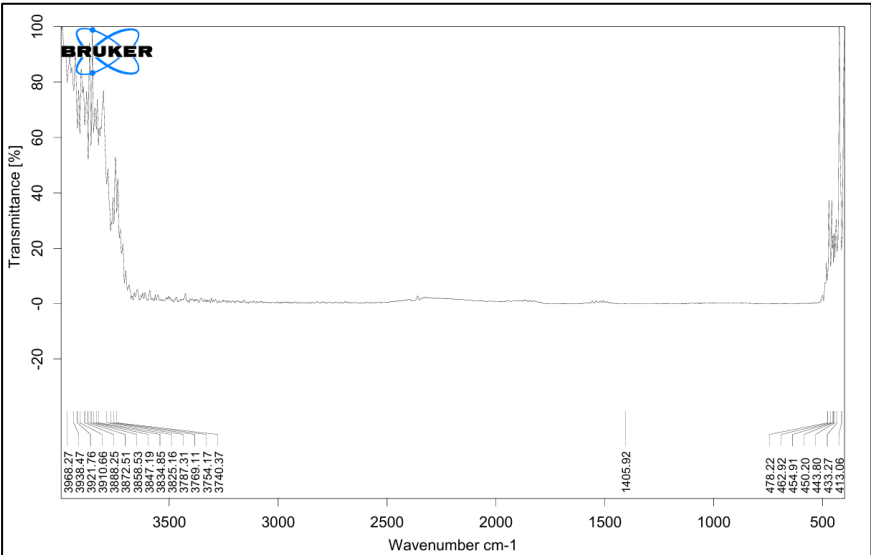
Sample detail

File Name	Creation Date	X-axis Start Value	X-axis End Value	X-axis Unit	Y-axis Unit
Pink China Rose	06-06-2024 01:41:00 PM	3500	500	Wavenumber cm^{-1}	Transmittance

Peak Table

Peak number	1	2	3	4	5	6
X(cm^{-1})	3898.49	3863.43	1989.27	793.24	457.22	426.94
Y(%)	80	80.1	10	5	40	39

f. FT-IR for Pink Kaner sample

The FT-IR spectral analysis of pink kaner dye shows peaks for following chemical characterisation:

Broad and strong peak at 2610.32 cm^{-1} shows presence of N=C=O stretching and 2944.82 cm^{-1} indicates peak of alkyne group. 1632.51 cm^{-1} absorption is due to C=C stretch. Absorption at 791.31 cm^{-1} shows presence of C-H bend (Phenyl ring).
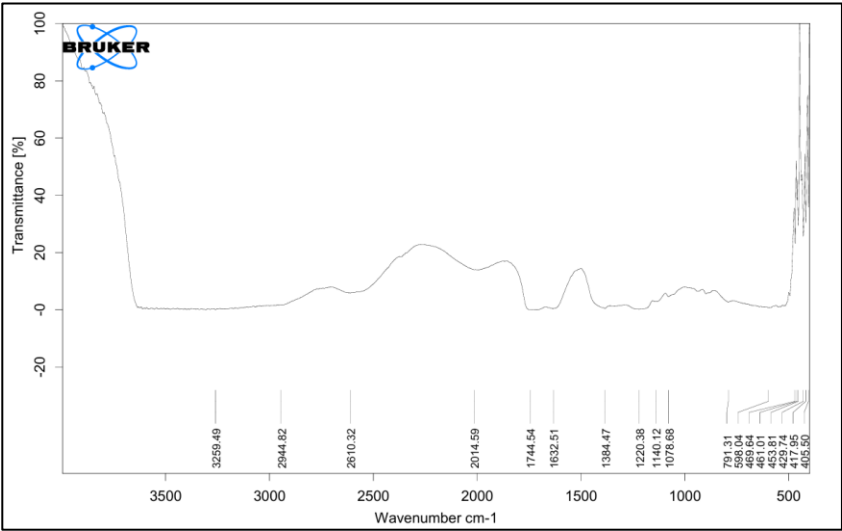
Sample detail

File Name	Creation Date	X-axis Start Value	X-axis End Value	X-axis Unit	Y-axis Unit
Pink Kanher	06-06-2024 01:50:02 PM	3500	500	Wavenumber cm^{-1}	Transmittance

Peak Table

Peak number	1	2	3	4	5
X(cm^{-1})	2610.32	2014.59	461.01	453.81	405.50
Y(%)	9.7	20	36.7	38.9	40

g. FT-IR for Aster sample

Aster, FT-IR spectral analysis shows broad and strong band of O-H stretch at 3442.84 cm^{-1} and C-H stretch alkane of group at 1384.32 cm^{-1}. From 1500-1650 cm^{-1} peaks shows N=O stretch of nitro compound.
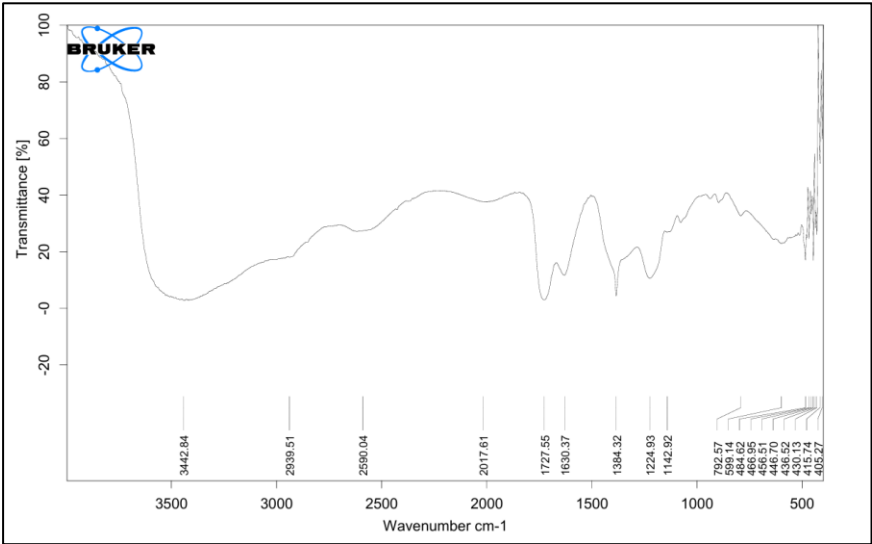
Sample detail

File Name	Creation Date	X-axis Start Value	X-axis End Value	X-axis Unit	Y-axis Unit
Aster	06-06-2024 02:20:00 PM	3500	500	Wavenumber cm^{-1}	Transmittance

Peak Table

Peak number	1	2	3	4	5	6
X(cm^{-1})	3442.84	2939.51	2590.04	2017.61	1630.37	792.5
Y(%)	1.5	18	24	40	10	37.5

h. FT-IR for Red Kaner sample

FT-IR spectral analysis of red kaner shows peak for the following chemical characterisation:

Peak from 2500 cm^{-1} to 3400 cm^{-1} shows O-H stretching. Peak at 1632.45 cm^{-1} shows C=O stretching and 1151.00cm^{-1} shows C-O stretch.
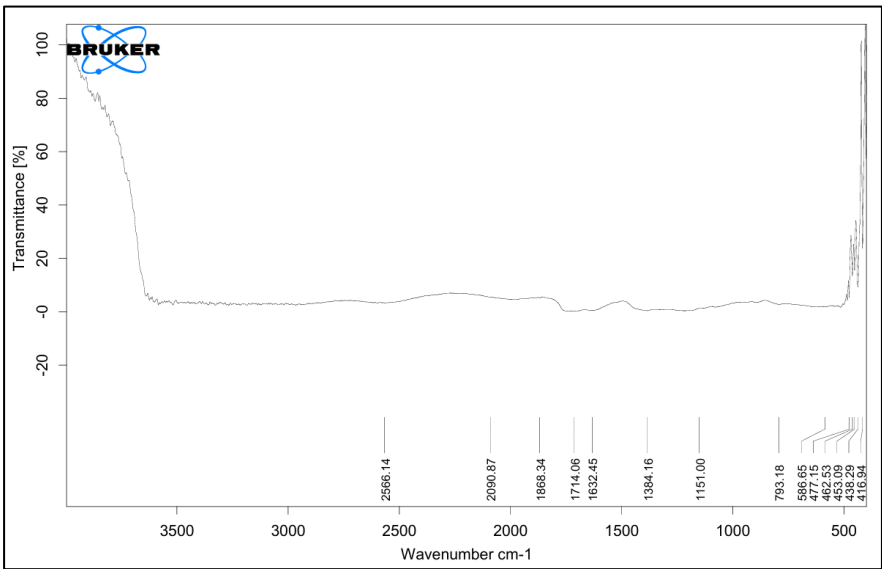
Sample detail

File Name	Creation Date	X-axis Start Value	X-axis End Value	X-axis Unit	Y-axis Unit
Red Kaner	06-06-2024 02:30:05 PM	3500	500	Wavenumber cm^{-1}	Transmittance

Peak Table

Peak number	1	2	3	4
X(cm^{-1})	3500	462.53	453.09	416.94
Y(%)	0.9	15	18.9	36

VII. RESULT AND DISCUSSION

Different colour shades were obtained from the extract of Red and Pink Rose, Yellow and Orange Rose, Pink and Red Kaner, Aster and Blue Butterfly Pea flowers. The cloth which is displayed get fixed to the respective dye with the help of mordant. The mordant used is Potassium dichromate. This mordant when added to dye gave different shades of colour. Different colour shades are possible by using the similar flower with the help of mordant. Also the fastness test has done. In this washing fastness and lightning fastness test has been done. The preparation of the lip balm has also done successfully by using the natural dye and do not show any effect when applied on the hand,

VIII.   APPLICATION

Prepared dyes were applied on the pure co on cloth and the lip balm is applied on the paper for the identification of the colour.
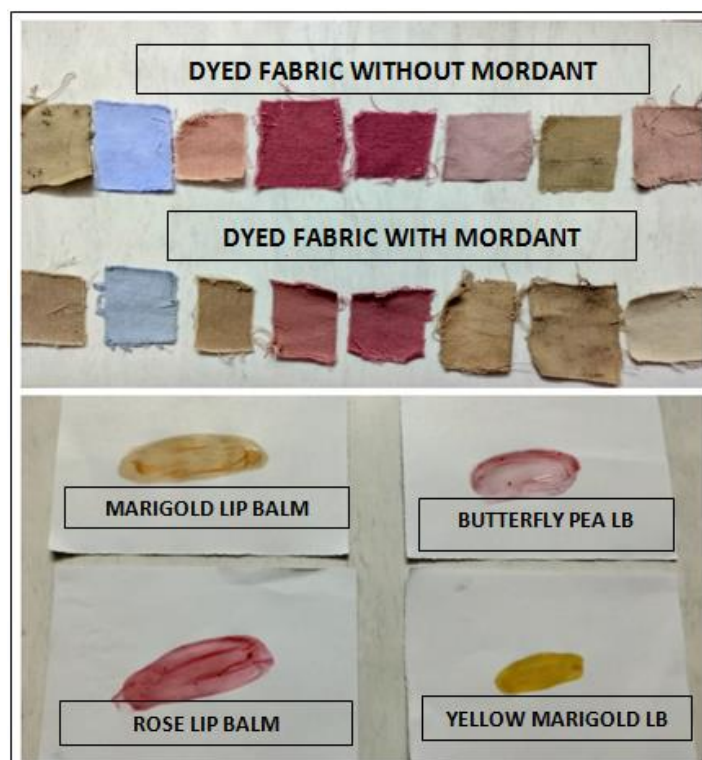
IX. CONCLUSION

The present study shows that the natural dye extracted from the different flowers can be successfully applied to the cotton fabric to obtain the wide range of colour shadings along with the application of the mordants as fixative agent. And have also successfully the prepared the natural lip balm for minimising the use of the lip balm containing the harmful chemicals. The whole process of the extraction is environmental friendly.

Fastness testing is done on the dyed fabric. The study revealed that the dyeing property of the fabrics a er washing with water and detergents was not affected much but fabric when exposed to the sunlight loose the colour and this causes colour to fade. This study also revealed that this natural lip balm have no adverse effect on the skin and lips and can have the scope in the future in the cosmetics.

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SUPRAMOLECULE SOLVENT-BASED EXTRACTION TECHNIQUES FOR EXTRACTION OF HEAVY METALS: A REVIEW

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ABSTRACT
This review explores the application of Supramolecule solvent-based liquid-liquid extraction (LLE) and microextraction (SSME), a novel green analytical technique for assessing trace metal concentrations in water. Supramolecular solvent-based micro-extraction stands out due to its ease of use, impressive pre-concentration factor, rapid execution, accuracy, affordability, minimal chemical reagent usage, and eco-friendliness. The rise in water contamination due to hazardous heavy metals has become a major global issue in recent decades. Numerous carriers and separation systems have been discussed in this review.

Keywords: Supramolecule, liquid-liquid extraction, heavy metal, ligand.

INTRODUCTION
Heavy metals, such as chromium, copper, lead, cadmium, zinc, and nickel, are crucial for environmental protection and ecosystem degradation. Traditional analytical techniques like ETAAS, FAAS, and ICP MS face challenges like matrix effects and trace metal detection. Researchers have introduced supramolecular solvent-based microextraction (SSME) for effective heavy metal analysis, aligning with green chemistry principles. [6] Supported Liquid Membranes (SLM) are gaining popularity for their efficiency in removing metal ions from wastewater, even at low concentrations, among other methods.[2]

Supramolecular chemistry is a field that focuses on designing and assembling super-molecules called supramolecules (SUPRASs) through noncovalent interactions. These entities are used in various applications, such as luminescent material sensors, light-emitting devices, biological systems, gels, and materials chemistry. The discovery of SUPRAS in 1987 led to its 2016 Nobel Prize in Chemistry. Their attributes are influenced by self-assembly processes, molecular structure, and environmental factors. SUPRAS are formed through sequential self-assembly of amphiphilic species at both nano and molecular scales.[25][26] Metal ions are major environmental contaminants in wastewater, leading to strict regulations. Various methods, including Liquid-Liquid extraction, adsorption, ion exchange, electrodialysis, and membrane technologies, are used to remove pollutants. Supported Liquid Membranes (SLM) are recognized for their effectiveness, cost-effectiveness, and ease of commercialization.

TYPES OF HEAVY METALS AND THEIR EFFECTS
Zinc, a key component of over 200 enzymes, should be kept below safe limits. Chromium, a toxic metal, can cause kidney failure, liver diseases, and respiratory issues. Ferrous metals should be controlled to prevent nausea, diarrhoea, cardiovascular complications, anemia, and neurological impairments. Copper, essential for enzyme structure, can cause jaundice, developmental delays, liver and kidney problems, and skin disorders. Lead, a hazardous heavy metal, is associated with chronic health complications. Cadmium contributes to cancerous tumors and kidney damage. Global health organizations and regulatory agencies are establishing limits and developing treatment solutions.[1-25][49]

The review explores various types of liquid membranes (LM) and their applications, focusing on emulsion and supported membranes for metal separation in model and industrial wastewater. It highlights various carriers and separation systems, including laboratory-scale models and actual wastewater separation.

1. SUPRAMOLECULAR COMPOUND FORMATION
Self-assembly is a synthetic method in chemistry and material science that involves organizing discrete components into functional arrangements through weak, noncovalent interactions. These components can vary in size and can be customized through careful design and environmental adjustments. The complexity of the final self-assembled system depends on the intrinsic properties of the components and the surrounding environment. The ability to reverse or modify interactions is crucial for ordered structures. Self-assembled supramolecular systems (SUPRASs) are formed by minimizing repulsive interactions between polar head groups of amphiphiles, with lower energetic costs. Enhancement of aggregate formation can be achieved through cosurfactants, electrolytes, counterions, or pH changes.[11] Supramolecular solvents (SUPRASs) are nano-structured liquids formed through self-assembly and coacervation, and they are extensively utilized in analytical chemistry for a range of extraction processes. [8].

1.1 Supramolecular macrocycles

Crown ethers

Crown ethers are cyclic compounds that interact with guest molecules through ionic interactions, hydrogen bonding, and hydrophobic forces. Developed by Pedersen in 1967, they are used as complexing agents due to their ability to selectively identify cations of different sizes. A stable complex is more likely to form when guest molecule dimensions align with crown ether cavity size. [44]

Cyclodextrins

Cyclodextrins (CDs), also known as Schardinger's dextrins and cellulosines, are cyclic oligosaccharides formed through starch breakdown. They have a macrocyclic structure with many glucopyranose units, making them useful in a variety of applications. Natural CDs include α-CD, β-CD, and γ-CD. β-CD is preferred due to its inclusion capabilities. [45]

Calixarenes

Calixarene, a cyclic polyphenol, is the most renowned member of the calixarene family. Its upper rim is typically adorned with tert-butyl or hydrogen atoms, while its lower rim contains phenolic hydroxyl or thiol groups. [44]

1.2 General Procedure

SUPRAS is a liquid phase formed in amphiphile extraction processes, resulting from the formation of supramolecular aggregates. These aggregates are influenced by factors like the amphiphile's structure, solvent choice, environmental conditions, and hydrocarbon chain dimensions. Coacervation occurs when these aggregates expand, leading to oily droplets clustering and forming SUPRAS. This abundant phase with a large surface area enhances solute mass transfer during extraction processes.[14]

SUPRAS, a nanostructured and reversible aggregate, offers exceptional capabilities for analyte extraction due to its unique properties. It provides diverse polarity microenvironments, enabling simultaneous solubilization of solutes across a broad range of polarities. This advantage over traditional solvents is due to hydrogen bonding, dipole–dipole interactions, and ionic interactions. SUPRAS is generated directly within samples, making its synthesis accessible and environmentally sustainable due to energy-efficient synthetic methods and the availability of low-cost, eco-friendly amphiphiles. [21-30]

1.3. Characterization techniques used for the SUPRAS analysis

1.3.1. Nuclear magnetic resonance (NMR) spectroscopy

NMR spectroscopy is a crucial technique for studying the structure and intricacies of SUPRAS networks, which resemble memory systems. It provides insights into component composition, aggregates, and interactions essential for network stability. [3]

1.3.2. Infrared (IR) Spectroscopy

Infrared spectroscopy is a crucial method for characterization, quality assurance, and monitoring of

self-assembled polymeric systems (SUPRAS), providing insights into hydrogen bonding and aggregation behavior. [3]

1.3.3. Ultraviolet-visible spectroscopy (UV/Vis)

UV/Vis spectroscopy is an absorption technique used to analyze molecules with non-bonding or pi electrons, detecting energy in ultraviolet or visible light and examining biological macromolecules and organic compounds. [3]

2. LIQUID MEMBRANE

Modular design configuration

i. Bulk Liquid Membranes (BLM)

ii. Emulsion Liquid Membranes (ELM)

iii. Supported Liquid Membranes (SLM)

Transport mechanism: Basic transport mechanisms include facilitated or carrier-mediated transport, coupled counter- or co-transport, and active transport. [45] [16]

Carrier type: Organic carriers that are not miscible with water, polymers that are soluble in water serving as membrane support, electrostatic and ion-exchange carriers, as well as neutral carriers that possess polarizable characteristics. [45] [16]

Membrane support type: Neutral hydrophobic and hydrophilic membranes, charged ion-exchange membranes, flat sheet and spiral module membranes, hollow-fiber membranes, and capillary hollow-fiber membranes. [45] [16]

Application: Metal separation and concentration involve various biotechnological or pharmaceutical applications. This includes the separation of gases, the recovery of valuable organic compounds, and the treatment of wastewater. Additionally, there are significant analytical applications related to carrier systems. [45] [16]

3. The composition of ELM: The primary driving force for solute transport across the membrane, similar to other liquid membranes, is the difference in chemical potentials between the external feed phase and the internal receiving phase. [45]

ELM consists of three phases

Feed phase (external, aqueous phase)

Organic membrane phase

Receiving phase (internal, aqueous phase)

3.1 SUPRASs, nano-structured solvents from amphiphiles, are characterized by their immiscibility with water and exceptional physicochemical attributes. The extraction efficiency is determined by binding energies between SUPRASs and solutes. Their nonflammability, nonvolatility, and varied polarities make them superior alternatives to hazardous organic solvents. This cost-effective, straightforward, and rapid method minimizes solvent usage, making it a sustainable alternative. [5]

3.1.1 Types and examples of extractant/ carrier
Numerous carriers commonly utilized in liquid membranes serve as commercial extractants, and several examples of the compounds employed in a membrane phase are provided. While LMs require fewer carriers than standard extraction methods, the utilization of macrocyclic and macromolecular extractants is severely limited due to the high cost involved with macrocycle carriers. [1] [45]

Table 1: Types and examples of commonly used extractants [1] [45].

Acidic, chelating	Trade name	Application in LM	Reference
β-diketone	LIX 54	ELM: Cu(II) transport	[45]
2-hydroxy-5-nonylbenzophenone oxime	LIX 64N	ELM: Cu(II) transport	[45]
Mixture of 5-nonylsalicylaldoxime and 2-hydroxy-5-nonylacetophenoneoxime	LIX 984N	BLM: Cu(II) transport	[45]
2-hydroxy-5-nonyl benzaldoxime with modifiers	ACORGA P50, ACORGO 5640, LIX 860	SLM: Cu(II) transport	[45]
Acidic, nonchelating			
bis(2-ethylhexyl)phosphoric acid	HDEHP, D2EHPA, DEHPA	ELM: Cu(II) and Zn(II) from wastewater, Cd(II), Pb(II), Ce(III), Hg(II), Ni(II)	[45]
bis(2,4,4-trimethylpentyl)phosphinic acid Cyanex 272	Cyanex 272	ELM: Co(II) from waste	[45]
2-ethylhexyl 2-ethylhexylphosphinate	PC88A	ELM: Co(II) from wastewater, Cr(III) transport	[45]

Basic			
methyltrioctylammonium chloride	Aliquat 336/TOAC	ELM: Cd(II), Cr(III) transport	[45]
trialkylamine, trioctylamine	Adogen 364, TOA	BLM: Hg(II) transport SLM: Zn(II) separation from Ni(II)	[45]
trihexyl(tetradecyl)phoshonium salts	Cyphos ILs	BLM: separation of Fe(III) from Ni(II) PIM: Zn(II), Fe(III), Cd(II)	[45]
Solvating			
tributylphosphate	TBP	SLM: Zn(II), Fe(II) separation, ELM: Zn(II) from wastewater	[45]
Macrocyclic and macromolecular			
calix[4]resorcinarene derivatives		PIM: Zn(II), Cd(II) transport	[45]

3.1.2 Surfactants

The preferred characteristics of an effective surfactant are the following: (i) membrane stabilization during mixing of the emulsion in the reactor, (ii) reduction of the osmotic transport of water between the phases, (iii) supporting the extraction of a component. Surfactants are mainly organic compounds that consist of two elements:– Ahydrophobic group (a tail),– Ahydrophilic group (a head). A hydrophilic group is soluble in the aqueous phase, whereas a hydrophobic group is soluble in the organic phase. Surfactants lower the interfacial tension between the organic and aqueous phases by adsorbing at the interface of both phases.

Table 2: Types and examples of surfactants [1] [45].

Type of surfactants	Examples
Anionic	Sodium dodecyl sulfate (SDS), Ammonium lauryl sulfate, Fatty acid salts
Cationic	Cetyltrimethylammonium bromide (CTAB)
Amphoteric	Dodecylbetaine, Dodecyldimethylamine oxide, Cocamidopropylbetaine, Cocoamphoglycinate
Nonionic	Alkylpoly(ethylene oxide), Copolymers of poly(ethylene oxide) and Poly(propylene oxide), Alkylpolyglucosides, Sorbitan monooleate (Span 80)

3.1.3 Carriers/extractants

Carriers and extractants utilized in ELM As previously stated, an extractant, also referred to as a carrier, primarily facilitates the selective diffusion transport of the solute from one phase, across the membrane, to another phase. The various types of extractants, along with examples of the metal species being transported, are detailed in Table 3.[45][16]

Table 3: Examples of extractants

Ion	Examples	Stripping agents
Cu(II)	Chloroform/DB18C6	Distilled water
Cd(II)	Kerosene/Aliquat336	EDTA
	Solvesso100/Cyanex923	Distilled water
	Exxol 100/Cyanex 923	Distilled water
	Kerosene/ D2EHPA	H2SO4
	NPOE/ thiacalix[4]arene	HCl
	Kerosene/ TOA	CH3COONH4
	Xylene/Cyanex 923	Distilled water
	Cyclohexane/TBP	EDTA
	Kerosene/ D2EHPA+	H2SO4
	Toluene/Aliquat 336	EDTA
Co(II)	Chloroform/Alamine336	NH3+TEA
	Exxsol D100/DP8R,Acorga M5640	H2SO4

	Kerosene/DP-8R	H2SO4
	Chloroform/Alamine300	NH3+TEA
	Kerosene/ cyanex 272	H2SO4
	Paraffin/Cyanex 272	H2SO4
Cr(III)	NPOE/Lasalocid A	HNO3
	Cyclohexanone/TEA	H2SO4
Cr(VI)	Chloroform/Alamine336	NaOH
	Toluene/ CYPHOS IL 101	NaOH
	Dichloromethane+5%NPOE/ Calix[4]arene	NaOH
	Xylene/ Cyanex 923	NaCl

3.1.4 Diluents

A carrier, surfactant, and diluent are all essential components in the transmission of emulsion liquid membranes (ELM). The diluent, also referred to as a solvent, is a liquid or a uniform mixture of liquids that can dissolve an extractant and, if applicable, a modifier such as a surfactant.

Commonly Used Diluents in ELM Processes	Concerns with Kerosene	Alternative Diluents
− n-Hexane − Kerosene − Cyclohexane − Benzene − Toluene − Chloroform − Carbon tetrachloride	Kerosene is the most commonly used organic diluent which is hazardous to human health Environmentally unsustainable	Vegetable oils such as: − Palm oil − Sunflower oil − Soybean oil − Sesame oil − Corn oil

An effective diluent should possess the ability to dissolve the extractant efficiently, exhibit low volatility, have a high flash point, maintain low surface tension, remain insoluble in the aqueous phase, be cost-effective and easily accessible, and not create a third phase with the extracted substances. [1] [45]

4. THE STUDY OF IMPACT OF DIFFERENT EXPERIMENTAL VARIABLES

The effect of pH, effect of the type of supramolecular solvent, effect of stripping agent, effect of carrier concentration, effect of metal concentration, effect of ligand concentration, and effect of diluent can also be studied during experimentation.

CONCLUSION

SUPRASs are a sustainable, cost-effective alternative to hazardous organic solvents for preparing and preconcentrating pollutants like pesticides and metal ions. They are environmentally benign, nonvolatile, and non-flammable. However, challenges persist, including potential environmental toxicity and difficulty in detecting trace pollutants in complex matrices. Researchers dilute enriched SUPRASs with solvents. [3][26-29]

Supercapacitors, or SUPRASs, are a sustainable, non-volatile, and non-flammable substitute for organic solvents, aiming to enhance compound extraction efficiency and address the growing demand for greener solvents in environmental, food, and biological sample analysis. [6]

Heavy metals, a major concern for human health, are introduced into the environment through natural processes and human activities. Traditional analytical methods struggle to detect trace amounts, leading to the development of SSME techniques for efficient separation. [10, 11, 13, 14] [26-29]

The SSME technique, which selectively extracts heavy metals from various matrices, has shown success in environmental, food, and biological samples. Future research will expand its use to more complex matrices, particularly in biological contexts. The selection of the appropriate solvent significantly influences the extraction amount. [6]

SUPRAS micro-extraction is an environmentally friendly method for pre-concentrating pesticide residues in food and environmental samples. It involves mixing an amphiphile with a dispersion solvent, utilizing tetrahydrofuran for high enrichment factors and recovery rates. [26-28, 30, 32, 35]

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SYNTHESIS AND CHARACTERIZATION OF SAGO STARCH GRAFTED WITH METHYL ACRYLIC ACID USING CERIC AMMONIUM NITRATE AS INITIATOR

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ABSTRACT

Using ceric ammonium nitrate as an initiator, methyl acrylic acid was grafted onto granular sago starch. Grafting has been examined in the context of several reaction parameters, spanning initiator concentration, monomer concentration, polymerization time, polymerization temperature, material to liquid ratio, and solvent. [CAN] = 0.008 mol/L, [MAA] = 0.3538 mol/L, time = 180 minutes, temperature = 30 ℃, material to liquid ratio = 1: 15.86, and solvent = water were the ideal grafting conditions. Grafting efficiency (%GE), percentage grafting (%G), and percentage add-on (% Add-on) are the grafting parameters that are employed. Scanning electron microscopy, X-ray diffraction, and infrared spectroscopy were used to analyse the grafted product.

Keywords: Sago starch, Methyl acrylic acid, Ceric ammonium nitrate, IR spectroscopy.

1. INTRODUCTION

Amylose and amylopectin units make up the polysaccharide known as starch [1]. It has qualities including solubility, crystallinity, gelatinization, and retrogradation, and it is abundant, renewable, biodegradable making it inexpensive [2,3]. Numerous physical, chemical, and enzymatic techniques can be used to alter these [4,5]. Grafting vinyl monomers onto starch is a successful chemical modification technique that adds desired qualities to starch without compromising its biodegradable nature. Numerous free radicals, including ceric ammonium nitrate [6,7], potassium persulphate[8,9], ammonium persulfate[10,11] AIBN, BPO[12], potassium tert-butoxide[13], and potassium oxalatomagnate [14], have been used to graft vinyl monomers onto starch. CAN is widely employed as an initiator due to its straightforward method of single electron transfer, creation of free radicals on the starch backbone, and synthesis of pure graft copolymer. Grafting vinyl monomers onto starch, such as acrylamide (AM)[15,16,17], methyl acrylamide (MAM)[18,19], acrylonitrile (AN) [20,21,22], methyl acrylonitrile (MAN)[23,24] and acrylic acid (AA)[15,25] has been extensively studied. However, grafting methyl acrylic acid onto sago starch has received less attention. Thus, implementing CAN as an initiator, the current study discloses grafting MAA onto sago starch.

2. EXPERIMENTAL

2.1) Materials

Sago Starch supplied was dried at 110 ℃ for 10 hours to remove absorbed moisture and store over anhydrous $CaCl_2$, Ceric ammonium nitrate (LOBA CHEMIE PVT. LTD.) was dried in hot air oven at 110 ℃ for 4 hours and stored over $CaCl_2$, Methylacrylic acid (MAA) supplied by LOBA CHEMIE PVT. LTD. stored in refrigerator, anhydrous $CaCl_2$ and Concentrated nitric acid supplied by LOBA CHEMIE PVT. LTD , Whatman filter paper no. 41 supplied by Cytiva.

2.2) Graft copolymerisation

2.0 g of starch and 70 mL of distilled water were combined and stirred to 400 rpm to create a homogenous slurry. After that, it was exposed to a fixed amount of CAN for ten minutes to promote the creation of free radicals on it. Additionally, a predetermined amount of monomer was added, and total volume of reaction mixture was made to 100 mL using distilled water. The reaction mixture was filtered using Whatman filter paper no. 41 once the reaction had finished for the chosen time. After washing with distilled water to get rid of the homopolymer, the residue was dried for 24 hours at 110 degrees in a vacuum oven. Apart from adding a monomer to each pair of reactions, control reactions were likewise conducted in a similar manner.

## 3. RESULTS AND DISCUSSION

3.1) Physical appearance:

Pure sago starch is off whit in colour, but starch-g-MAA was slightly yellowish-white amorphous powder.

Evidence of grafting
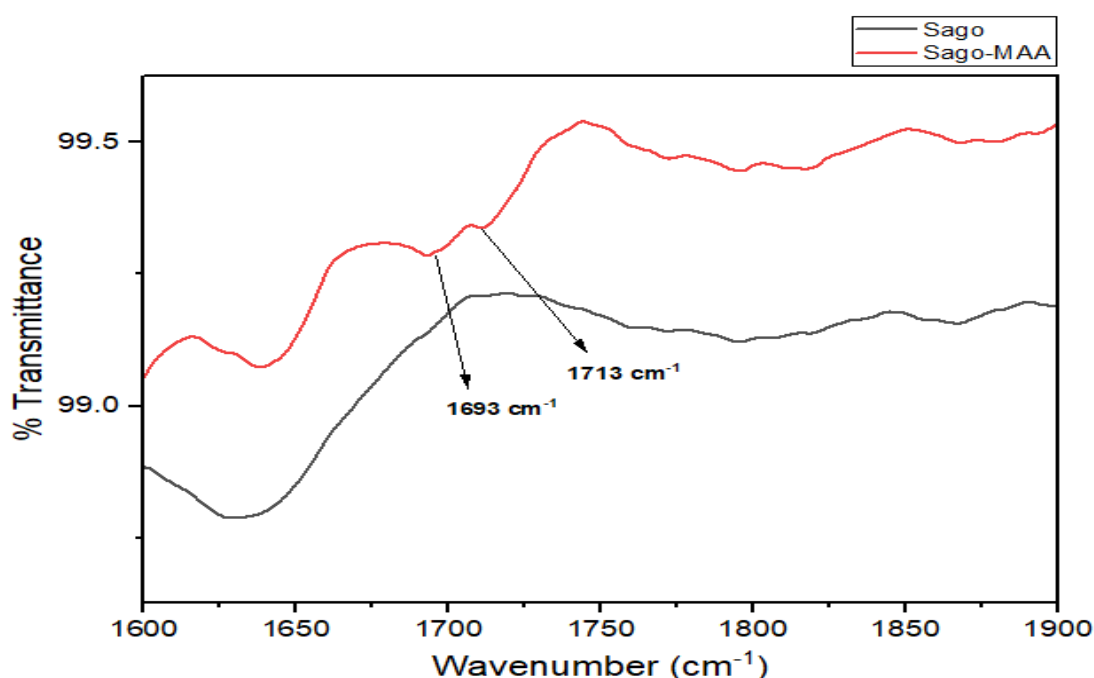
3.1.1) Gravimetric estimation

The grafting of starch is verified using the gravimetric technique. The weight of the residue from the control reaction was compared to the weight of the grafted product. Utilizing 2.0 g of starch and 0.004 M CAN at a room temperature, the control reaction was executed.

3.1.2) Infrared spectroscopy

At ICT Mumbai, infrared (IR) spectra of grafted and pure sago starch have been measured in the 4000–400 cm-1 region. The image below displays the IR spectra of starch-g-MAA and pure sago starch. In this case, the grafting of starch with MAA is confirmed by the presence of two additional peaks at 1693 cm-1 and 1713 cm-1, which reflect C=O stretching vibrations.
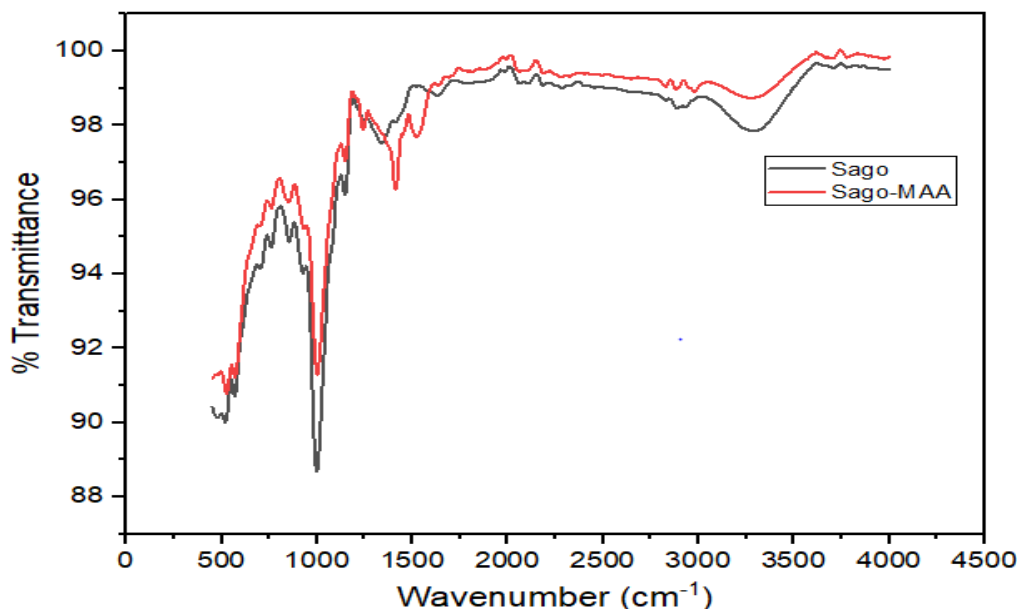
(Fig.1): a] IR of pure sago starch and methyl acrylic acid grafted sago starch. b] Enlarged IR of pure sago starch and methyl acrylic acid grafted sago starch

3.2) Impact of several factors on grafting:

Based on gravimetric estimation, the following formulas were used to figure out the grafted parameters: percentage grafting (%G), grafting efficiency (%GE), and percentage add on (% Add on) [6,19]:

$$\%GE = 100(W_2 - W_1) / W_3$$

$$\%G = 100(W_2 - W_1) / W_1$$

$$\%Add\ on = 100(W_2 - W_1) / W_3$$

Here, W_1, W_2, and W_3 are the weights of pure starch, grafted starch copolymer and monomer respectively,

3.2.1) Impact of initiator concentration

Table 1 demonstrates how CAN concentration impacts MAA grafting onto sago starch. It has been noted that as CAN concentration rises from 0.001 M to 0.008 M, the %G rises as %GE and % grow. At 0.008 M, the highest percentages of GE, G, and add-on were 9.51%, 14.48%, and 12.65%, respectively. The rise in free radical sites on the backbone of starch is the reason of this. Due to i) the unavailability of sites on the starch backbone and ii) the homopolymerization of MAA caused by the high concentration of CAN, further increases in CAN concentration result in a drop in all grafting parameters.

(Table 1) Sago starch 2.0 g, [MAA] = 0.3538 M in 100 mL of distilled water 30℃ for 180 min.

[CAN] M	% GE	%G	% Add on
0.001	3.68	5.61	5.31
0.002	4.82	7.34	6.84
0.003	5.77	8.78	8.08
0.004	6.01	9.14	8.38
0.006	7.59	11.56	10.84
0.008	**9.51**	**14.48**	**12.65**
0.010	8.96	13.64	12.00
0.012	8.57	13.06	11.55

3.2.2) Impact of monomer concentration

The impact of monomer (MAA) concentration on grafting % and grafting efficiency is shown in Table 2. %GE and %G rise in tandem with the MAA concentration, that rises from 0.1179 M to 0.3538 M. Therefore, given a concentration of 0.3538 M MAA, the maximum %GE achievable is 9.51%. The percentage of GE decreases as the MAA concentration rises further. Because MAA homopolymerizes rather than grafts onto the starch backbone, the percentage of GE decreases at high MAA concentrations.

(Table 2) Starch 2.0 g, [CAN] = 0.008 M in 100 mL of distilled water 30℃ for 180 min.

[MAA] M	% GE	%G	% Add on
0.1179	2.28	1.17	1.15
0.2359	5.66	5.74	5.43
0.3538	**9.51**	**14.48**	**12.65**
0.4718	7.27	14.75	12.85
0.7076	5.42	16.52	14.17
0.9435	4.68	19.05	15.98
1.1794	3.38	17.17	14.65

3.2.3) Impact of polymerization time:

The impact of time on MAA grafting onto sago starch is displayed in Table 3. Grafting is seen to occur at a slow rate, which eventually levels off after slowing down even more. More and more monomers react with free radical sites on starch with time. Ultimately, the levelling off is caused by a decrease in the concentration of monomer and a reduction in the amount of monomer available for additional grafting.

Table 3) Starch 2.0 g, [CAN] = 0.008M, [MAA] = 0.3538 M in 100 mL of distilled water 30℃.

Time(min)	% GE	%G	% Add on
30	7.88	11.99	10.71
60	8.05	12.26	10.92
90	8.72	13.28	11.72
120	8.91	13.57	11.94
150	9.14	13.91	12.21
180	**9.51**	**14.48**	**12.65**
210	9.55	14.54	12.69
240	9.59	14.60	12.74

3.2.4) Impact of reaction temperature

Table 4 illustrates how temperature affects MAA grafting onto sago starch. The %G and %GE are shown to increase with an initial temperature increase of up to 30℃. However, both %G and %GE drop as the temperature rises further. This is due to the high activation energy and favourable nature of chain transfer processes.

(Table 4) Starch 2.0 g, [CAN] = 0.008M, [MAA] = 0.3538 M in 100 mL of distilled water at 30℃ for 180 min.

Temperature (℃)	% GE	%G	% Add on
25	6.56	9.98	9.08
30	**9.51**	**14.48**	**12.65**
35	8.09	12.32	10.97
40	7.82	11.91	10.64
45	6.41	9.76	8.89
50	5.48	8.35	7.71
55	4.66	7.09	6.62

3.2.5) Impact of material to liquor ratio

The consequence of the material to liquor ratio on grafting is shown in Table 5. By altering the amount of water in the reaction medium, the material to liquor ratio was modified. Grafting parameters are found to increase with an initial volume drop from 100 mL to 80 mL. The %G and %GE likewise drop with further volume reduction. This results from the limited mobility of monomer molecules as their volume decreases.

Table 5) Starch 2.0 g, [CAN] = 0.008M, [MAA] = 0.3538 M in 100 mL of distilled water at 30℃ for 180 min.

Material to liquor ratio	Total volume of water	% GE	%G	% Add on
1:19.82	100	9.51	14.48	12.65
1:15.86	**80**	**10.37**	**15.78**	**13.63**
1:11.89	60	9.56	14.55	12.70
1:7.93	40	8.81	13.42	11.83

3.2.6) Impact of solvent

Table 6 displayed the influence of several solvents on MAA grafting onto sago starch. Here, the highest percentages of GE and %G have been detected in water. When alcohol is added to water, the percentages of GE and G drop, and the order is methanol > ethanol > iso-propanol.

Table 6) Starch 2.0 g, [CAN] = 0.008M, [MAA] = 0.3538 M in 100 mL of distilled water at 30℃ for 180 min.

Solvent	Water: alcohol	% GE	%G	% Add on
Water	**100: 00**	**9.51**	**14.48**	**12.65**
Methanol	80:20	7.42	11.30	10.16
Ethanol	80:20	6.50	9.90	9.01
Iso-propanol	80:20	1.71	2.61	2.54

3.3) Characterisation of graft copolymer

3.3.1) X-ray diffraction studies

Granules of starch exhibit a semi-crystalline structure. Because of the amylopectin proportion, crystallinity is essential. About 20–25% of the starch granules' total volume is made up of the crystallinity regions. Pure granular sago starch's wide angle X-ray diffraction pattern highlights three roughly sharp peaks with low counts only up to 1200 between 2theta values of 10–30 degrees. These peaks appear to have compressed into a broad, smoothed peak upon drying and grafting, changing the crystallinity of pure sago starch (fig. 2) Therefore, it may be concluded that grafting engages both the crystalline and amorphous regions of the granular starch.
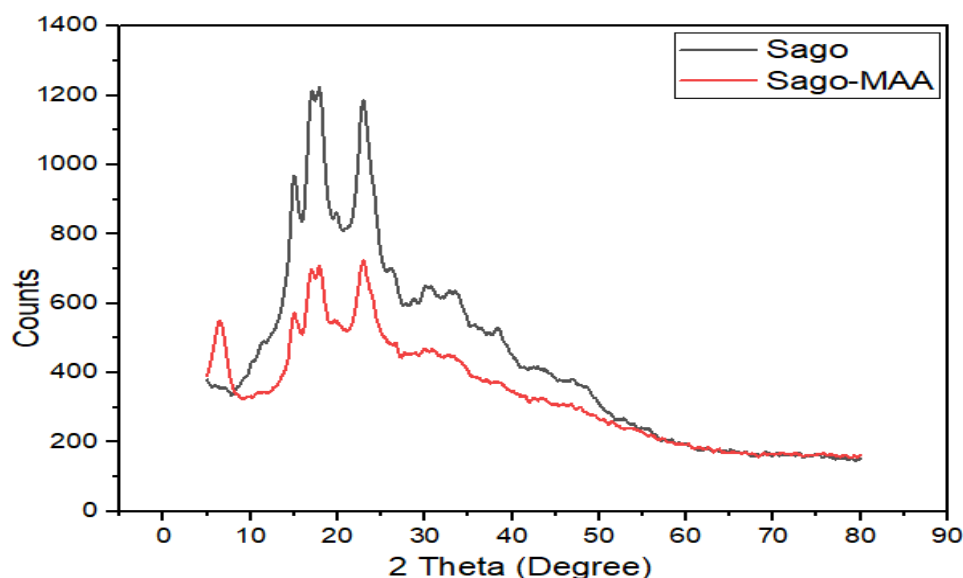
Fig.2) X-ray Diffraction Pattern of pure sago starch and methyl acrylic acid grafted sago starch

3.3.2) Scanning electron microscopy

The best method for directly observing the microstructure of spheroid varying in size from 10 to 50µm sago starch grains is SEM. The granular structure of pure starch is evident in the electron micrographs of the samples (fig.a). The heavy polymeric coating on the granules' surface, which is clearly of grafted poly (methyl acrylic acid), and the change in granule conformation upon grafting are apparent in (fig.b). It is evident that throughout the grafting process, individual starch granules are attached together owing to these surface coatings.
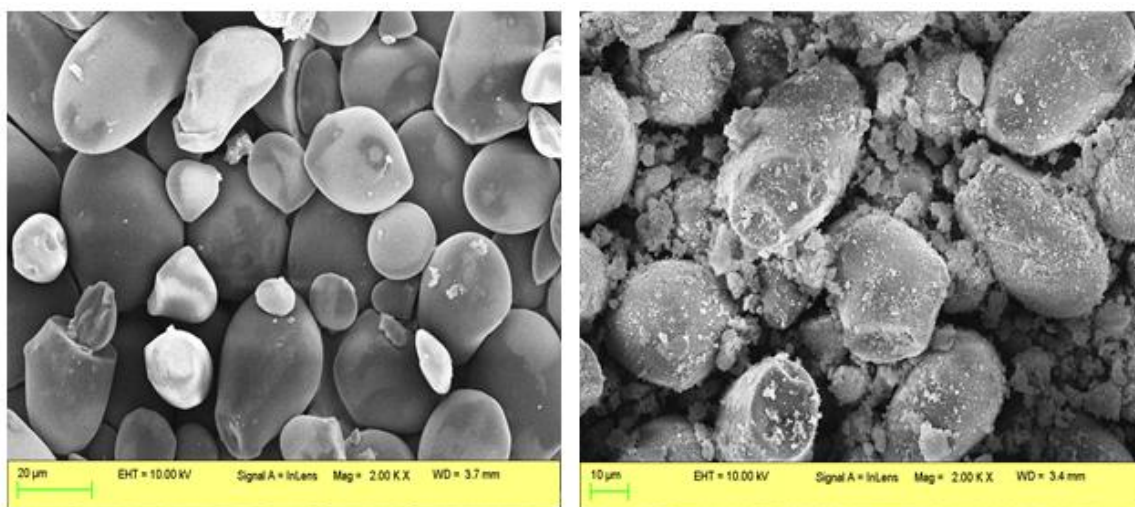
Fig3] SEM photographs of pure sago starch and methyl acrylic acid grafted sago starch

4. CONCLUSION

- The optimum conditions for grafting of MAA on sago starch obtained are as follows:

[CAN] = 0.008 M

[MAA] = 0.3538 mol/L

Reaction time = 180 minutes

Polymerization Temperature = 30℃

Solvent = water

- In addition to the amorphous component, grafting also utilizes the crystalline component of starch.

- Over individual starch granules, a thick layer of grafted starch is formed.

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APPLICATIONS OF GRAPH THEORY IN FINANCE

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ABSTRACT

Graph theory, a fundamental area of discrete mathematics, provides a powerful framework for modeling and analyzing financial systems. Financial markets, risk assessment, portfolio optimization, and fraud detection are some of the many areas where graph-based approaches enhance decision-making and efficiency. This paper explores key applications of graph theory in finance, discussing network structures, market modeling, and algorithmic trading. Additionally, it highlights how graph-based machine learning techniques are revolutionizing financial analytics. This paper also delves into constructing the minimal spanning tree of stocks that captures the essential relationships between them while reducing complexity.

Keywords: Financial network, Distance metric , Minimal spanning tree.

1. INTRODUCTION

Finance is inherently complex, involving relationships among various entities such as investors, stocks, banks, and financial instruments. These relationships can be effectively represented using graphs, where nodes represent entities and edges represent interactions. Graph theory enables the visualization and quantitative analysis of such interactions, aiding in risk assessment, optimization, and fraud detection.

This paper explores the major applications of graph theory in finance, including financial networks, portfolio management, systemic risk analysis, and fraud detection.

2. FUNDAMENTAL CONCEPTS OF GRAPH THEORY

Graph theory studies mathematical structures used to model pairwise relationships between objects. A graph is defined as G (V,E) where V is a set of vertices (nodes) and E is a set of edges (connections). Key types of graphs relevant to finance include:

Directed Graphs: Where edges have a direction (e.g., transaction flows).

Weighted Graphs: Where edges have weights representing relationship strengths (e.g., correlation between stocks).

Bipartite Graphs: Where two distinct sets of nodes interact (e.g., banks and borrowers).

Dynamic Graphs: Evolving over time (e.g., changing market structures).

3. APPLICATIONS OF GRAPH THEORY IN FINANCE

3.1 Financial Networks and Systemic Risk Analysis:

Financial systems involve interconnected institutions such as banks, insurance companies, and investment firms. Graph theory helps to analyze these relationships and assess systemic risk of collapse due to interdependencies.

Interbank Lending Networks: Represented as directed graphs, where nodes are banks and edges represent lending relationships. Detecting central nodes helps identify institutions critical to financial stability.

Contagion Modeling: Graph algorithms, such as PageRank, help model how financial distress spreads through a network.

Stress Testing: Simulations on financial graphs help regulators predict the impact of shocks on the system.

3.1.1 Model: Minimum Spanning Tree (MST) in Stock Correlation Networks

Overview of the Model

A Minimum Spanning Tree (MST) is a subgraph of a weighted network that connects all nodes (stocks) with the minimum total edge weight (correlation distance) while avoiding cycles. This model simplifies complex financial networks by retaining essential relationships and removing redundant connections.

How MST Works in Finance

Each stock is a node in the graph. The correlation between stock returns is used as the edge weight (distance measure). The goal is to construct a tree that captures the essential relationships between stocks while reducing complexity. The Prim's or Kruskal's algorithm is commonly used to find the MST.

Example: Applying MST to Nifty 50 Stock Correlation Network

Step 1: Construct the Stock Correlation Network

Collect historical stock price data for 5 stocks of Nifty 50 companies.

Compute the Pearson correlation coefficient between each pair of stocks.

Convert correlations into a distance metric by applying $d_{ij} = \sqrt{2(1 - \rho_{ij})}$

Step 2: Apply Minimum Spanning Tree (MST) Algorithm

Treat each stock as a node. Use Kruskal's or Prim's algorithm to build the MST, ensuring all stocks relate to the minimum total distance. These algorithms iteratively add edges to form the MST.

Step 3: Interpret the Results

The MST reveals industry clusters (e.g., tech stocks form a tight group). Stocks with central roles (high degree) serve as market influencers. Helps in portfolio diversification by identifying weakly connected stocks. Following example illustrate the theory.

Example Output (Simplified MST for 5 Stocks)

Let's go through a concrete example using five Indian stocks (for simplicity) and construct a Minimum Spanning Tree (MST) based on their correlation.

Example: Applying MST to Indian Stocks

We choose five Indian stocks from different sectors:
1. Reliance Industries Ltd. (RELIANCE) - Energy

2. Tata Consultancy Services Ltd. (TCS) - IT

3. HDFC Bank Ltd. (HDFCBANK) - Banking

4. Infosys Ltd. (INFY) - IT

5. State Bank of India (SBIN) - Banking

Step 1: Get Historical Stock Prices

Assume we collected daily closing prices for one year.

Step 2: Compute Log Returns

We calculate the logarithmic returns for each stock using:
$r_t = \ln\left(\frac{P_t}{P_{t-1}}\right)$ Where P_t is the closing stock price at the time t.

Step 3: Compute Correlation Matrix ρ_{ij}.

After calculating log returns, we compute the correlation matrix:

Stock	RELIANCE	TCS	HDFCBANK	INFY	SBIN
RELIANCE	1.00	0.65	0.75	0.60	0.70
TCS	0.65	1.00	0.50	0.85	0.55
HDFCBANK	0.75	0.50	1.00	0.55	0.80
INFY	0.60	0.85	0.55	1.00	0.50
SBIN	0.70	0.55	0.80	0.50	1.00

Step 4: Convert Correlation to Distance using formula

$d_{ij} = \sqrt{2(1 - \rho_{ij})}$ where ρ_{ij} is the correlation between stock i and stock j.

After applying this formula, we get the distance matrix:

Stock	RELIANCE	TCS	HDFCBANK	INFY	SBIN
RELIANCE	0.00	0.91	0.71	1.10	0.85
TCS	0.91	0.00	1.26	0.55	1.17
HDFCBANK	0.71	1.26	0.00	1.17	0.63
INFY	1.10	0.55	1.17	0.00	1.26
SBIN	0.85	1.17	0.63	1.26	0.00

Step 5: Apply the Minimum Spanning Tree (MST) Algorithm

We apply Kruskal's Algorithm to find the MST:
1. Start with an empty graph (no edges).

2. Sort the edges by increasing weight (distance).

3. Add edges one by one, ensuring no cycles are formed.

Visualise MST as a graph, where each node represents a stock, and the edges represent the correlation distances.

After applying MST, we get the following network:
(HDFCBANK -SBIN) (0.63)

(HDFCBANK -RELIANCE) (0.71)

(TCS- INFY) (0.55)

(RELIANCE - TCS) (0.91)

Step 6: Interpret the Results

a) HDFCBANK and SBIN have the strongest connection, indicating that private and public banks are closely related.

b) TCS and INFY are directly connected, as both belong to the IT sector.

c) Reliance is linked to banking (HDFCBANK), showing a significant connection between energy and financial markets.

3.1.2 Conclusion
By constructing the Minimum Spanning Tree, we eliminate weaker relationships and highlight the most significant connections. This method helps in:

1. Portfolio Diversification -Identify weakly connected stocks for better diversification.

2. Risk Management - Understand how stocks movement might impact others.

3. Market Insights - Observe how different sectors are interrelated.

This approach can be expanded to 10+ stocks for a more detailed financial network analysis.

3.2 Portfolio Optimization and Asset Allocation
Modern portfolio theory (MPT) benefits from graph-based approaches, particularly in clustering and network analysis.

Correlation Networks: Stocks can be represented as nodes, with edges weighted by correlation coefficients. Community detection algorithms help identify clusters of highly correlated assets, aiding diversification.

Minimum Spanning Trees (MST): Used to simplify asset correlation networks, identifying key assets that drive market movements.

Graph-Based Portfolio Optimization: Machine learning algorithms using graph embeddings improve asset selection and allocation.

3.3 Market Structure and Trading Strategies
Graph theory plays a significant role in understanding financial market microstructure and optimizing trading strategies.

Limit Order Book as a Graph: Orders in financial markets can be structured as a graph where buyers and sellers are nodes, and bids/asks form edges. Graph-based learning improves order matching efficiency.

Algorithmic Trading: Graph neural networks (GNNs) analyze market trends, improving algorithmic trading models.

Liquidity Networks: Understanding liquidity flows in financial markets helps detect potential crises.

3.4 Fraud Detection and Anomaly Detection
Financial fraud, such as money laundering and insider trading, often involves complex networks of transactions that can be detected using graph theory.

Transaction Graphs: Suspicious transactions are identified using anomaly detection algorithms on transaction graphs.

Community Detection: Helps identify fraudulent groups involved in insider trading or coordinated trading schemes.

Graph Machine Learning for Fraud Detection: GNNs classify entities as fraudulent or non-fraudulent based on transaction patterns.

4. EMERGING TRENDS AND FUTURE DIRECTIONS

The application of graph theory in finance is expanding with advancements in artificial intelligence and big data analytics. Key emerging areas include:

1. **Graph Neural Networks (GNNs) in Financial Forecasting:** Using deep learning on financial graphs to improve risk predictions and trading models.

2. **Blockchain and Graph-Based Cryptography:** Enhancing security in decentralized finance (DeFi).

3. **Real-Time Financial Graph Analytics:** Detecting market anomalies and risks in real time.

5. CONCLUSION

By constructing the Minimum Spanning Tree, we eliminate weaker relationships and highlight the most significant connections. This method also helps in Portfolio Diversification

Risk Management and market Insights. Graph theory provides a robust mathematical foundation for analyzing fraud detection. As financial data becomes increasingly complex, integrating graph-based machine learning techniques will further revolutionize financial analytics. Future research should focus on real-time financial graph analysis and the integration of GNNs for enhanced predictive modelling.

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SYNTHESIS AND CHARACTERIZATION OF COPPER OXIDE (CUO) NANOPARTICLES VIA CHEMICAL PRECIPITATION (THERMAL TREATMENT EFFECT)

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ABSTRACT

This study investigates the effect of calcination temperature on the structural, functional, and physical properties of copper oxide nanoparticles (CuO-NPs). CuO-NPs were synthesized using a chemical precipitation method with sodium hydroxide as the precipitating agent, followed by calcination at 400°C, 600°C, and 800°C. The nanoparticles were characterized using X-ray diffraction (XRD) to determine crystallite size, microstrain, and dislocation density, while Fourier- transform infrared (FTIR) spectroscopy was used to analyze functional groups. XRD analysis revealed an increase in crystallite size from 51.14 nm at 400°C to 168.50 nm at 800°C, with an intermediate size of 61.70 nm at 600°C, accompanied by a decrease in microstrain and dislocation density, indicating enhanced crystallinity. FTIR spectroscopy confirmed the presence of Cu-O bonding and variations in functional groups influenced by calcination temperature. These findings highlight the significant role of thermal treatment in modifying the structural, functional, and physical properties of CuO-NPs, which is crucial for their potential applications in various fields.

Keywords: chemical precipitation method, copper oxide nanoparticles, microstrain, dislocation density.

HIGHLIGHTS

- CuO nanoparticles (CuO-NPs) were synthesized via chemical precipitation method using copper (II) chloride dihydrate.

- Calcination was performed at 400°C, 600°C, and 800°C to study temperature effects.

- Characterization of CuO nanoparticles by XRD and FTIR.

GRAPHICAL ABSTRACT
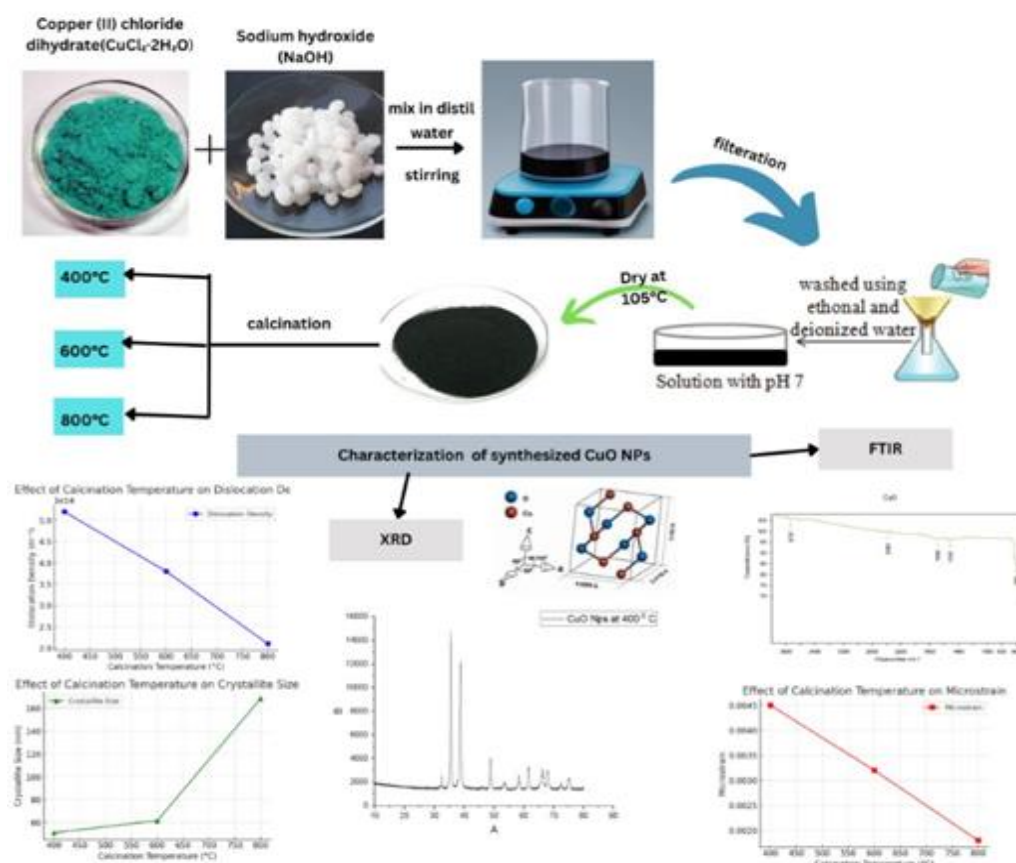
1. INTRODUCTION

Nanoscience has gained significant interest for its crucial innovative role in controlling materials at the elemental and chemical levels to significantly regulate the material characteristics. Materials minimized to the nanoscale exhibit noticeably unique properties compared to their large-scale or micro-scale counterparts. Because of their properties, nanomaterials are extensively used in lots of applications. These nanoparticles can play an important role in growing the properties of substances. Nanoparticles are emerging as an increasing number of critical daily as they play a useful position in an extensive form of medical sectors. Overall, the scale of a nanoparticle covers the variety between 1 and 100 nm. Nanoscience deals with the structure, fabrication, and application of useful systems with, as a minimum, one function size measured in nanometers. At present, nanoparticles are extensively used in various fields [1]-[17].

Copper oxide nanoparticles (CuO-NPs) have captured widespread focus due to their unique physicochemical characteristics and versatile applications across multiple domains. With large specific areas, exceptional catalytic activity, enhanced conductivity and heat resistance, it is widely utilized for advanced technological uses. Compared to bulk copper oxide, CuO-NPs exhibit enhanced reactivity, selectivity, and structural integrity, making them appropriate for a wide range of applications. They have shown exceptional antibacterial performance against multiple microbial species [2] and are widely employed in pollution control strategies, such as pigment extraction [3], the fabrication of ultrafine layers [4], air pollutant detection [5], microelectronic components [6], organic catalysis [7], and photovoltaic energy transformation [8]. Furthermore, CuO-NPs are essential for heat transfer applications, significantly improving the heat efficiency of nanoparticle suspensions over traditional alternatives [9]. Their multifunctional properties fuel technological progress in fields such as nanotechnology, electronics, and batteries.

Copper oxide nanoparticles can be synthesized using both chemical and physical processes. These consist of electrochemical deposition, hydrothermal techniques, sol-gel processing, reductive synthesis [10], photochemical reduction, the utilization of emulsifiers and passivating compounds, low-pressure infiltration [11], thermal decomposition [12], and precipitation methods [13]. In this research, copper oxide nanoparticles were prepared using the chemical precipitation method, selected due to its simplicity, cost-effectiveness, and one-step synthesis process. Temperature is a key parameter in affecting both the purity and size of nanoparticles. Increased thermal conditions provide additional thermal energy, promoting elemental dispersion and enhancing structural formation, which leads to larger crystallite sizes. This effect is clearly observed during the calcination process, where elevated temperatures assist in purifying material composition, improve crystallinity, and reduce structural defects. This CuO-NPs was perfect, indicating a well-organized crystal structure and phase purity. However, excessively high temperatures could cause nanoparticle clustering, which can compromise the intended morphology and its characteristics. Therefore, optimizing temperature is crucial for regulating crystal structure and producing refined copper oxide nanomaterials with specific characteristics. Luna et al. (2015) [14] highlighted the significance of thermal treatment in improving the structural and functional properties of nanomaterials.

In this study, CuO nanoparticles (CuO-NPs) will be subjected to thermal treatment at 400°C, 600°C, and 800°C to analyze their effect on phase purity, nanostructure scale, and crystallinity. The synthesized nanoparticles will be investigated using Fourier-transform infrared spectroscopy (FTIR) to verify the presence of Cu-O bonds and X-ray diffraction (XRD) to estimate the average crystallite size and other structural parameters.

2. MATERIALS AND METHODS

2.1. Materials

All chemicals were of analytical grade and used without further purification. Copper (II) chloride dihydrate [(CuCl·2HO), 98%], Sodium Hydroxide Pellets [(NaOH), 99.8%], Ethanol [(C2H5OH), 99.9%], double distilled, which were purchased from Ami Chemical, kalbadevi, Mumbai (India). All reagents and chemicals were pure and used with no further treatment.

2.2. Methods

Procedure for synthesis of CuO NPs

Copper oxide (CuO) NPs were synthesized by the Chemical Precipitation Method by utilizing Copper (II) chloride dihydrate as the precursor, NaOH precipitating agent, and ethanol as the solvent. 9 g of copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$) was measured and dissolved in 50 mL of deionized water with continuous stirring using a magnetic stirrer for half an hour. 6 g (3 M) NaOH has been added as much as 50 mL into the $CuCl_2 \cdot 2H_2O$ solution slowly in increments with continuous stirring and thermal application until the color changed, turning deep black.

The process was permitted to continue with stirring for 90 minutes at room temperature. The resulting precipitate was separated by centrifugal force to separate the solid and liquid phases at 6000 rpm for 20 minutes. Additionally, the precipitate is washed with deionized water 3-4 times to remove the salt that is still contained in the precipitate. The final material is dried in an oven at 105 °C for 4 hours. Samples were calcined at 400°C, 600°C, and 800°C in a furnace for 4 hours to study its effect. Fig. 1 shows a pictorial presentation of synthesis of CuO NPs obtained after calcination.

(a) Copper (II) chloride dihydrate + deionized water solution

(b) Sodium Hydroxide + deionized water solution

(c) Mixing both solution

(d) Black precipitate formed

(e) Centrifuge done

(f) CuO NPs formed at 800°C
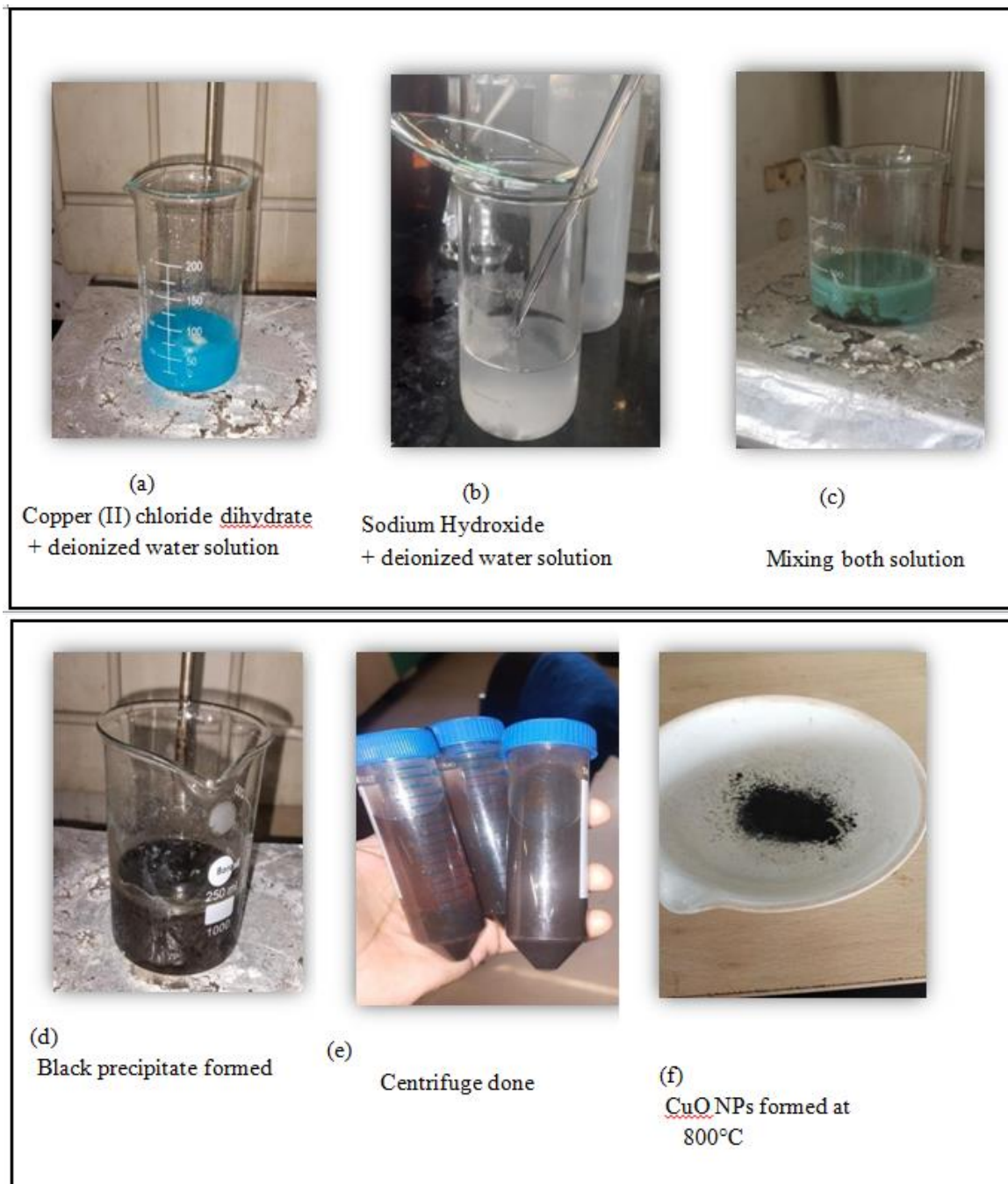
Fig. (1). Pictorial presentation of synthesis of CuO NPs by chemical precipitation method.

In this synthesis, the copper (II) chloride dihydrate integrates with sodium hydroxide in a hydrated solution, generating copper (II) hydroxide as a solid precipitate and salts. During thermal treatment, the copper (II) hydroxide passes through thermal decomposition, resulting in the development of black copper (II) oxide and the emission of water vapor. The reaction is presented as follows:

CHEMICAL REACTION

$CuCl_2 \cdot 2H_2O(aq) + 2NaOH(aq) \rightarrow Cu(OH)_2(s)\downarrow + 2NaCl(aq)$ $Cu(OH)_2(s) \rightarrow CuO(s) + H_2O\uparrow$
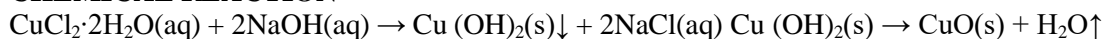
After successfully synthesizing CuO NPs, they were characterized using structural & spectroscopic techniques.

3. RESULT AND DISCUSSION

3.1. Characterization of CuO nanoparticles

The characterization of synthesized nanoparticles was done by following analytical techniques, such as Fourier Transform Infrared spectroscopy (FTIR) to identify the functional groups present in the synthesized material. X-ray Diffraction (XRD), to determine the structures, crystalline phase, and particle size.

3.1.1 Fourier Transform Infrared spectroscopy (FT-IR)

Fourier-transform infrared spectroscopy has been used to identify the functional groups and chemical bonds present in the synthesized CuO NPs. Functional groups with electrostatic interaction have resulted in strong absorption in the IR region. The FTIR spectra indicated that the tested CuO nanoparticles displayed characteristic vibrational modes corresponding to the tenorite (CuO) phase in all three samples. The FTIR spectrum of CuO NPs calcinated at 400°C, 600°C and 800°C, which were recorded in a wavenumber range of 500 cm^{-1}–3800 cm^{-1} (Fig. 2).

In this spectrum, the peak located at 528 cm^{-1} and 604 cm^{-1} is the monoclinic phase of pure CuO NPs. The small peaks at 1514 cm^{-1} and 1690 cm^{-1} are due to the carbonyl C=O stretching bonds. The small peak shift in the phonon modes is associated with the related variation in the surface area of the prepared CuO-NPs [18]. The broad peaks observed around 3739 cm^{-1} and 2382 cm^{-1} correspond to the stretching vibrations of hydroxyl (-OH) functional groups, indicating the presence of residual moisture or surface-adsorbed water molecules [19]. Therefore, the FTIR spectrum confirms the formation of CuO NPs.
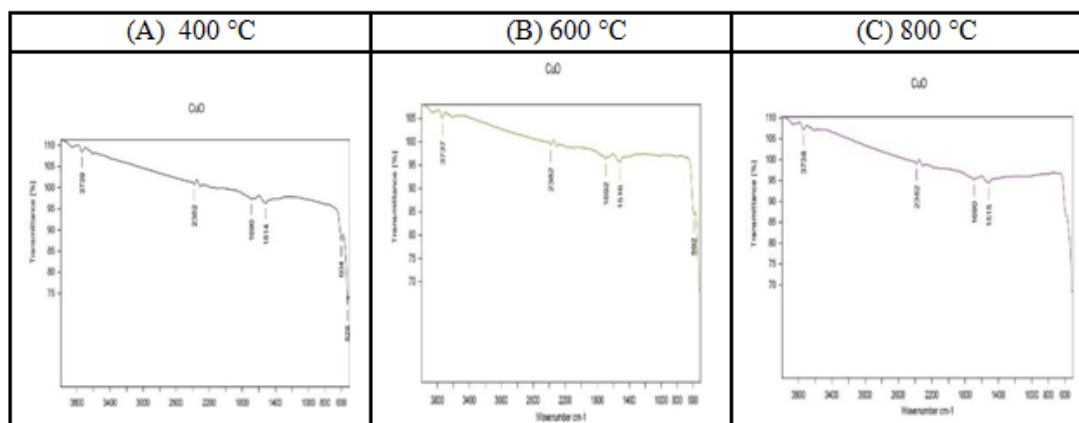
Fig. 2: Fourier transform infrared spectroscopy spectra of CuO NPs at different temperatures.

3.1.2 XRD (X-Ray Diffraction) Study

Structural identification of synthesized CuO NPs is done using this technique. The diffraction peaks signified that the analyzed particle possessed a structural pattern of CuO (tenorite) nanoparticles. The reflection outcome observed in the three CuO samples was visible, and each sample exhibited structural characteristics that were nearly identical. Fig. 3 shows the XRD pattern of CuO NPs annealed by thermal treatment at 400°C, 600°C, and 800°C along with the reference tenorite (CuO), which produced a diffraction pattern similar to the monoclinic phase of CuO (tenorite) nanoparticles. The strengths and position of the peaks were in good agreement with the documented values. The observational results were also found to be similar to the previously reported data of CuO NPs [20]. From the diffractogram at CuO NPs, the miller indices (hkl) were estimated within the 2θ range of 20° to 80° and were indexed to 31.69° (110); 35.48° (11-1); 38.74° (111); 48.83° (20-2); 52.83° (020); 58.23° (202); 61.67° (-113); 66.26° (31-1); 68.09° (220); 72.45° (311); 74.95° (22-2). The diffraction read indicated that the CuO nanoparticles had a monoclinic phase with a = 4.585 Å, b = 3.323 Å, and c = 5.122 Å at 400°C, a = 4.485 Å, b = 3.243 Å, and c = 5.242 Å at 600°C, and a = 4.681 Å, b = 3.423 Å, and c = 5.232 Å at 800°C.

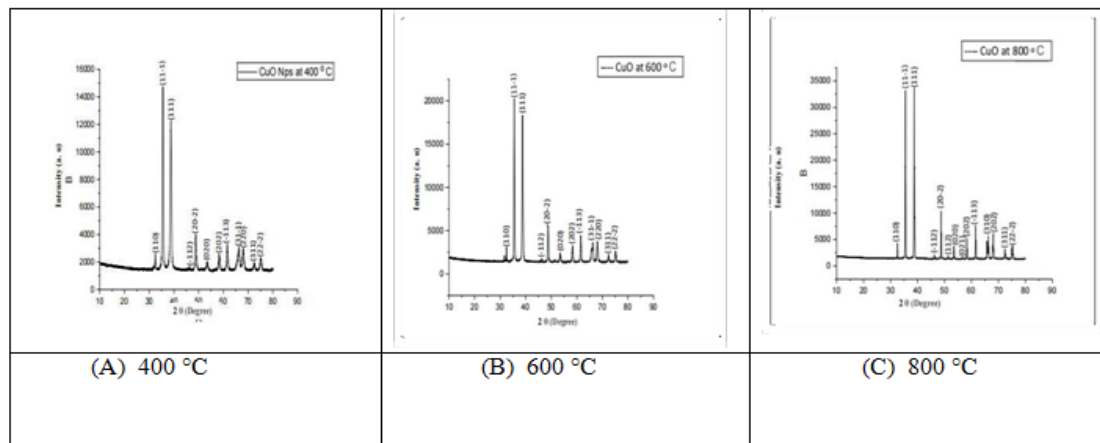|		
(A) 400 °C	(B) 600 °C	(C) 800 °C

Fig. 3. The XRD pattern of synthesized CuO NPs at different temperatures

The average crystallite size is calculated from XRD peak broadening by using Debye Scherrer's equation [21].

$$\text{Crystallites size (D)} = \frac{0.9\lambda}{\beta \cdot \cos\theta}$$

Where D is the average crystallite size, λ is the X-ray wavelength (1.5406 Å), β is the full width at half maximum (FWHM) of each peak in radians, and θ is the Bragg diffraction angle. The obtained crystallite size (D) increases with increasing the temperature (Table.1).

The dislocation density in CuO nanoparticles is calculated using relation [22]. Where δ is the dislocation density, the number of defects and vacancies in the crystal, and can be decided using the crystallite size (D) with the below formula. The obtained dislocation density is decreasing with increasing temperature (Table 1).

$$\text{Dislocation density } (\delta) = \frac{1}{D^2}$$

Microstrain (ε) indicates the distribution of crystal deformations within a crystal and can be determined using the Williamson-Hall equation.

Using this equation, we get

$$\beta\cos = \frac{k\lambda}{D} + 4\varepsilon\sin\theta$$

$$\text{Microstrain } (\varepsilon) = \frac{\beta}{4\tan\theta}$$

Table 1: Structural Parameters of CuO Nanoparticles at Different Calcination Temperatures

Calcination Temperature (°C)	2θ in degrees	Miller Indices (hkl)	Crystallite Size (D, nm)	Micro Strain (ε)	Dislocation Density (δ, nm⁻²)	Crystal Structure
400°C	31.686	(110)	51.14	0.1400	3.82×10^{-4}	Monoclinic
600°C	32.5050	(110)	61.70	0.1130	2.63×10^{-4}	Monoclinic
800°C	35.4430	(11-1)	168.50	0.0380	3.52×10^{-5}	Monoclinic

From the diffractogram, it was found that peak intensity is maximum for CuO nanoparticle annealing at 800°C in comparison to 400°C and 600°C. This shows an increase in the degree of crystallinity of synthesized CuO NPs, showing reduced microstrain, improving the crystal parameters. At the annealing temperature of 400°C, CuO NPs have high defects and strain, which leads to a smaller crystallite size and lower crystallinity. Further increase in annealing temperature to 800°C leads to larger crystallite sizes of CuO NPs. Therefore, the degree of crystallinity of CuO NPs annealed at 800°C was the highest.

The effect of thermal treatment on the synthesized CuO NPs at 400°C, 600°C and 800°C is as shown in Fig. 4.
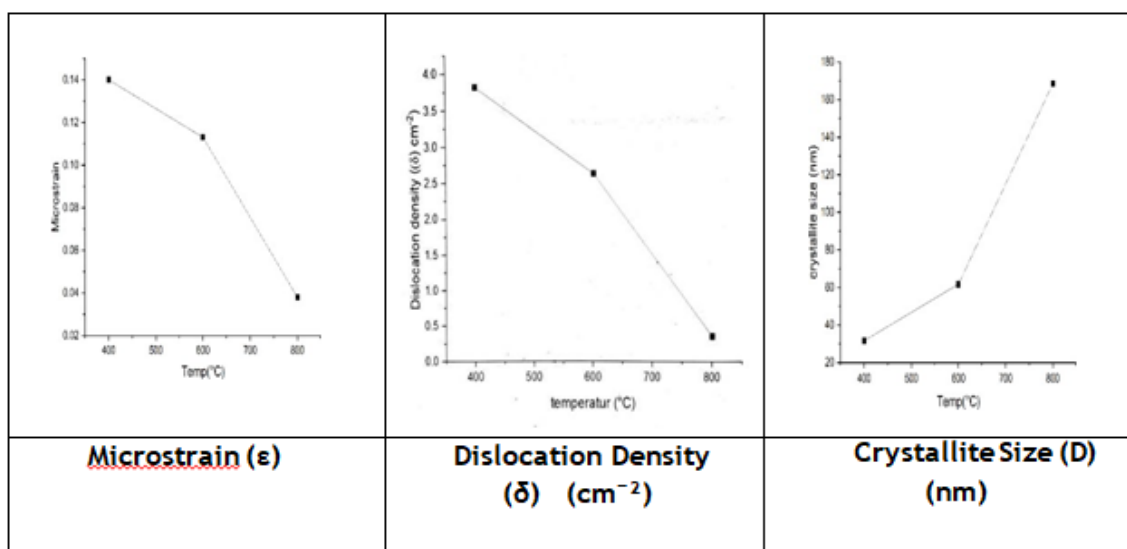
Fig. .4. Thermal treatment as CuO NPs

As the temperature increases, the moment between the particles size increases, resulting in a reduction in microstrain and dislocation density. This results in the agglomeration of CuO NPs, giving them a higher crystal size.

4. CONCLUSION

In the present work, we conclude that CuO nanoparticles has been effectively synthesized by a simple co-precipitation method. This method provides a large-scale production of CuO nanoparticles at relatively high purity and very low cost. The effect of calcination of the nanoparticles at $400^{\circ}C$, $600^{\circ}C$ and $800^{\circ}C$ was studied through FTIR and XRD characterizations. FTIR analysis showed presence of carbonyl and hydroxyl stretching bonds. XRD indicates the formation of pure CuO nanoparticles with a monoclinic phase at all temperatures with an increase in crystallite size, making it suitable for gas sensing applications.

5. ACKNOWLEDGEMENT

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NANOCRYSTALLINE COBALT FERRITE THIN FILM DEPOSITED USING ECOFRIENDLY ELECTROCHEMICAL ROUTE AND THEIR APPLICATIONS AS SUPERCAPACITORS

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ABSTRACT

In the present research work, electrochemical route was used for synthesis of cobalt ferrite thin films. The Potentiostat was used for synthesis as well as to study the electrochemical behavior. AR grade 0.1M Cobalt sulphate and 0.1 Iron sulphate was complexed with citric acid and electrodeposition of CoFe alloy was carried out from this bath. Ethylene glycol was used as an organic solvent for preparation of all solutions. Deposition of Cobalt Iron alloy was carried out at room temperature. After electrodeposition, this alloy film was used as an anode and anodization of CoFe alloy was carried out for the formation of Cobalt ferrite. Small heat treatment converts this $CoFe_2$ into $CoFe_2O_4$.

Using XRD technique, structural studies were carried out which confirm cubic spinel crystal structure of Cobalt ferrite thin films. SEM images confirm nanocrystallinity as well as smooth, uniform and well growth of Cobalt ferrite thin films over the surface.

These films were used as an electrode in formation of electrochemical capacitor. The observed value of specific and interfacial capacitance is 81.6 Fg^{-1} and 0.28 Fcm^2 respectively.

KeyWords: Electrochemical route, Cobalt ferrite, XRD, SEM, Supercapacitor.

1. INTRODUCTION

Research on cobalt ferrite thin films has been very active because they are good candidates for magneto-opto devices. It is ferromagnetic material with interesting properties such as high coercivity, moderate saturation magnetization, remarkable chemical stability and mechanical hardness [1-5]. It has large-scale technological applications such as transformer cores, recording heads, antenna rods, loading coil memory, microwave devices, catalysts, ferro fluids, magnetic refrigeration, solar energy conversion and biomedical applications [6-11]. Oxide film based thin film supercapacitors have been the subject of considerable attention as energy storage systems, particularly for applications which involve a micro power sources for microelectronic mechanical systems (MEMS) and for back up sources for computer memory chips [12-15]. Many of the other transition metal oxide materials viz. Co_3O_4, NiO, MnO_2 SnO_2 etc have already been tested as an electrode for supercapacitors. Iron based compounds have drawn much attention for their potential applications in various electrochemical devices due to low cost and low toxicity. Some reports are available on the iron-based compound in electrochemical devices such as Li-ion batteries [16].

Various chemical and physical techniques such as deposition with ion beam, Rf sputtering, sol-gel method, spray pyrolysis, ferrite plating, etc. have been used in the preparation of Cobalt ferrite thin films. [17-27]. The electrochemical reaction arises on the working electrodes, where either oxidation or reduction observed during the electrosynthesis.

Principally, electro-deposition can be done from aqueous and non-aqueous baths. By using non-aqueous solvents, serious problems such as precipitation of ferric (Fe $(OH)_3$) can be avoided that were faced in case of aqueous solutions. [28]. During electro-deposition various electro-active species can be added to the electrolytes for improving coating characteristics. The addition of these electro-active species can also improve surface morphology and physical properties of deposits. Intercalation of oxygen can be possible in electrodeposited species and is a well-known phenomenon. The presence of oxygen in the electrodeposition bath gives oxidation of the deposited metal. An increase in pH near the cathode results in the hydrolysis phenomena and consequent precipitation of any iron group [E.g., Co (II), Ni (II)]. An alkaline bath generally depends on the presence of a complexing agent and electrodeposition from an alkaline bath helps incorporate the oxygen species [29-32].

In the present article, the room temperature deposition of Cobalt ferrite thin films from non-aqueous bath was carried out. Using electrosynthesis from an alkaline non-aqueous bath, in a single step cobalt ferrite thin film were deposited. The Cobalt ferrite thin film was deposited from a mixture of cobalt sulfate, iron sulfate, citric acid (complexing agent), and sodium hydroxide using ethylene glycol as an organic solvent. Preparative parameters were optimized to get good quality of cobalt ferrite thin films. Post-heat treatment was given for enhancement of the properties. Structural characterizations of thin films of Cobalt ferrite were done with the help of X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The electrochemical performance of these films were tested using cyclic voltammetry technique.

2. METHODS

Electrodeposition of the Cobalt ferrite thin films:

The deposition of the thin film of Cobalt ferrite was carried out from an electrolyte mixture of 0.1 M $CoSO_4$, 0.1 M $FeSO_4$, 0.1 M citric acid, and 1 M NaOH solutions in various proportions. Bath composition was confirmed with the use of atomic absorption spectroscopy (AAS) technique. Three-electrode system was used for the electrosynthesis of thin films of Cobalt ferrite, graphite was used as a counter electrode, the substrate acts as a working electrode and saturated calomel electrode (SCE) acts a reference electrode. The electro analytical measurements and deposition of thin films of Cobalt ferrite were carried out by using potentiostat/galvanostat model 263. Preparative parameters for depositing smooth, uniform cobalt ferrite thin films are given in Table 1. After deposition, thin films of Cobalt ferrite small post heat treatment was given because as deposited films may contain defects, the air annealing helps to remove such types of defects and improvement in crystallinity. Annealing of electrodeposited Cobalt ferrite thin films was carried out in air at 773 K for 4 hours.

3. CHARACTERIZATION OF COBALT FERRITE FILM

The composition of films was carried out using the atomic absorption spectroscopy (AAS) spectroscopic technique with a Perkin Elmer model 3030B spectrophotometer. At room temperature, Cobalt ferrite thin films were deposited onto a stainless-steel substrate. After the deposited films were dissolved into concentrated nitric acid and further that solution was diluted into known volume for measurement of the weight percentage of metal deposited in the film.

X-ray diffraction patterns of as deposited and heat-treated Cobalt ferrite thin films deposited onto stainless steel substrates were carried out using X-ray diffractometer PW 3710. The SEM images of Cobalt ferrite thin films were obtained using the Scanning electron microscope model JSM 5600. Cyclic voltametric curves (CV) depict information about charging- discharging process occurring across the electrode-electrolyte interface. In addition, CV can be used for evaluation of capacitance. The electrochemical performance of cobalt ferrite thin films was evaluated in terms of its capacitance. The electrochemical measurements carried out at room temperature in between voltage range 0.5 V to -0.5 V vs SCE. The number charge-discharge cycles were tested for the stability of cobalt ferrite film as an electrode for supercapacitors.

4. RESULTS AND DISCUSSION

Bath composition

Cobalt ferrite thin films were deposited from the mixture of 0.1 M $CoSO_4$, 0.1 M $FeSO_4$, 0.1 M citric acid and 1 M NaOH solutions. In this solution, total quantity is constant of 20 ml, variation in quantities of 0.1 M $CoSO_4$ and 0.1 M $FeSO_4$ solutions was made in different ratios. Fig 1 shows plot of percentage of iron in deposited film with volume of 0.1 M $FeSO_4$ solution in the fixed quantity of electrolyte. It is observed that for (10cc) 0.1 M $CoSO_4$ + 0.1 M $FeSO_4$ (10cc) bath solution, the deposited film contained atomic percentage of Co ~34% and Fe ~66% composition. Various preparative parameters for deposition of Cobalt ferrite thin films are listed in
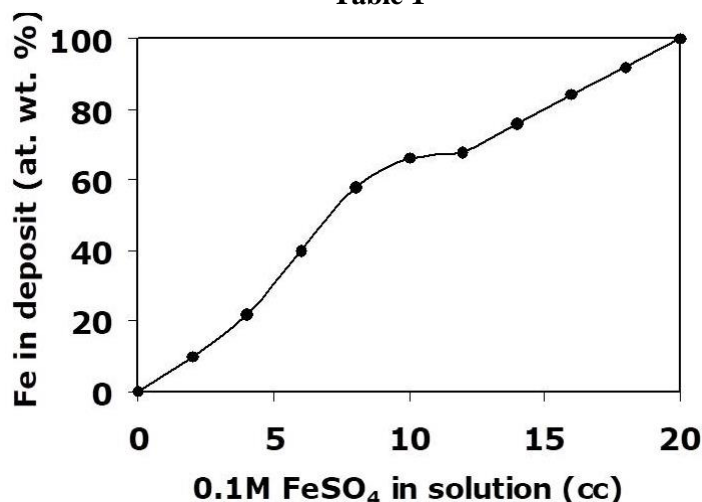
Table 1

Fig.1 A Plot of Fe in deposit against quantity of 0.1 M $FeSO_4$ solution in bath.

Table 1: Parameters for thin films of Cobalt ferrite deposited from non-aqueous bath

Optimized preparative parameters	For Cobalt ferrite thin films deposited from non-aqueous bath at pH 12
Bath composition	0.1 M $CoSO_4$ (10 cm^3) + 0.1 M $FeSO_4$ (10 cm^3) + 0.1 M Citric acid (in ethylene glycol) + 1 M NaOH (in distilled water)
Deposition potential, V/SCE	-0.65
Deposition time (min)	20

Structural and Morphological Studies

Fig. 2 shows X-ray diffraction patterns for as deposited and heat-treated cobalt ferrite thin films. Well-defined peaks of $CoFe_2O_4$ films for as deposited and heat-treated films were observed. After heat treatment preferred orientation along (311) plane was observed which is comparable to bulk $CoFe_2O_4$ [33], and one more peak (422) was observed, which confirms formation of spinel cubic $CoFe_2O_4$ phase. Lattice parameters were calculated and are found to be matches with standard value [7] for $CoFe_2O_4$. Observed and standard 'd' values [34] are in good agreement with each other and are tabulated in Table 2.

Table 2. X-ray diffraction studies for thin films of Cobalt ferrite

Films	Standard 'd' values	Observed 'd' values	Plane	Lattice parameters
As deposited	2.531	2.531	(311)	8.3943
	2.08	2.0866	(400)	8.3044
Heat treated	2.531	2.531	(311)	8.3995
	2.08	2.076	(400)	8.3464
	1.713	1.793	(422)	8.3256
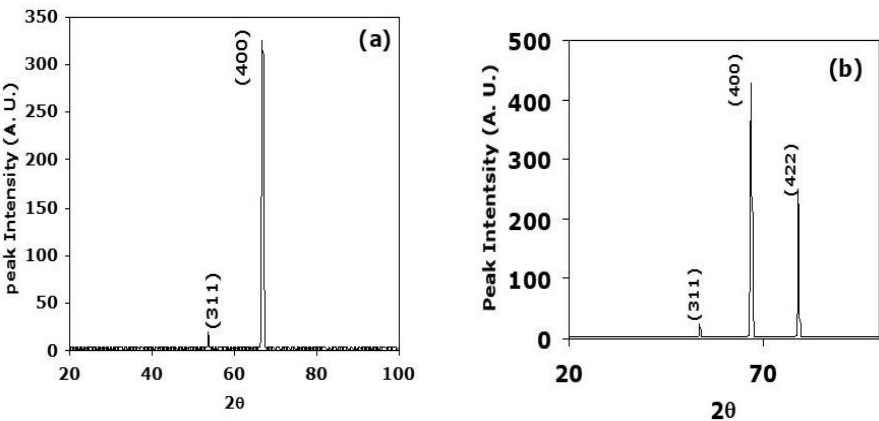
Fig. 2 XRD patterns for (a) as deposited and (b) heat treated cobalt ferrite thin films.

Figures 3 (a) and (b) show SEM's of as deposited and heat treated Cobalt ferrite thin film. From images, it was observed that the films uniform, smooth and well covered to the substrate. Heat treated cobalt ferrite thin films showed an increase in grain size and compactness of film. Thus from SEM studies, necessity of post annealing is confirmed and well covered, completely grown cobalt ferrite thin film formation was observed.
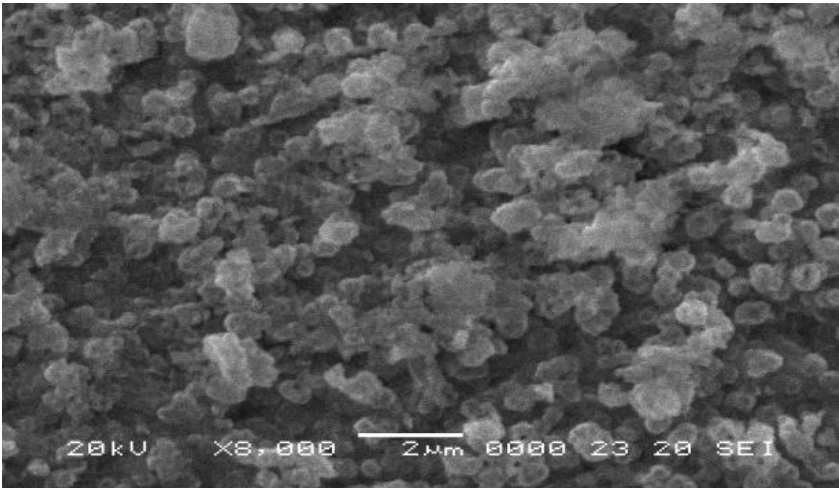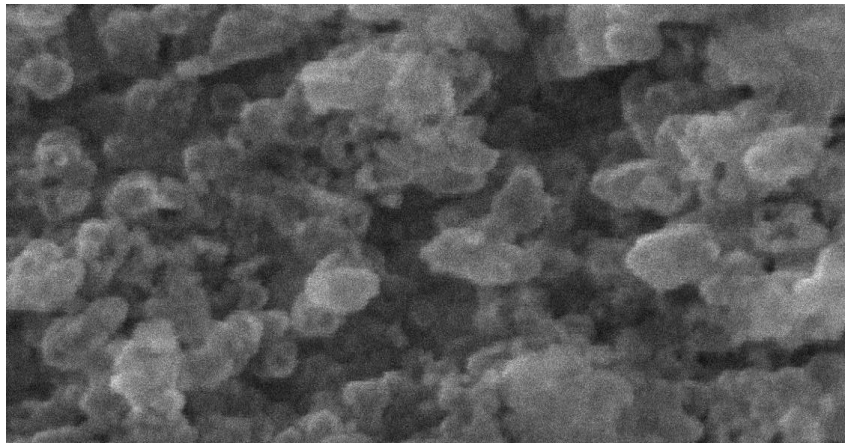
Fig. 3 SEM images for (a) as deposited and (b) heat treated cobalt ferrite thin films.

Supercapacitive Performance of Cobalt ferrite thin films

With the use of cobalt ferrite thin films as an electrode in electrochemical cell, electrochemical supercapacitive performance was tested. Figure 4 shows cyclic voltametric curves obtained for cobalt ferrite thin films for (a) 50 and (b) 400 charge discharge cycles.
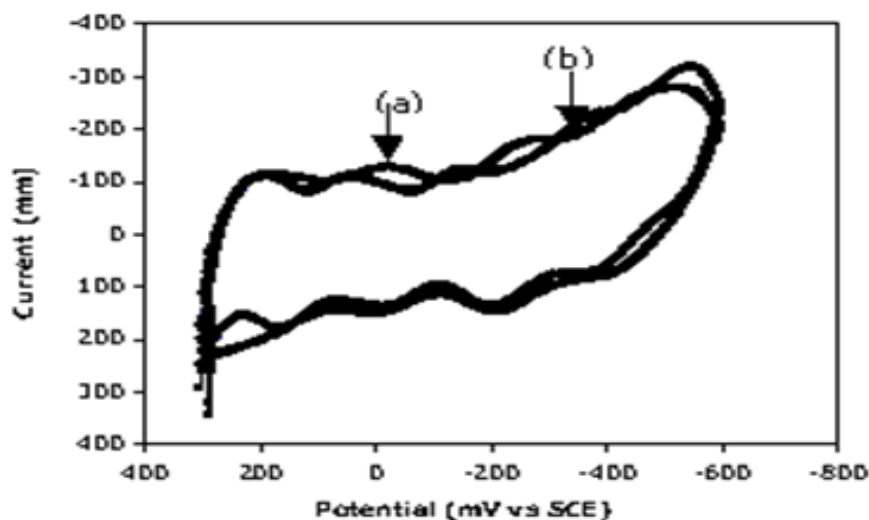
Fig. 4 cyclic voltametric curves obtained for cobalt ferrite thin films for (a) 50 and (b) 400 cycles.

Area under curve 'b' is 1.70 mC, indicating charge storage capacity of these films. Values of specific and interfacial capacitance obtained from CV for cobalt ferrite thin films are summarized in Table 3. The current was decreased slightly with increase in number of cycles and was stable after 500 cycles. Thus, stability of cobalt ferrite thin film electrode was confirmed. From the observed values of specific and interfacial capacitance, cobalt ferrite thin films are significant for their use in supercapacitor device applications.

Table 3: Observed specific and interfacial capacitance values for cobalt ferrite thin films. (Conc. of NaOH =5 N and scan rate = 100 mVS^{-1}).

Values observed	Cobalt ferrite	
Number of cycles	50	400
Specific capacitance (Fg^{-1})	81.6	67.6
Interfacial capacitance (Fcm^2)	0.28	0.16

4. CONCLUSIONS

Cobalt ferrite thin films were deposited at room temperature in a single step electro-deposition. Non-aqueous bath enhanced quality of thin films of Cobalt ferrite. Due to alkaline bath, thin films of Cobalt-ferrite formation at room temperature is possible. Small post heat treatment enabled to achieve good quality of Cobalt ferrite thin films. Electrodeposition is an eco-friendly method and does not require sophisticated instrumentation. XRD studies showed formation of cubic spinel Cobalt ferrite thin films with preferred orientation along (311) plane. SEM images showed smooth, well covered growth to surface of substrate, uniform and compact Cobalt ferrite thin film formation. From electrochemical studies, it was observed that cobalt ferrite thin films were electroactive materials and showed supercapacitive behavior. These films shows significant values of capacitance.

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SYNTHESIS OF ZNO AND BTO (BATIO₃) NANOPARTICLE USING HYDROTHERMAL METHOD AND COMPARE ITS APPLICATIONS

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ABSTRACT

Synthesized using the hydrothermal method, a low temperature and low cost synthesis method Barium Titanium and ZnO are popular capacitor dielectric materials because of their high dielectric constant and ferroelectric properties. Rod like ZnO and Spherical BTO nanoparticle were prepared by the Hydrothermal Method. Structural characterization of the synthesized powders was investigated by XRD, transmission electron microscopy (TEM). From Dynamic light scattering (DLS) the average size of the Zno is 40 nm and BTO 50 nm is found. Selected area electron diffraction measurement show that nanoparticle have good crystalline properties. Extending the synthesis time has no significant influence on the size and morphology The well aligned and high surface area make them a potential candidate for application in solar cell, field emission device and ultra-sensitive gas sensor.

Keywords: Barium Titanium, Zinc Oxide , Hydrothermal Method , Nanoparticles

1. INTRODUCTION

ZnO has wide variety of technological applications such as sensor devices, electroluminescent devices, piezoelectric devices, optical wave guide, catalysis and many more. It has various applications such as conductive oxide, antistatic coating, touch display panels and high band gap optoelectronic devices. The Hydrothermal method has attracted considerable attention because of its unique advantages—it is simple, low temperature (60-160 ^{0}C), high yield and more controllable process.

Barium titanate (BaTiO3) was discovered in the 40s when its high dielectric constant was reported worldwide. The BaTiO3 belongs to the perovskite family, and its structure has a low Curie temperature of nearly 120^0C.Which attributes to this material an elevated dielectric constant at environmental temperature ($\epsilon = 3600$ at 25^0C and 105 Hz).Due to excellent piezoelectric properties (polarization occurs after applying pressure), BTO is used in developments of counters, data collectors, sound detectors, as well as in microelectronic devices fabrication

Moreover, the dielectric characteristics of this material are important in the electronic industry for the fabrication of multilayer ceramic condensation devices, ceramic capacitors, super capacitors. Zinc oxide nanoparticles (ZnO NPs) have many uses, including in medicine, cosmetics, and manufacturing. In Medicine Used as an astringent to treat wounds, Antibacterial properties due to their small size and high surface area-to-volume ratio ,Shown anticancer activity against human cervical cancer cell lines .In Cosmetics , Sunscreens: ZnO NPs are used in sunscreens. In Manufacturing Ceramics, Cement, Plastics, Glass, Batteries, Fire retardants. Some Other uses Food: used as source of Zinc nutrient, Bioimaging: have potential use in bioimaging, Photocatalytic activity, Antioxidant activity

2. EXPERIMENT DETAILS

Material

Barium (Ba(OH)2·8H2O), Titanium (TiOCl21,4HCl·7H2O), Zinc Nitrate, Sodium Hydroxide, All material are AR and obtained from Chemscope Labsolution Indian LLP100 ml Teflon Autoclave, Smart lab studio II 4.3, Shimadzu SALD-7500(WingSALD II:Version 3.1.1) Flow Cell with Sampler, Tecnai G2 FEI 120 KV

2.1 Synthesis of ZnO

Hydrothermal method is opted for the synthesis of nanoparticles.

0.5 M Zinc Nitrate solutions were prepared in 30 ml distilled water under stirring for 30 min. Meanwhile 5 M Sodium Hydroxide solutions were prepared by mixing weighed pellets of NaOH in 30 ml distilled water under stirring for same duration.

NaOH solution is added dropwise to former solution under continuous stirring until pH of the reactants becomes 12.

This solution mixture was transferred into Teflon lined sealed stainless-steel autoclaves and kept in hydrothermal oven at a temperature of 100 °C for 2 h.

Then the beaker was taken outside and allowed to cool naturally to room temperature. The resultant solution was filtered, then washed with distilled water and kept for drying in oven.

2.2 Synthesis of BTO

Take 20ml of distilled water in beaker and add 3.15g of Barium (Ba(OH)2·8H2O) into it. Similarly add 2.32ml of Titanium (TiOCl21,4HCl·7H2O) into 20ml of distilled water Kept the ratio 1:1 Stirred both solutions for 15 min. at 1000 RPM Mix both chemicals and stir again for 10 min. After mixing newly formed chemical placed into oven for 15 hrs at 175^0 C Cooled at room temperature Washed with methanol and again kept it into the oven at 60^0 C for 24 hrs.

3. RESULT AND DISCUSSION

X-ray diffraction of the powders showed the characteristic peaks of $BaTiO_3$ and ZnO. XRD and TEM results confirm the crystalinity of ZnO and BTO and a small primary crystal size below 100 nm as will discuss later. The sample were characterized by X-ray diffraction (XRD), using a Smart lab studio II 4.3diffractometer from 5° to 75°, with a graphite monochromator using Cu Kα radiation (λ= 1.5406 Å). The morphology and size of the ZnO and BTO were observed using transmission electron microscopy

Assuming a uniform strain across the deposited film, the size of the crystallites D, in the grains can be estimated by Scherrer's formula

$$D = \frac{k\lambda}{B \cos \vartheta}$$

where k is the shape factor of the crystallite (the expected shape factor is 0.9), k is the X-ray wavelength (0.154 nm), B is the full width at half maximum (FWHM) of the diffraction peak, and θ is the Bragg diffraction angle.

It is known there are many factors (such as solution chemistry, substrate, and heat treatment) that affect the crystalline characteristics of films produced by the hydrothermal process.

The typical XRD pattern of the as-prepared ZnO products. All the reflections can be indexed to hexagonal structure of ZnO with lattice parameters a = 3.247 A and ° c = 5.20 A, in good agreement with the reported data for ZnO ° (a = 3.249 A, ° c = 5.205 A, JCPDS File, 074-0534).

The typical XRD pattern of the as-prepared $BaTiO_3$ products. All the reflections can be indexed to cubic structure of BTO with lattice parameters a = $5.71 A^0$ and c = $13.92 A^0$, in good agreement with the reported data for BTO (a = $5.72 A^0$, c = $13.96 A^0$, JCPDS File, 074-1968).

Dynamic light scattering (DLS) is a non-invasive technique used to measure the size and distribution of particles and molecules in a solution User Parameters Required

$$d_H = \frac{kT}{3\pi\eta D}$$

d_H = Hydrodynamic diameter, k = Boltzmann's constant, T = Absolute temperature, η = Viscosity, D = Diffusion constant

The size of ZnO nanoparticle is 34 nm and size of $BaTiO_3$ nanoparticle is 44 nm

Transmission electron microscopy (TEM) is a technique that uses a beam of electrons to image the internal structure of thin specimens, such as tissue sections, molecules, and organisms. TEM is a major analytical method in the physical, chemical, and biological sciences.
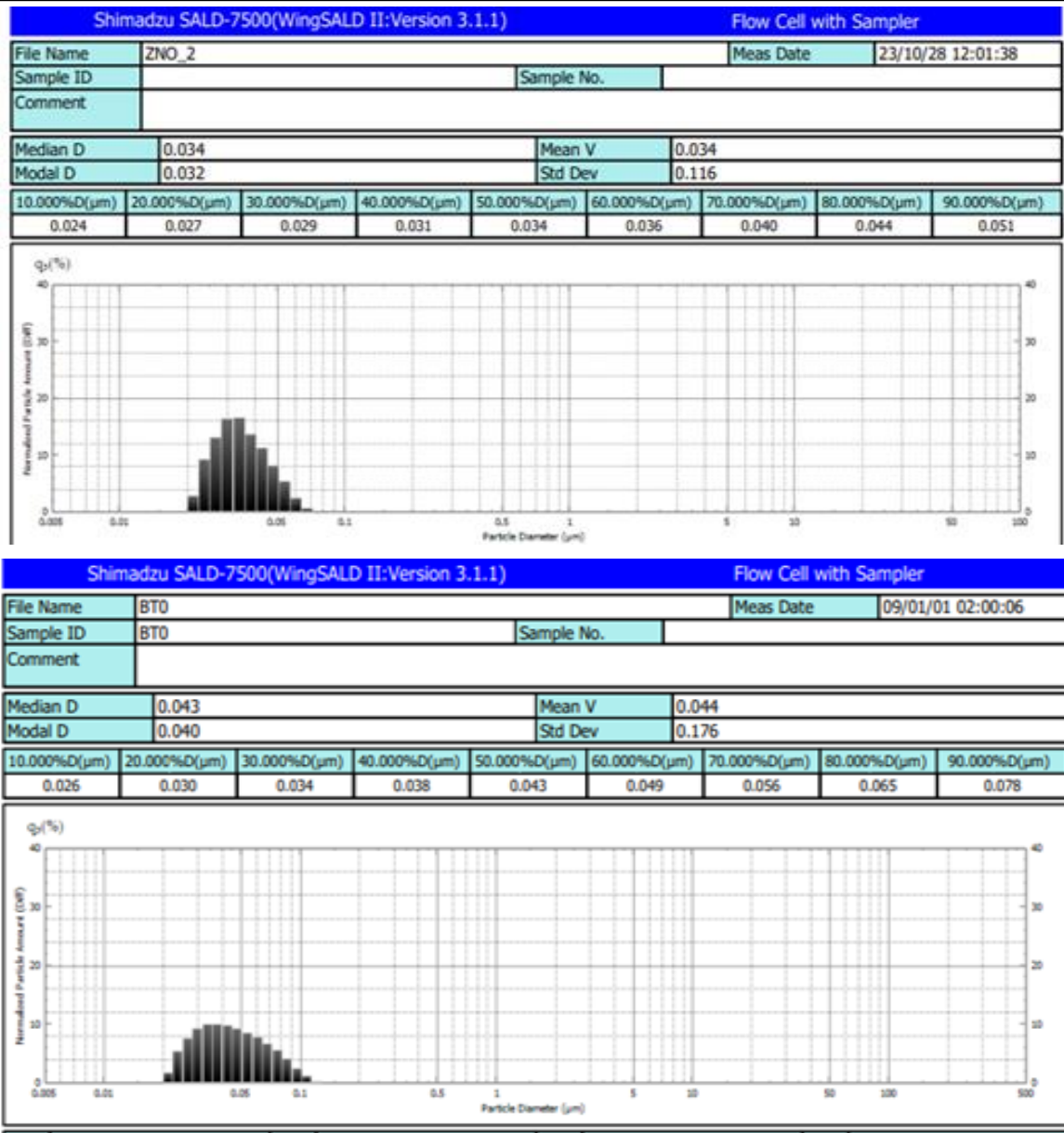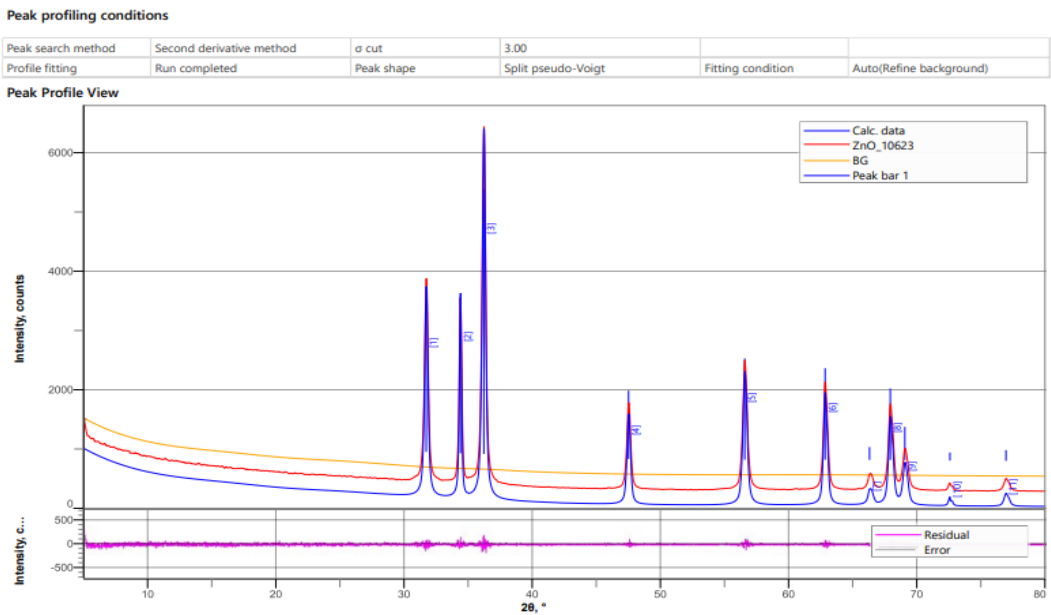
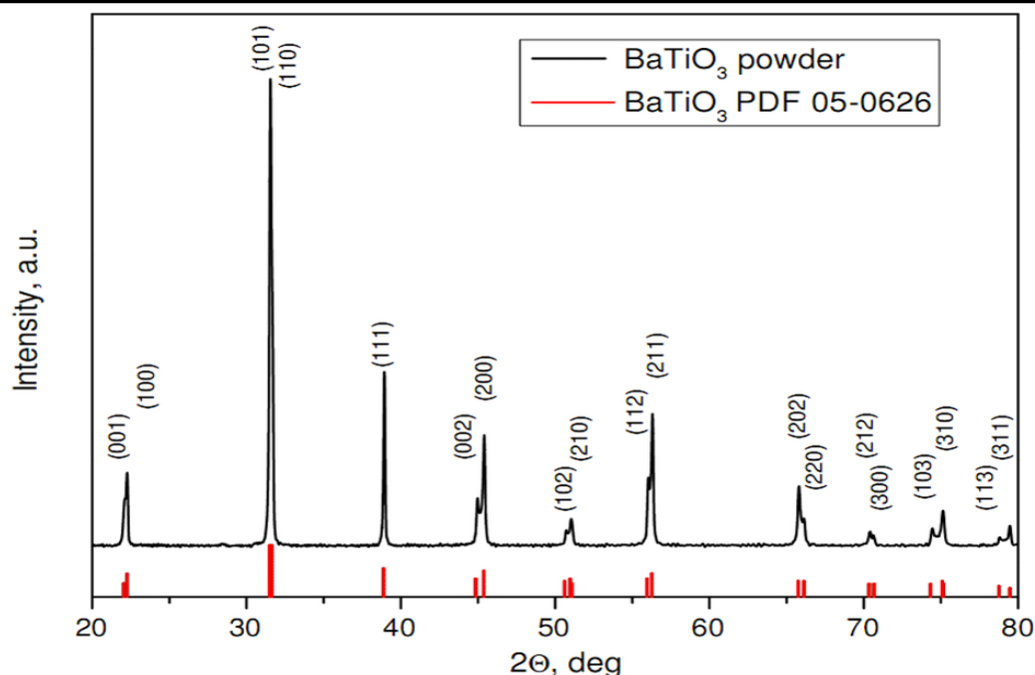**Fig 1.** DLS method to determine size of ZnO and BTO Nanoparticle which is around 34 & 44 nm respectively

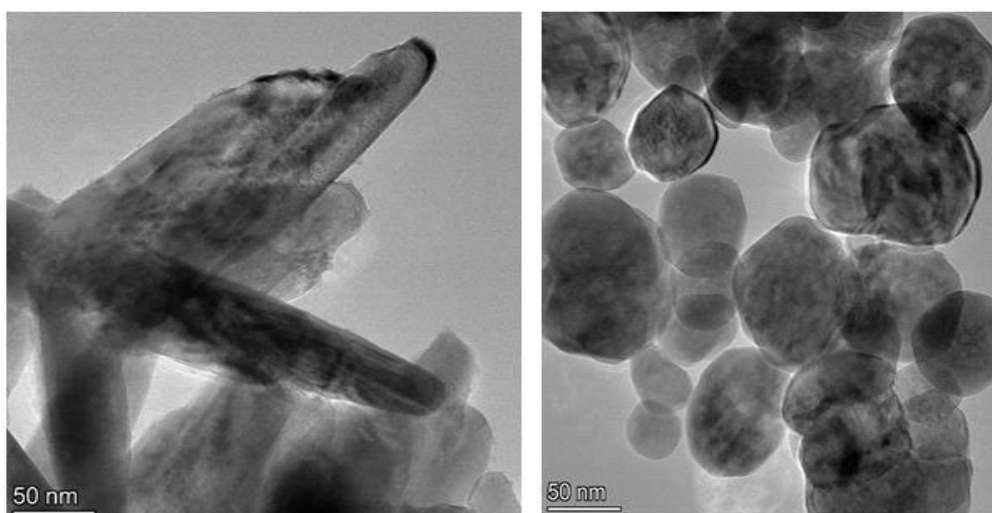**Fig 2** XRD spectra of ZnO and BTO Nanoparticle which is prepared by hydrothermal method

Fig 3. TEM image of ZnO and BaTiO$_3$ prepared using hydrothermal method respectively

4. CONCLUSION

From this study, it is evident that the optimal hydrothermal process parameters produce a ZnO and BaTiO$_3$. The optimized composition corresponds to standard ZnO and BaTiO$_3$ phase as per international JCPDS card 074-0534.mean particle size of 34 nm and 44 nm. The crystal structure of ZnO is hexagonal and BaTiO$_3$ is cubic. ZnO and BTO is formed only after hydrothermal heating at 100^{0}C and 175 ^{0}C respectively.

5. ACKNOWLEDGMENT

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TO STUDY STRUCTURAL CHARACTERISATION OF CERIUM DOPED CESIUM COPPER CHLORIDE NANOCRYSTAL BY SOLVENT-BASED THERMAL SYNTHESIS TECHNIQUE

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ABSTRACT

The different physical, chemical, mechanical, electrical, optical, catalytic, and magnetic characteristics of nanoparticles (NPs) in comparison to their bulk counterparts have recently attracted a lot of study interest. As numerous in nature, non-toxic, biodegradable, and having an uncomplicated production technique, copper-based perovskite (CSCuCl3) is one of the most promising nanoparticles. This paper presents powdered CsCuCl3 perovskite doped with Ce3+ ions prepared using the hydro-solvo thermal reaction method. The crystal structure of the CsCuCl3 and Ce-doped CsCuCl3 NCs was characterized using X-ray diffraction. The Field Emission Scanning Electron Microscope (FESEM) was used to examine the surface morphology of the NCs, and the results showed that Ce doping reduced the particle size. It was observed that dopant content strongly influences the obtained results. Furthermore, the cubic crystal structure of the early phases remained in Ce3+ doped CsCuCl3 NCs. Ce3+ ion doping successfully removed the surface roughness of CsCuCl3 NCs. An efficient and cost-effective method of synthesizing Ce-doped CsCuCl3 NCs could lead to a flexible way to increase the photoelectrical uses of CsCuCl3 NCs.

Keywords: Copper based perovskite, cerium doped, photoelectrical application

1. INTRODUCTION

Organic–inorganic hybrid lead halide perovskites have come-up as an attractive choice because of their excellent optoelectronic qualities, which include appropriate band gaps, long hole–electron diffusion lengths, and high carrier mobility. Scientists have swiftly become interested in the most promising core light-absorbing material for affordable and high-performing photovoltaic devices [2] [1]. But they also have to overcome several significant obstacles:1) Inability to maintain stability over extended periods of time when exposed to light, dampness, or extreme temperatures, significantly reducing the device's lifespan Lead's natural toxicity and ecological biological accumulation place restrictions on its use and growth in the commercial sector. Due to these issues, research has been going on stable, eco-friendly metal halide perovskite materials that have comparable optoelectronic qualities and can replace lead-based perovskites. [1]. Lead free halide perovskite give the different directions have been taken to diminish toxicity of lead halide perovskite. In this paper we doped Cerium into host material $CsCuCl_3$. We synthesized the Cerium Doping $CsCuCl_3$ perovskite nanocrystals and characterized their optical, structural, and environmental stability. The material exhibits the peak of photoluminescence and extremely long-lasting materials also have appealing absorption qualities that reach the near-infrared spectrum with a suitable band gap [1]. Essential functions in PL tuning and optoelectronic devices, like LEDs, lasers, screens, solar cells, and photodetectors, are morphology modification, size control, and compositional alloying. Furthermore, doping or the addition of impurity ions is a viable technique for regulating the structural stability, optical, and electrical characteristics of halide perovskite NCs. [2]. The good alignment of conduction band between perovskite and lanthanide ions has great impact on the fast electron injection which can result in high efficiency. From now on, the composites between lead free halide perovskites and lanthanide ions have earned great concern due to the enhancement of energy conversion efficiency and charge transportation [15,16]. However, its self-inherent trapping and surface defects caused by strong excitation-phonon coupling mainly control the process of capturing a charge carrier. So, its quantum efficiency of this photoluminescence is greatly reduced, thus the photoluminescent signal cannot be detected, which limits the study of its optical properties. To solve this problem, this paper introduces the Cerium elements to passivate internal and surface defects which were successfully prepared by the solvent based thermal synthesis method. Cerium doped $CsCuCl_3$ crystal structure, luminescence and photoluminescence properties were characterized, its cerium doped $CsCuCl_3$ NCs PLQY increases by 52 % providing a benchmark for the design of lead-free perovskite optoelectronic devices with good optical properties [3].
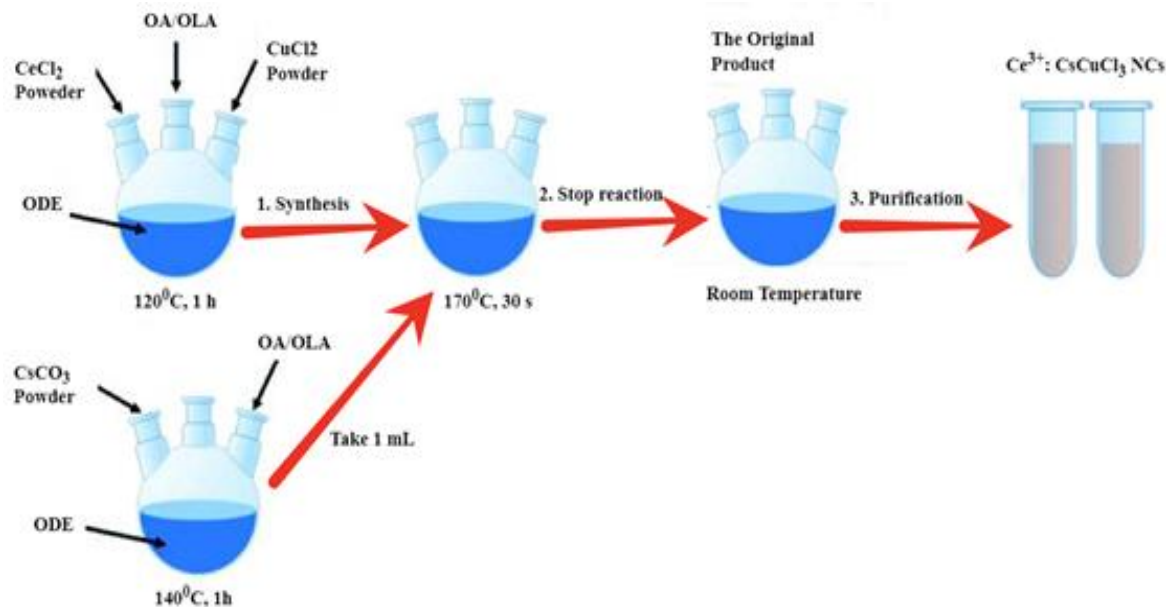
2. EXPERIMENTAL SECTION

Figure 1 Schematic of the synthesis of Ce^{3+}: $CsCuCl_3$ NCs.

2.1 Materials and chemicals

Cs_2CO_3 (SRL, 99%), $CuCl_2$ (SRL, 98%), 1-octadecene (ODE, ALFA AESAR, 90%), oleic acid (OA, SDF, 90%), oleyl amine (OLA, SRL, 95%), $CeCl_3$ (TCI, 99%), and n-hexane (SDF, 99%) were purchased. All chemicals were used without any further purification.

2.2 Preparation of the Cs-oleate solution

2.5 mL OA, 30 mL ODE and Cs_2CO_3 (0.8 g, 2.5 mmol) powder were put into a 100 mL three-neck flask at 140 C for 1 h under magnetic stirring until the Cs_2CO_3 powder completely dissolved and the solution became transparent.

2.3 Synthesis of $CsCuCl_3$ NCs

1.5 mL Oleic Acid + 1.5 mL oleyl amine (OLA) + 15 mL 1-Octadecene (ODE) + 0.15 gm, 0.54 mmol $CuCl_2$ powder, put into 100mL 3 neck round flask at 1200C for 1 hour to obtain $CsCuCl_3$ NCs. After reaction Temperature increase to 1700C. the Cs-oleate solution (1 mL) was quickly injected for reacting and after 30 s, the solution was cooled to room temperature in an ice bath.

2.4 Synthesis of Cerium doped $CsCuCl_3$ NCs

We prepared Cerium doped $CsCuCl_3$ NCs with the molar ratios of $CeCl_3$ and $CuCl_2$ of 0.9:1. The typical synthetic procedure of Ce^{3+}:$CsCuCl_3$ NCs with the Ce-to-Cu molar ratio of 0.9 : 1 as follows: 1.5 mL OA, 1.5 mL OLA, 15 mL ODE, $CuCl_2$ (0.097 g, 0.35 mmol) and $CeCl_3$ (0.053 g, 0.31 mmol) powders were loaded in a 100 mL three-neck flask heated to 1200C for 1 h. The reaction temperature was increased to 170 C, and the Cs-oleate solution (1 mL) was quickly injected, and after 30 s, the reaction was cooled to room temperature on an ice bath.

2.5 Purification

$CsCuCl_3$ & Ce^{3+}doped $CsCuCl_3$ NCs were extracted from the original product via centrifugation at 8000 rpm for 5 min. and precipitate was taken out. The resulting precipitates were dispersed in n-hexane at room temperature and were centrifuged for 5 min. at a speed of 6000 rpm. The supernatant was taken, and this process was repeated twice to get $CsCuCl_3$ & Ce^{3+}doped $CsCuCl_3$.Then they were kept aside for 24 h in a freezer, and were taken out again for centrifugal purification, obtaining a clear colloidal $CsCuCl_3$ & Ce^{3+}doped $CsCuCl_3$ NCs.

2.6. Characterization analysis

XRD measurements were performed using a PAN analytical, The Netherlands, model EMPYREAN X-Ray tube with Cu target. (Anode Material) Wavelength – 1.54184 Å and X-ray generator at 45kv & 40 mA. Field Emission Scanning electron microscopy (FESEM) was carried out using a Philips XL30 FEG SEM. Energy-dispersive analysis of X-rays (EDAX) spectroscopy was performed using a DX4 detector. All samples were carbon coated using Edwards coating system E306A prior to SEM analysis.

3. RESULTS AND DISCUSSION

3.1 Powdered X-ray Diffraction

The XRD patterns of $CsCuCl_3$ presented in Figure 2 shows the sharp peaks at 2Θ = 20.7, 29.44, 36.27, and 42.13° corresponds to the (103), (110), (203) and (213) planes of hexagonal CsCuCl3 (ICDD 00-018-0349). The XRD patterns of the $CsCuCl_3$ samples doped with Ce^{3+} are shown in Figure 2. The patterns exhibit the characteristic peaks of the $CsCuCl_3$ phase, indicating that the lanthanide ions were successfully incorporated into the $CsCuCl_3$ host lattice. No secondary phases or impurities were detected, suggesting that the doping did not affect the phase purity of the samples. The crystallite size of the $CsCuCl_3$ samples also decreases with the doping concentration of the lanthanide ions. This can be explained by the effect of doping on the grain growth of the samples. The doping of the lanthanide ions introduces lattice defects and strain, which can hinder the grain growth and result in smaller crystallites [4].

3.2 Morphology Studies

The morphology of $CsCuCl_3$ & Ce^{3+} doped $CsCuCl_3$ NCs was investigated by field emission scanning electron microscopy (FESEM) they are as follows:

3.2.1 FESEM Analysis of CsCuCl3 NCs

The CsCuCl3 NCs were analyzed through Field Emission Scanning Electron Microscope and as a result, the image with cluster of uniformly distributed particles was obtained as shown in Figure 3 (a). The distribution of the Cs, Cu and Cl in the compound was examined by EDX mapping. Figure 3 (b) shows that the Cs, Cu and Cl are distributed uniformly in the interrogated area of the inorganic perovskite material. Energy dispersive X-ray spectroscopy (EDX) revealed Cs: Cu: Cl atomic ratio of almost 1:1:3 which matches the theoretically calculated stoichiometry of $CsCuCl_3$ as shown in Figure 4 (a) It demonstrates that the bulk of the particles have morphologies that are almost spherical. The distribution of particles is uniform, but their sizes vary. On measuring the nanoparticles using the image J software, average size of the particle for sample has been estimated by fitting the particle size distribution histogram to the log-normal distribution function, which is represented as

$$f(D) = \left(\frac{1}{\sqrt{2\pi\sigma_D}}\right)\exp[-\frac{ln^2\frac{D}{D_0}}{2\sigma^2}]$$

where D corresponds to average particle size and σ_D is the standard deviation. Typical fitting of log normal distribution function to particle size distribution histogram for sample is illustrated in Figure 6 (a) the average size of the particles obtained was in the range of 20 nm to 30 nm thereby confirming the existence of nanoparticles [8].

3.2.2 FESEM Analysis of Ce3+: CsCuCl3 NCs

The $CsCuCl_3$ NCs were analyzed through Field Emission Scanning Electron Microscope and as a result, the image with cluster of uniformly distributed particles was obtained as shown in the Figure 3 whereas the EDX mapping of perovskite confirm the co-existence and homogeneous distribution of Cs, Cu and Br in the cross-examined area of the material shown in the Figure 4 (b) Energy dispersive X-ray spectroscopy (EDX) revealed Cs, Cu, Cl and Ce elements as shown in Figure 5 (a) Typical fitting of log normal distribution function to particle size distribution histogram for sample is illustrated in Figure 6 the average size of the particles obtained was in the range of 2 nm to 10 nm thereby confirming the existence of nanoparticles [1].
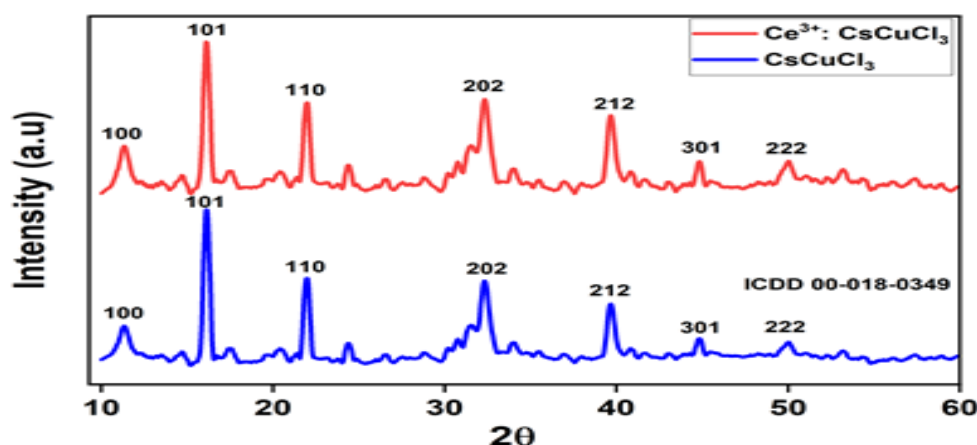
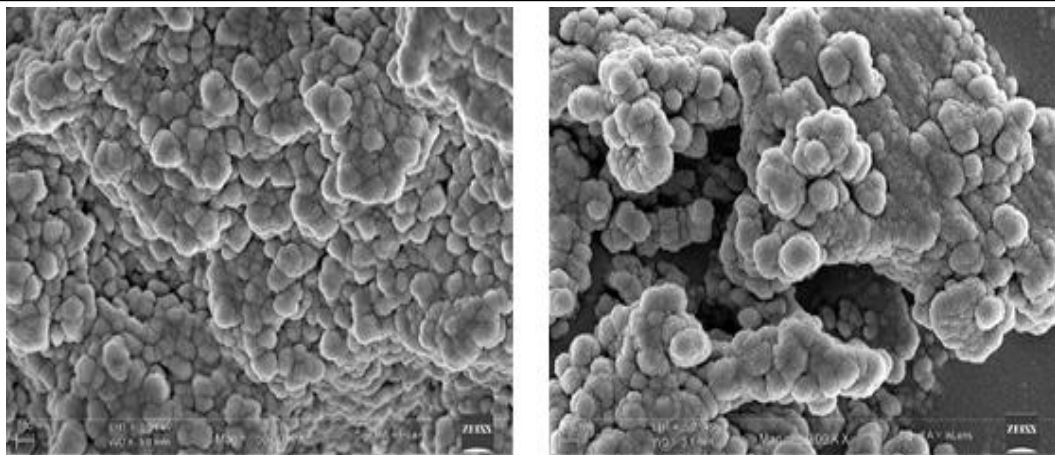**Figure 2** patterns of as-prepared all-inorganic $CsCuCl_3$ and Ce^{3+}: $CsCuCl_3$ NCs

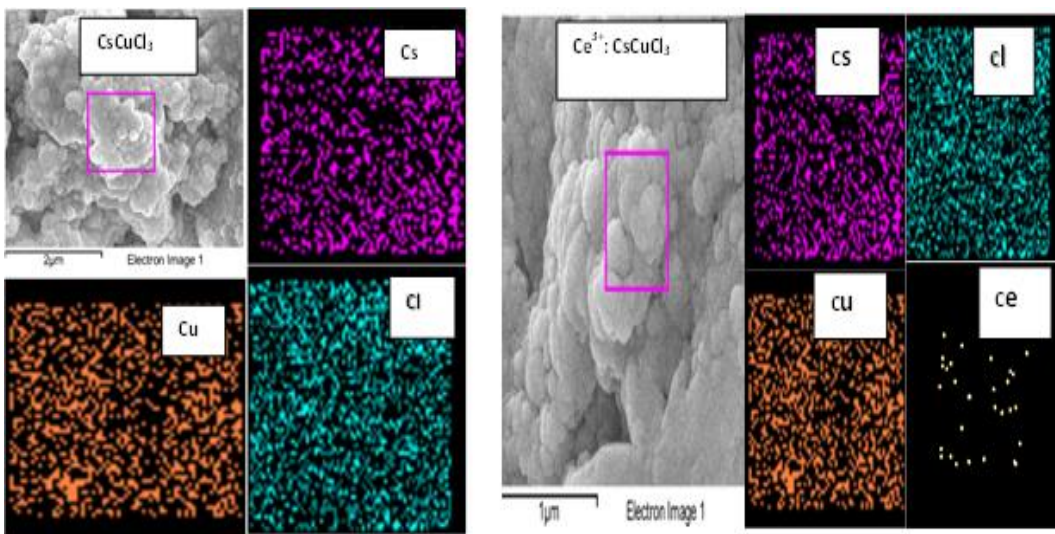**Figure 3** (a) FESEM of particle distribution of $CsCuCl_3$ NCs and (b) FESEM of particle distribution of $Ce^{3+:}$ $CsCuCl_3$ NCs

Figure 4 EDX images of $CsCuCl_3$ NCs (b) SEM-EDX images of Ce^{3+}: $CsCuCl_3$ NCs
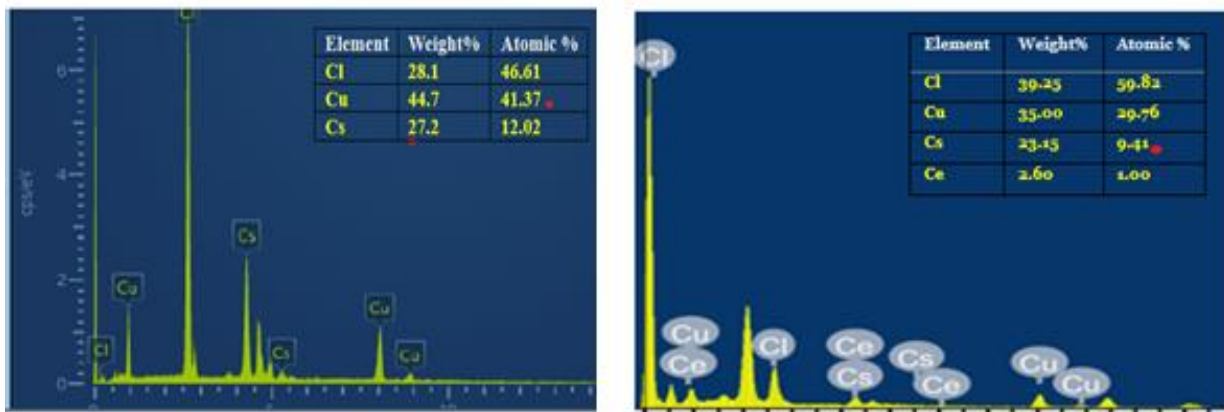

Figure 5 *(*a) EDX weight %age spectra of as-prepared Ce^{3+}: $CsCuCl_3$ NCs (b) EDX weight %age spectra of as-prepared $CsCuCl_3$ NCs
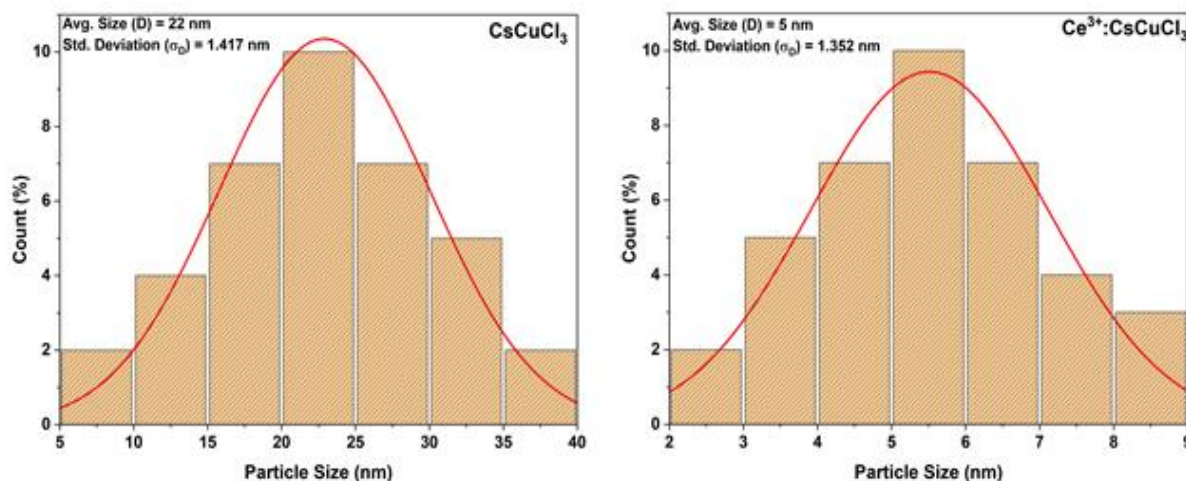
Figure 6 (a) Particle size distribution for CsCuCl3 NCs fitted with a log normal distribution function (b) Particle size distribution for Ce^{3+}: $CsCuCl_3$ NCs fitted with a log normal distribution function.

CONCLUSION

Using the hydro-solvo thermal reaction technique, Ce^{3+}-doped $CsCuCl_3$ NCs have been successfully synthesized. While morphological investigations showed a decrease in particle size and surface roughness following doping, structural research verified that the cubic crystal structure of $CsCuCl_3$ remained stable. The results demonstrate how Ce^{3+} ion doping significantly affects the physical characteristics of $CsCuCl_3$ NCs, potentially increasing their potential for photoelectrical applications. A potential strategy for the advancement of copper-based perovskite materials in cutting-edge optoelectronic and catalytic applications is provided by this economical and effective synthesis process.

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FABRICATION AND CHARACTERIZATIONS OF WO$_3$ DECORATED MNO$_2$ THICK FILMS FOR LPG DETECTION

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ABSTRACT

Mixed metal oxide gas sensors are an emerging class of sensing materials that leverage the synergistic properties of two metal oxides to enhance gas detection performance. In this study, 5 wt. % WO$_3$ decorated MnO$_2$ (WO$_3$-MnO$_2$) thick films were fabricated using a cost-effective screen-printing technique and evaluated for liquefied petroleum gas (LPG) sensing. Structural and electrical characterization revealed that WO$_3$ doping significantly influenced the crystallite size, morphology, resistivity, temperature coefficient of resistance (TCR), and activation energy of MnO$_2$ films. Gas sensing analysis demonstrated a maximum sensitivity of 93.26 % at 300 ppm of LPG and an optimal operating temperature of 120 °C. The sensors exhibited rapid response (26 sec) and recovery (52 sec) times, along with excellent selectivity towards LPG. These results highlight the potential of WO$_3$-decorated MnO$_2$ films as efficient and reliable gas sensors for LPG detection.

Keywords: Binary metal oxide, Sensors, screen-printing technique, characterizations.

1. INTRODUCTION

Binary metal oxide gas sensors have emerged as a promising new area in the field of gas sensing technology, driven by the need for more sensitive, selective, and stable detection systems [1]. Traditional single metal oxide sensors, such as those based on SnO$_2$, ZnO, or TiO$_2$, have been widely used for detecting gases like carbon monoxide, nitrogen dioxide, and volatile organic compounds (VOCs). However, these sensors often face limitations in selectivity and long-term stability, particularly in complex and variable environments [2, 3]. The development of binary metal oxide sensors addresses these challenges by combining two different metal oxides into a single sensing material, leveraging the synergistic interactions between them to enhance performance [3, 4]. One of the key advantages of binary metal oxide gas sensors is their ability to offer improved sensitivity and selectivity. By carefully selecting and combining metal oxides with complementary properties, researchers can create sensors that are more responsive to specific target gases while minimizing interference from other gases [5, 6]. The exploration of binary metal oxide gas sensors is also opening new avenues for applications in areas where traditional sensors may have struggled. For instance, these sensors are increasingly being considered for use in harsh industrial environments where temperature fluctuations, humidity, and the presence of multiple gases could be pose significant challenges [6-8]. The enhanced thermal stability and robustness of binary metal oxides make them suitable for such demanding conditions. Additionally, their potential for integration into miniaturized and portable devices is expanding their use in consumer safety products, environmental monitoring systems, and automotive emission controls. As this new area of research continues to evolve, there is growing interest in exploring novel combinations of metal oxides, as well as optimizing synthesis techniques to further enhance sensor performance [8, 9]. Advanced fabrication methods, such as sol-gel processes, chemical vapor deposition, and hydrothermal synthesis, are being employed to create finely tuned nanostructures with controlled morphology and composition. These developments are expected to lead to the next generation of high-performance gas sensors that are not only more efficient but also more adaptable to the diverse needs of modern gas detection applications [9, 10].

Liquefied petroleum gas (LPG) is a common fuel source used in households, industries, and transportation, primarily consisting of propane and butane [10]. It is stored in pressurized cylinders and used for cooking, heating, and powering vehicles. While LPG is efficient and widely accessible, its use and exposure carry certain health risks. Inhaling LPG in small quantities over time can lead to mild symptoms such as headaches, dizziness, and nausea [10, 11]. The exposure to high concentrations, particularly in poorly ventilated areas, cause more severe health effects, including respiratory problems, unconsciousness, and even death due to asphyxiation [12, 13]. LPG is also highly flammable, and leaks lead to explosions or fires, posing significant safety hazards [14, 15]. Prolonged exposure to LPG can have cumulative effects, particularly for individuals with pre-existing respiratory conditions, making proper ventilation, leak detection, and safety measures essential when using this fuel [16, 17].

Manganese dioxide (MnO_2) is a widely studied material in the field of gas sensors due to its unique properties, including high surface area, good electrical conductivity, and strong catalytic activity [18, 19]. These characteristics make MnO_2 an excellent candidate for detecting various gases, particularly in environmental monitoring and safety applications. MnO_2 is a promising material for gas sensing applications but, it also faces several limitations that can impact its performance. One of the primary challenges is its relatively low sensitivity and selectivity when used alone. MnO_2 tends to exhibit a generalized response to a variety of gases, making it difficult to distinguish between different analytes in complex environments [20, 21]. This lack of selectivity might be lead to false positives or inaccurate readings, particularly in environments with multiple interfering gases. The intrinsic properties of MnO_2 may also result in lower sensitivity to certain gases at lower concentrations, making it challenging to detect trace amounts of harmful substances [21, 22]. Hence to overcome these limitations, researchers are exploring the combination of MnO_2 with other metal oxides or nanomaterials to enhance its sensing performance. By forming composites or doping MnO_2 with other materials, it is possible to improve its sensitivity, selectivity, and stability, making it more suitable for practical gas sensing applications. Tungsten trioxide (WO_3) is a widely studied metal oxide in gas sensing due to its excellent sensing properties, particularly for detecting nitrogen dioxide (NO_2), ammonia (NH_3), ozone (O_3), and various volatile organic compounds [23, 24]. WO_3 exhibits high sensitivity to these gases, making it a valuable component in gas sensors. When WO_3 is added to another metal oxide, such as tin dioxide (SnO_2), titanium dioxide (TiO_2), or manganese dioxide (MnO_2), it could be significantly enhance the overall gas sensing performance of the composite material [25, 26]. WO_3 contributes strong catalytic properties that facilitate faster and more complete reactions with target gas molecules, leading to greater sensitivity [26]. This catalytic activity, combined with an increased surface area and active sites provided by WO_3, allows for more effective gas adsorption. Hence in the present research work WO_3 is selected as an additive [26-28].

The aim of present research work is to investigate the impact of WO_3 additive on structural, electrical and gas sensing properties of MnO_2 thick films.

2. MATERIAL AND METHODS

All AR grade (99.99% purity) commercial available nanoparticles of host (MnO_2) and additive (WO_3) materials were used in this work. Chemicals were purchased from Sigma enterprises, Nashik, India. Initially, the 70% inorganic and 30 % organic ratio was used to prepare films. Inorganic materials consist of nanoparticles of host material MnO_2 and additive material WO_3 (5 wt. %). The 5 wt. % WO_3 additive is loaded into the MnO_2. The organic material consist of ethyl cellulose and butyl carbitol acetate [28]. All films were prepared on glass substrate via screen printing technique. All glass substrate were properly cleaned by double distilled water and acetone then dried under IR lamp. The thixotropic paste was prepared using molten and pestle. The prepared paste of WO_3 decorated MnO_2 was paste on glass substrate by using screen printing setup. Films were deposited after that, all prepared thick films were dried under IR lamp for 20-25 minutes at ambient temperature. The prepared thick films were annealed at 400 °C in a muffle furnace for 2 hours [28-30]. Then all films were used for further characterizations such as XRD, FESEM, EDX, electrical and gas sensing. XRD characterizations X-ray generator [Miniflex Model, Japan] Rigaku diffractometer (DMAX-500) was employed. For FESEM and EDX characterizations SEM [Model JOEL 6300(LA) Germany] and EDX (JOEL, JED-2300, Germany) were used respectively. For electrical and gas sensing characterizations half bridge as well as static gas sensing system was used. The thickness of films was calculated by weight difference method [31].

3. RESULT AND DISCUSSION

The Field Emission Scanning Electron Microscopy (FESEM) is an advanced imaging technique used to analyze the surface morphology and microstructural features of materials at a nanoscale resolution. Unlike conventional SEM, FESEM employs a field emission gun (FEG) as an electron source, which provides a highly focused electron beam with lower energy dispersion. Fig. 1 shows the FESEM image of WO_3-MnO_2 thick films. FESEM results reveals a highly porous and agglomerated microstructure, characteristic of metal oxide composite films [31, 32]. The morphology consists of irregularly shaped plate-like and granular structures, indicating the co-existence of WO_3 and MnO_2 phases. The porosity observed in the image suggests enhanced surface area, which is beneficial for applications such as gas sensing, catalysis, and energy storage. Also the presence of nanostructured and agglomerated grains indicates strong interparticle interactions which is useful for gas LPG detection [32, 33].
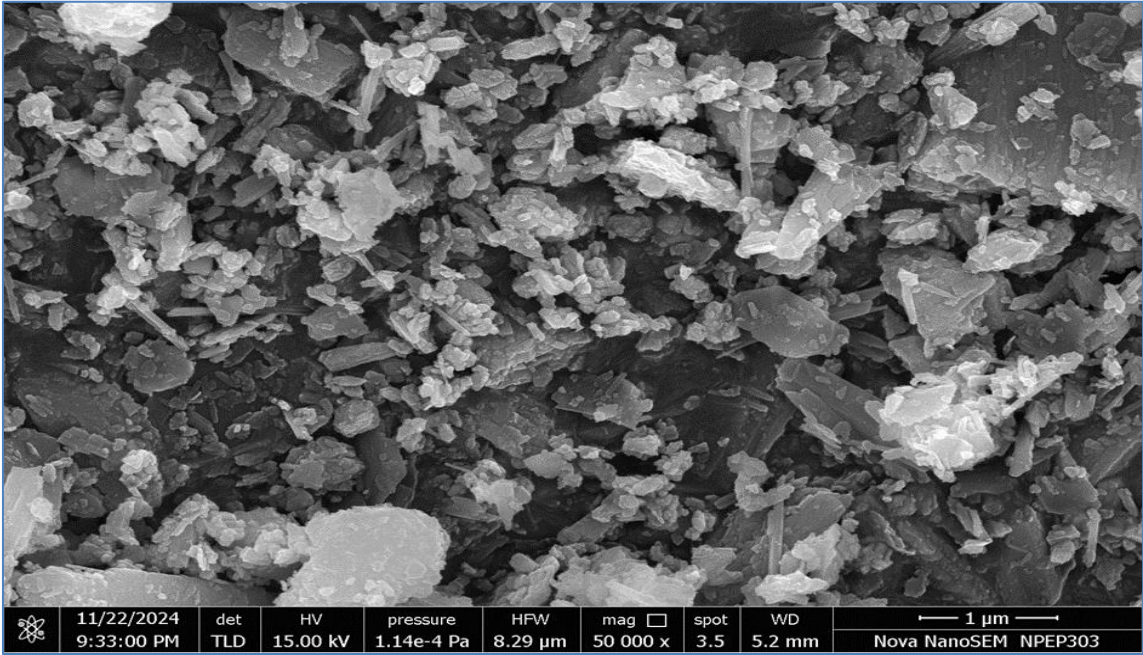
Figure 2. FESEM image of WO_3-MnO_2 thick films

Energy Dispersive X-ray Spectroscopy (EDX) is confirms the elemental composition of the material. Fig. 2 shows the EDX spectrum of WO_3-MnO_2 thick films.
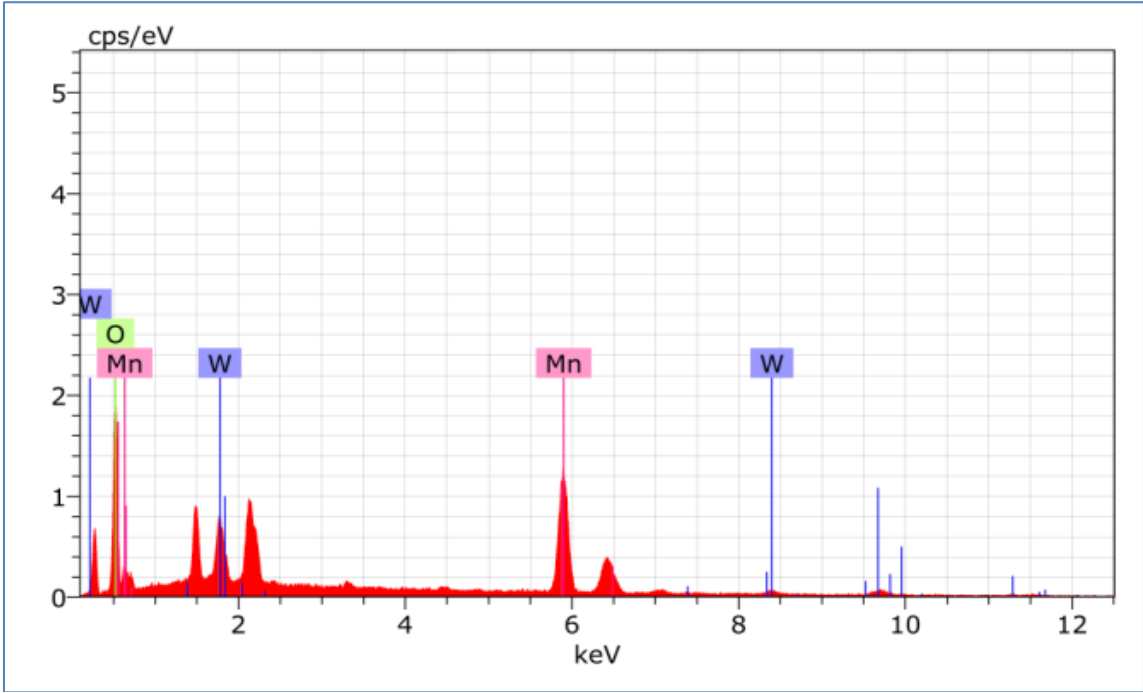

Figure 2. EDX spectrum of WO_3-MnO_2 thick films

The characteristic peaks corresponding to tungsten (W), manganese (Mn), and oxygen (O) are observed at different energy levels (keV), validating the presence of the intended metal oxides in the composite film as shown in Fig 2. Tungsten (W) peaks detected at multiple positions, particularly around 1.7 keV, 8.3 keV, and 9.7 keV, confirming the presence of WO_3 in the film. Manganese (Mn) peaks notably present at 0.6 keV and 5.9 keV, indicating the incorporation of MnO_2 in the composite. The oxygen (O) peak is appears at around 0.5 keV, signifying the formation of metal oxides. The EDX results strongly support the FESEM observations, where a well-distributed and agglomerated morphology was observed, correlating with the presence of the mixed oxide phases [28].

The electrical properties of WO_3-MnO_2 thick films, including resistivity, Temperature Coefficient of Resistance (TCR), and activation energy, were analyzed to evaluate their suitability for gas sensing applications. The resistivity, TCR and activation energy of WO_3-MnO_2 thick films were estimated using Eqs. 1, 2 and 3 respectively [31].

$$\rho = \left(\frac{R \times b \times t}{l}\right) \Omega - m \qquad (1)$$

Where,

ρ = Resistivity of prepared film, R = resistance at normal temperature, b = breadth of film,

t = thickness of the film, L = length of the film.

$$TCR = \frac{1}{R_o}\left(\frac{\Delta R}{\Delta T}\right) /^o C \qquad (2)$$

Where, ΔR = change in resistance, ΔT = temperature difference, and R_o = Initial resistance of the film.

$$\Delta E = \frac{\log R}{\log Ro} \times KT \qquad (3)$$

Where, ΔE = Activation energy, R = Resistance at raised temperature, R_0 = Resistance at room temperature.

The resistance vs. temperature graph (Fig. 3) illustrates the temperature-dependent electrical behavior of WO_3-MnO_2 thick films. The resistance decreases exponentially as the temperature increases from 300 K to 650 K, indicating a typical semiconducting behavior. This trend suggests that the electrical conduction follows a thermally activated mechanism, where charge carriers gain sufficient energy to overcome potential barriers, leading to enhanced conductivity at elevated temperatures [31, 32]. The resistivity and TCR WO_3-MnO_2 thick films were estimated using Fig. 3. The electrical characterization of thick films revealed a resistivity of 637330 $\Omega \cdot m$ and a temperature coefficient of resistance (TCR) of -0.00171/K. The negative TCR value indicates the typical semiconducting behavior of the material, where resistance decreases with increasing temperature. These parameters are crucial for gas sensing applications, as they influence the sensor's response mechanism by modulating charge carrier dynamics in the presence of target gases [32, 33].
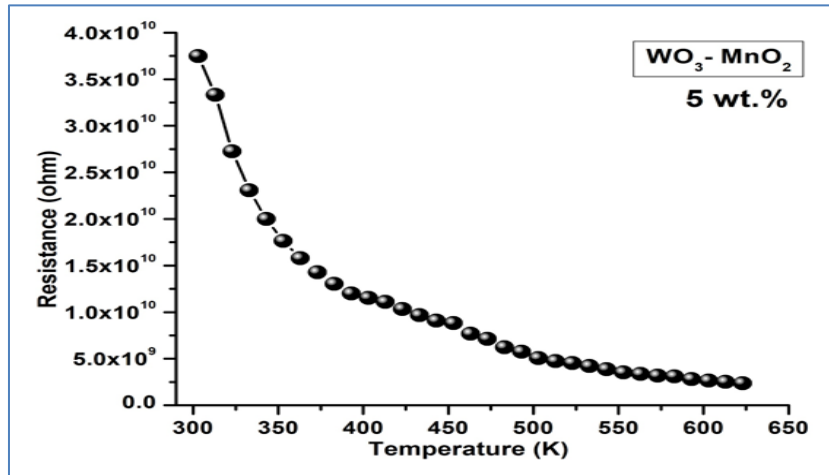
Figure 3. Resistance versus temperature plot of WO_3-MnO_2 thick films
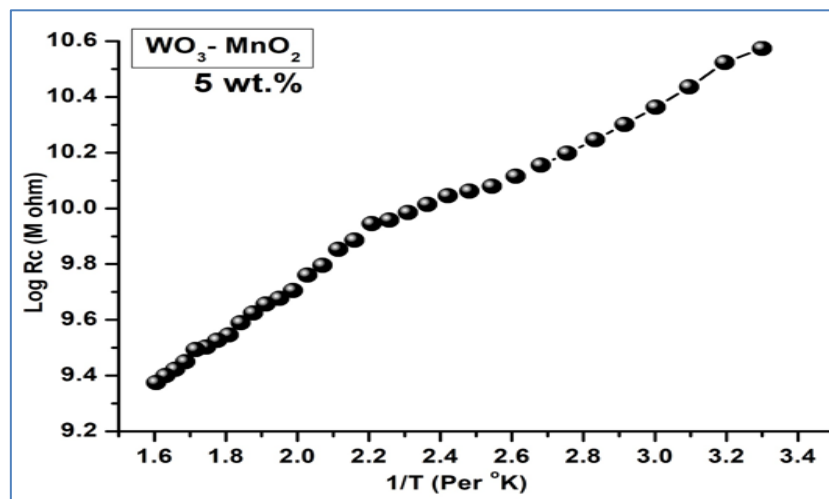
Figure 4. Log Rc versus 1/T plot of WO_3-MnO_2 thick films

The logarithmic resistance (Log Rc) vs. reciprocal temperature (1/T) plot is shown in Figure 4, follows an Arrhenius-type behavior, confirming that the electrical conduction in WO_3-MnO_2 thick films is thermally activated. The slope of the linear fit in the Log Rc vs. 1/T graph was used to determine the activation energy (Ea), which is critical in understanding the conduction mechanism. The increase in Log Rc with increasing 1/T supports the thermally activated transport process, where charge carriers require energy to move across potential barriers. The activation energy was found to be 0.1942 eV at higher temperature region and 0.1483 eV at lower temperature region respectively for WO_3-MnO_2 thick films. It is found that, the behavior aligns with the n-type semiconducting properties of MnO_2 is conduction is facilitated by oxygen vacancies and free electrons and influenced by WO_3 incorporation [28, 31].

The gas sensing properties of WO_3-MnO_2 thick films were analyzed based on sensitivity, selectivity, response to LPG concentration, and response-recovery times, as shown in Figure 5 (a-d).
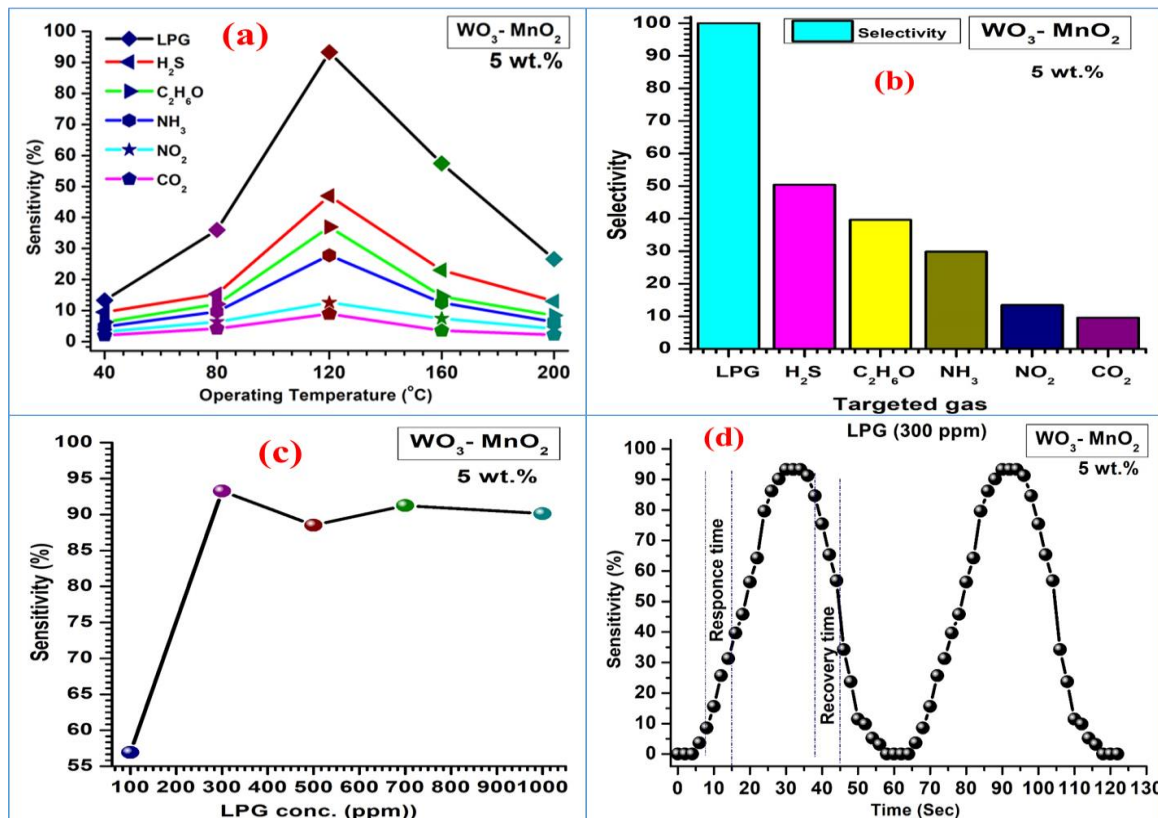
Figure 5. (a) Sensitivity versus operating temperature, (b) Selectivity histogram,(c) Sensitivity versus LPG gas concentration (ppm) and (4) Response and recovery time plot of WO_3-MnO_2 thick films

Fig. 5 (a) shows the sensitivity versus operating temperature plot of WO_3-MnO_2 thick films. The sensitivity WO_3-MnO_2 thick films was evaluated across different operating temperatures such as 40, 80, 120, 160 and 200 °C for various gases, including LPG, H_2S, C_2H_6O, NH_3, NO_2, and CO_2. The plot shows that sensitivity increases with temperature, reaching a peak at 120°C, after which it decreases. LPG exhibits the highest sensitivity (93.26%), indicating that this material is well-suited for LPG detection. The peak at 120°C suggests the optimum working temperature for effective gas sensing. Selectivity is a crucial factor for gas sensors, determining the sensor's ability to differentiate between gases. The histogram Fig. 5 (b), indicates that WO_3-MnO_2 exhibits the highest selectivity towards LPG, followed by H_2S, C_2H_6O, NH_3, NO_2, and CO_2. This preference for LPG suggests that the film's surface chemistry and adsorption-desorption dynamics favor interactions with LPG molecules over other gases [30, 31]. Sensitivity as a function of LPG concentration (100–1000 ppm) shows a rapid increase up to 300 ppm, reaching above 90% sensitivity as shown in Fig. 5 (c). Beyond this concentration, the sensitivity stabilizes, indicating a saturation effect where additional LPG molecules do not significantly alter resistance. This demonstrates the sensor's high responsiveness to LPG at lower concentrations, making it highly efficient for LPG leakage detection [32, 33]. The WO_3-MnO_2 thick film-based gas sensor demonstrated remarkable sensing performance with a rapid response time of 26 seconds and a recovery time of 52 seconds when exposed to 300 ppm of LPG. The response-recovery curve in Fig. 5(d) indicates the efficient adsorption and desorption of LPG molecules on the sensor surface, ensuring real-time gas monitoring capability [33, 34].

4. CONCLUSION

The WO$_3$-MnO$_2$ thick films were successfully fabricated using the screen-printing technique and evaluated for LPG sensing applications. Structural characterization confirmed the formation of a mixed metal oxide system, with WO$_3$ doping significantly influencing the crystallite size and surface morphology. Electrical measurements revealed a high resistivity of 637330 Ω·m and a negative TCR of -0.00171/K, indicating the semiconducting nature of the films. Gas sensing analysis demonstrated a maximum sensitivity of 93.26 % at 300 ppm of LPG, with an optimal operating temperature of 120 °C. Furthermore, the sensors exhibited rapid response (26 sec) and recovery (52 sec) times, along with excellent selectivity towards LPG, making them highly suitable for practical gas sensing applications. These findings highlight the potential of WO$_3$-decorated MnO$_2$ films as efficient, cost-effective, and reliable materials for LPG detection, paving the way for their integration into commercial gas sensor devices.

CONFLICTS OF INTEREST

The author declare no conflict of interest.

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A REVIEW ON ROLE OF DOPANT IN SODIUM ION BATTERY ELECTRODES

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ABSTRACT

Sodium-ion batteries (SIBs) are gaining popularity as alternatives to lithium-ion batteries, owing to their cheaper prices and plentiful sodium supplies. The choice of cathode materials has a considerable impact on SIB performance, since they are important for energy density, capacity retention, and cycle stability. Despite their abundance on earth SIB faces low energy density, low specific capacity and unstable structure which hinder its performance on large scale of application. There is lot of work is going on to improve the stability and performance of SIB. Majority are working on its parts like Cathode materials, anode materials, electrolytes and doping of electrodes. Many researchers have also tried to improve the overall performance of SIB by modifying structure and charge discharge mechanism of battery. Further, It has been also found that doping of electrode material significantly enhance the performance of SIBs. This review covers significant enhancement of SIB by adding dopant in the cathode materials.

1. INTRODUCTION

Since 19th century the rechargeable battery took the birth. Researchers found their first ever rechargeable battery lead acid in 1859, invented by Gaston Plante , a French engineer. Where it was a great power source of automobiles and other application. In mid of 20th century the Ni-Cd battery has become more demanding as it was greatly commercialized. They were more compact and could be recharged hundreds of times. These batteries were used in a variety of consumer electronics, power tools, and emergency backup systems.

The idea of using lithium, a highly reactive metal, in rechargeable batteries was explored in the late twentieth century; the breakthrough of the lithium-ion battery marked the beginning of the modern era of rechargeable batteries, which now power not only small electronics but also electric vehicles (EVs), solar energy storage, and other applications. The ability to recharge a battery several times without considerable reduction in performance was groundbreaking. [1]

With increased demand for lithium and concerns about supply chains and environmental impact, sodium-ion batteries are gaining appeal. Sodium, which is more abundant and less costly than lithium, is an attractive candidate for large-scale energy storage systems. Sodium-ion batteries are not yet as efficient as lithium-ion batteries, although research is underway to improve their energy density and cycle life. [2]

The cathode of sodium-ion batteries (SIBs) is crucial to the battery's overall performance, particularly in terms of energy density, charge/discharge rates, stability, and cycle life. Even while SIB has many benefits, its performance is hampered by some cathode materials because they do not have long cycles and cycle stability can be compromised. To relive the development of sodium ion batteries, research is being conducted on new age cathodes or doped cathode materials. [3,4]

Dopants, which are atoms or molecules that are purposely injected into the cathode material, can have a major impact on the cathode's electrochemical characteristics and improve battery performance. By judiciously doping the cathode, researchers can improve the material's structural, electrical, and electrochemical properties. The major cathode materials are Layered metal oxide, Prussian blue analogues and polyanionic compounds or NASICON based materials. These materials are effectively studied with doping of alkaline earth metals such as Mg, K Ca etc., transition metals such as Ti, V , Fe , Mn ,Ni and Co etc. and non-metallic dopants such as F ,N , S and C.[5]

This review discusses the three cathode materials that have been doped with such dopants, as well as their implications on rate capability, cycle stability, and retention in sodium ion batteries.

2. DISCUSSION

2.1 Layered Transition Metal Oxide

Transition metal layered oxides Na_xTMO_2, are one proposed cathode material for SIBs. (Na_xTMO_2, in which TM=transition metal; $0 < x \leq 1$). It is critical for the commercialization of LTMO cathode materials to maintain their performance throughout the battery's life span, which can only be accomplished if the cathode is designed with higher cycle stability.

Because of their simple structures and straightforward synthetic processes, sodium ion layered oxide materials, particularly manganese-based layered oxide materials such as P2-$NaxMnO_2$, P′2-$NaxMnO_2$, P2-Na0.67Ni0.33Mn0.67O2, and O3- NaNi0.5Mn0.5O2, have demonstrated significant commercial viability. However, a common issue for these materials is poor cycling performance due to irreversible phase changes. Elemental doping is an effective method to inhibit irreversible phase transitions and increase performance.[6,7]. Ding et al. has performed the synergetic doping of Zn/Ti/F in P2 – NaxMnO2, achieved a rate capability 79.5 mAg^{-1} at 10C and excellent cycling stability 86% capacity retention after 1000 cycles at 10C.[8]

Van et al has investigated the boron or boron and fluorine co-doped NLMC (sodium- lithium-manganese-cobalt oxide material) cathode with excellent capacity of 149 to 166 mAg^{-1} at a current density of 10 mA g−1.and 67-73% retention after 100 cycles were noted [9].

The NFM doped with different concentration of F is found by huang et al. the synthesis of F doped NFM with different stoichiometric carried out by simple solid state method, the NFM-F0.01 material exhibit the higher capacity of 110 $mAhg^{-1}$ at current density of 150 mAg^{-1} after 70 cycles.[10]

2.2 Prussian blue Analogues (Pbas)
Prussian blue analogues (PBAs) are emerging as potential materials for sodium-ion batteries (SIBs) due to their good electrochemical characteristics and cost-efficiency. These materials have great capacity and stability, making them appropriate for large-scale energy storage applications, particularly in renewable energy systems.

They feature a porous, open framework structure created by the self-assembly of metal ions and cyanide groups, enabling the intercalation of Na ions. The general formula for PBAs is sometimes written as $AM[M'(CN)6]n.H_2O$, where A, M and M' are distinct metal ions. Where A is Li , Na and K etc, M is Fe and M' are transition metals as Mn, Ni and Co etc [11].The crystal structure of PBA contains some concentration of alkali metals and some water content which creates symmetry disorder and hence affects the electrochemical performance. by regulating its crystal symmetry the cyclic stability of PBAs can be improved.[12]

Doping of Prussian blue analogues (PBAs) has emerged as an important approach for improving the performance of sodium-ion batteries. Several doping strategies, including codoping with metals like as Ni, Cu, and K, have been investigated to increase PBA structural stability, electrical conductivity, and overall electrochemical performance.[13]

Iron-based Prussian blue analogues (Fe-PBA) and manganese-based Prussian blue analogues (Mn-PBA) have been widely investigated as cathode materials for sodium ion batteries. They also performed substantially above theoretical levels of specific capacity, and their easy production and inexpensive cost made them an ideal choice for SIB. They continue to have poor cycle stability and low conductivity as a result of irreversible phase transitions with high Na concentrations.[14]

Yang et al. has produced vanadium-doped PBAs with Fe, Co, and Ni using chemical co- precipitation and a water bath procedure. Sodium vanadium ferrohexanocyanate (VFeHCF) has better electrochemical characteristics as compared to VCoHCF and VNiHCF an alternate materials design with vanadium, due to the fact that V and Fe has the right ratio, which produced a synergistic action, preserving the skeleton of the PBAs. Further (VFeHCF) material exhibit an initial specific capacity of 110 mAg^{-1} , a coulombic efficiency of 93.7%, capacity retention of 92.4%, and a rate capability of 70 mAh g^{-1} at 120 mAg^{-1}.[15] Chang et al. has discovered the multi metal PBA Na1.92($Mn_{0.3}Fe_{0.23}Co_{0.3}Ni_{0.17}$)[Fe(CN)$_6$]$_{0.88}$·2.16H2O prepared by one step co precipitation method has shown discharge capacity of 120 mAg^{-1} with retention up to 82 % after 1000 cycles.[16]

Jiang et al. utilized interstitial K-doping to enhance the structural stability of $Na_{2-x}FeMn[Fe(CN)_6]$ (FeMnPBA), resulting in improved sodium storage efficiency. They achieved a specific capacity of 139.1 $mAhg^{-1}$ at 100 mA g^{-1}, with 77.1% capacity retention after 700 cycles and the pouch cell of FeMnPBA3/hard carbon (HC) shows steady cyclability of 82.6% after 600 cycles.[17]

2.3 Polyanionic Compounds
Polyanion-type electrode materials are metal oxide frameworks, composed of networks formed by strong covalent bonding between polyanionic polyhedrons and transition metal ion polyhedrons. The general molecular formula of polyanionic compound is $Na_xM_y(X_aO_b)n$ (where M = V, Fe, Mn, etc., and X = P, S, Si, etc.).[18]

The most extensively researched polyanions are NASICONS. Polyanion type cathodes in sodium ion batteries provide improved cycle stability and superior rate capability. Furthermore, their polyanion networks are inefficient during Na ion intercalation and deintercalation, resulting in a blockage of electron transport and a limited output of electronic conductivity which can affect the overall capacity of battery.

Recent study suggests that elemental doping can enhance the conductivity of polyanion cathode materials. but it has also been noted that doping can be accomplished through specific choices of materials and structures [19]. Numerous researchers have explored the extremely effective NASICON-type material sodium vanadium phosphate $Na_3V_2(PO_4)_3$, which has been reported to demonstrate higher cycles at appropriate retentions. Zhu et al. discovered that adding tungsten W to $Na_3V_2(PO_4)_3$ resulted in a specific capacity of 116 mAh g^{-1} at a 1C rate, with retention up to 94% over 18000 cycles. The constructed $Na_{(3-x)}V_{(2-x)}W_x(PO_4)_3$@C (x = 0, 0.05, 0.1, 0.2, 0.3) was manufactured by solgel technique cathode with carbon coatings [20].

One of the cathode named as $Na_{3.3}K_{0.2}V_{1.5}Mg_{0.5}(PO_4)_2F$ has been designed by double metal doping and nitrogen doped carbon coatings which provide porous structure and produces active sites, Liu et al. doped binary metals K and Mg to NVPF $(Na_3V_2(PO_4)_2F_3)$ achieving

124.3 mAhg^{-1} at a rate of 0.1C and 1000 cycles with a capacity retention of 93.1% at 10 C. [21]. Doping at transition metal sites in NASICON based cathode with Cr, Al, Mn Mg, K etc can effectively produce high redox which in returns increases the conductivity of materials.[22]. Mahato et al. has investigated strategy of co doping NVPF material by Fe and Cr. They employed the rota-tumbler assisted sol–gel method to synthesized the carbon coated $Na_3V_{1.9}Fe_{0.095}Cr_{0.005}(PO_4)_2F_3$ cathode. After 500 cycles at 1C it retains 89% capacity. The initial specific capacity was 119 mAhg^{-1} at 0.1 C. [23]
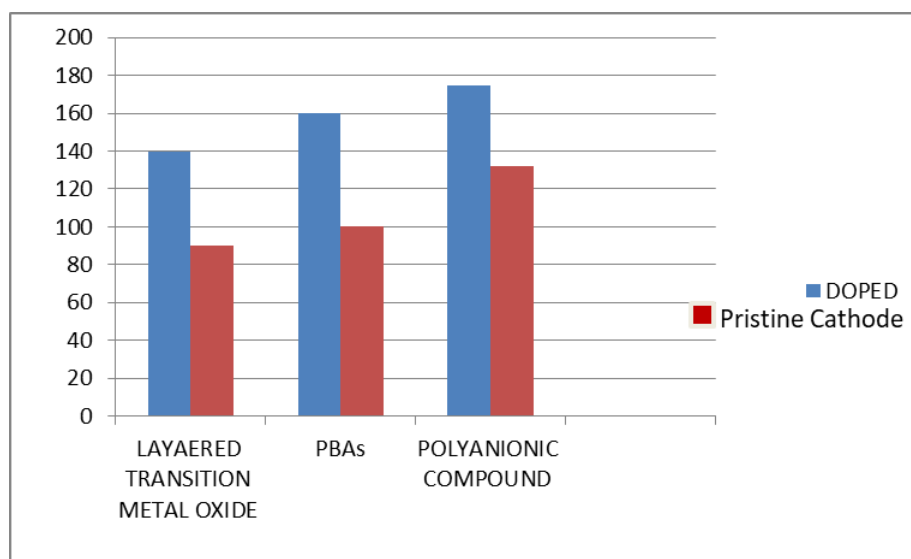
Fig 1. Shows comparison of doped and pristine cathodes having different specific capacities at 1 C rate in layered transition metal oxide, PBAs, Polynomic compound (Specific Capacitance Along Y- Axis)

3. CONCLUSION

In this review we have summarized the application of dopants to optimize the efficiency of cathode material such as layered metal oxides, PBAs or polyanionic compounds. in proper concentration, dopants can effectively enhance the full cell performance of battery also by stimulating different sites at host materials is one of the strategies to enhance its cycles and retention, Additional study can focus on ecologically friendly, cost effective and novel or innovative dopants. Therefore, Dopant has Played crucial role in enhancing battery overall performance.

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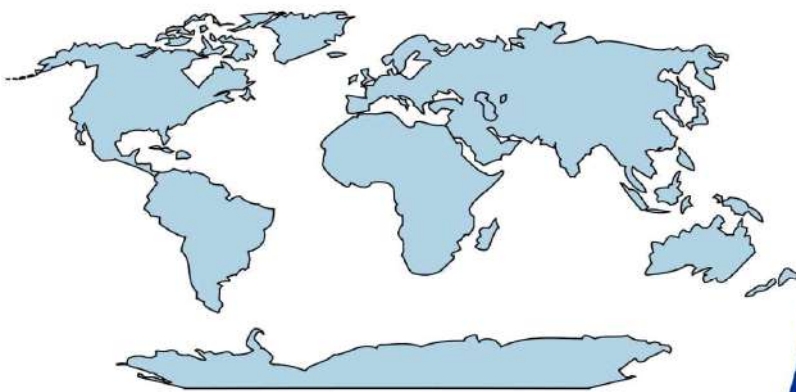
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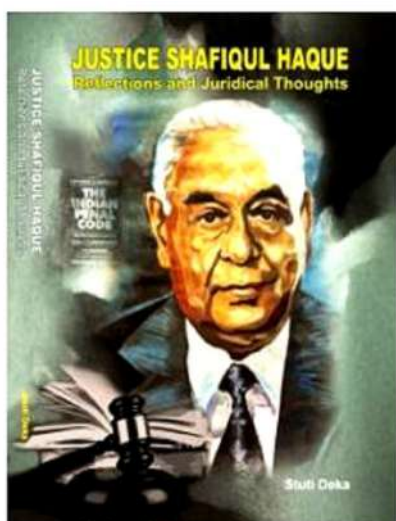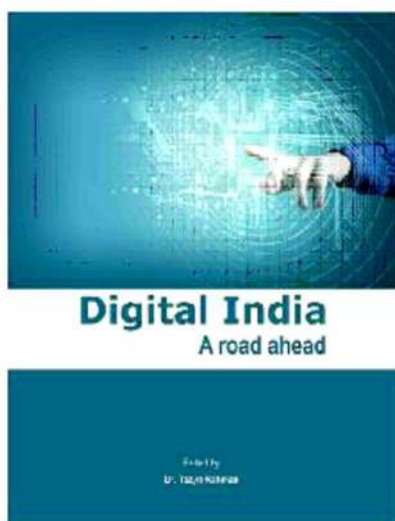
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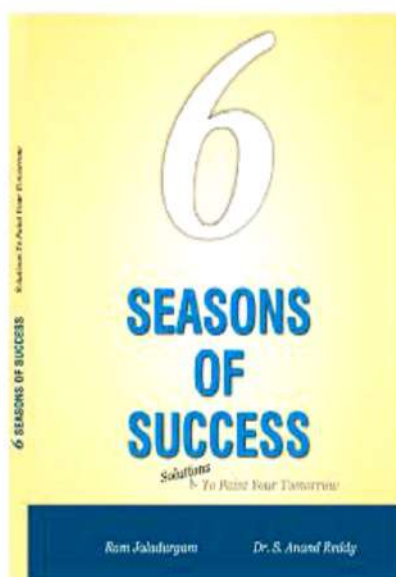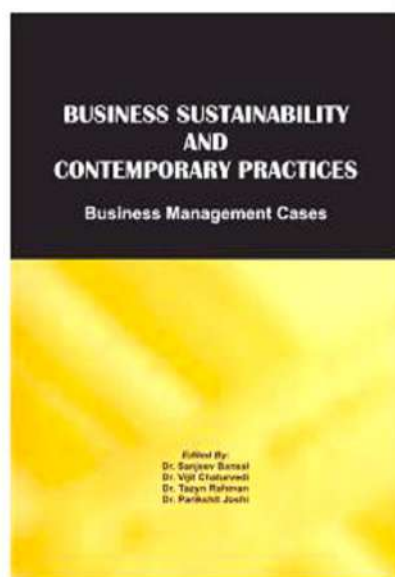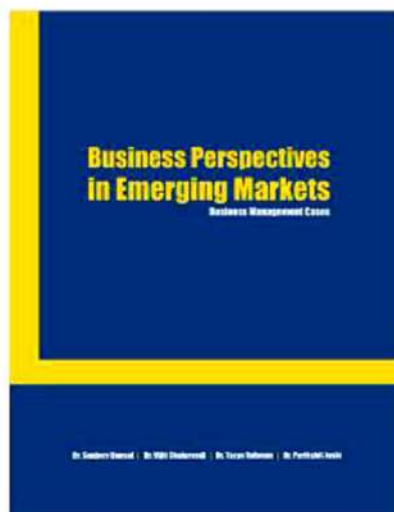
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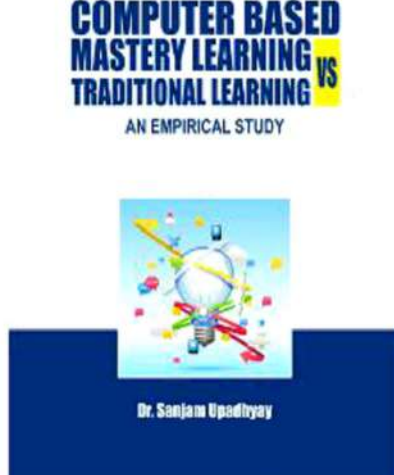
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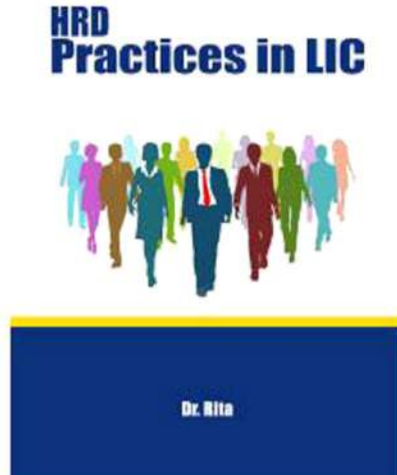
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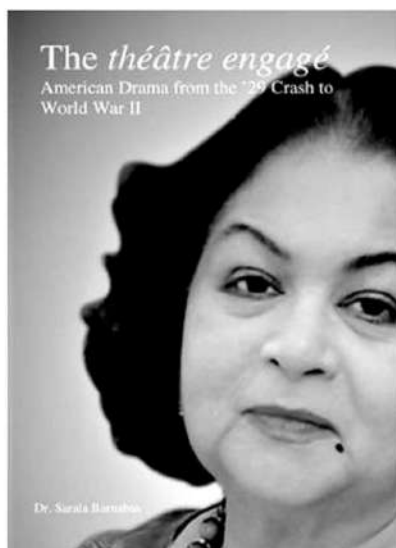
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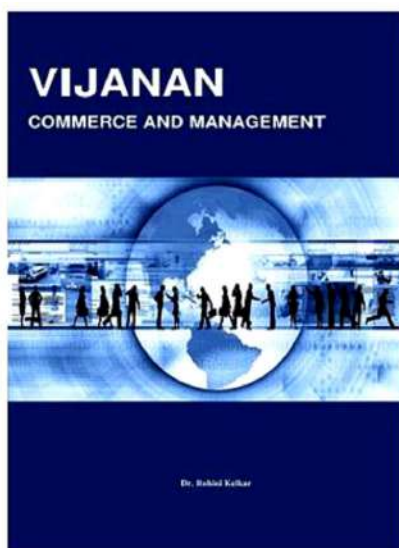
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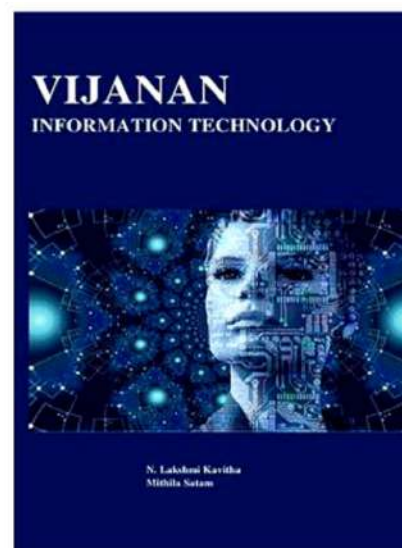
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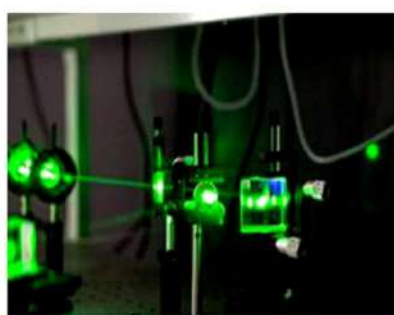
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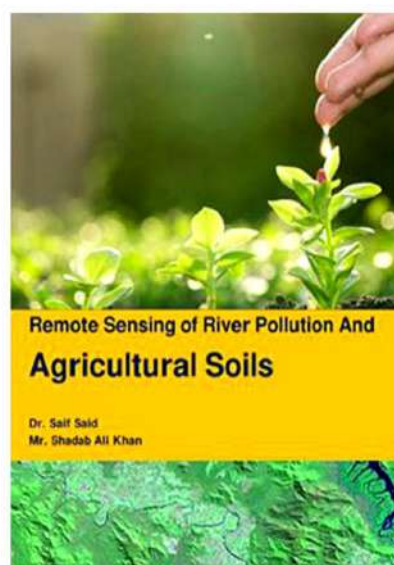
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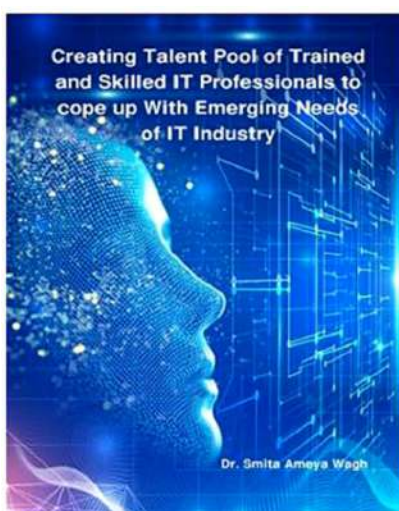
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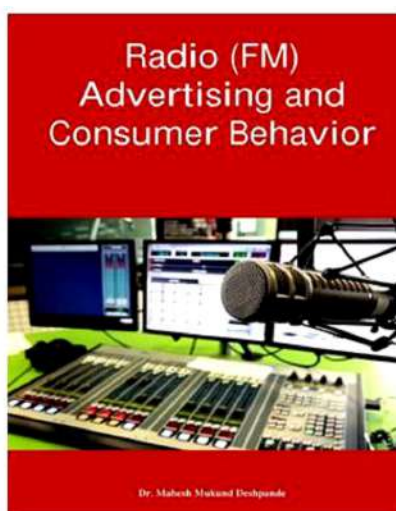
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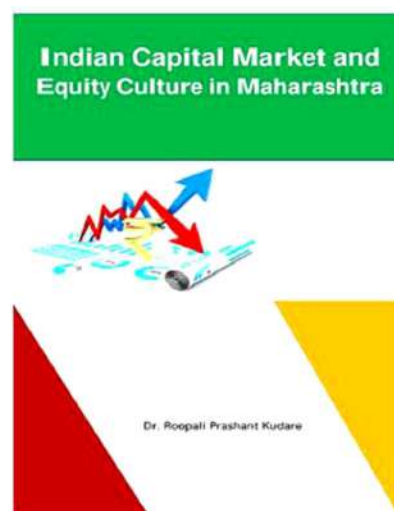
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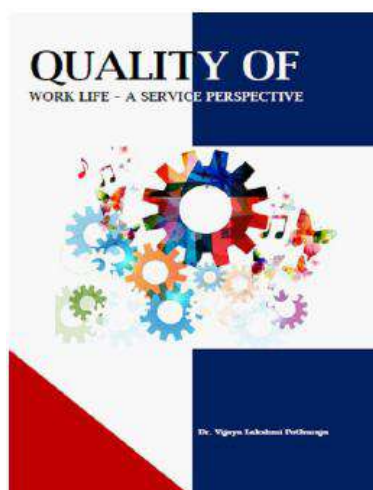
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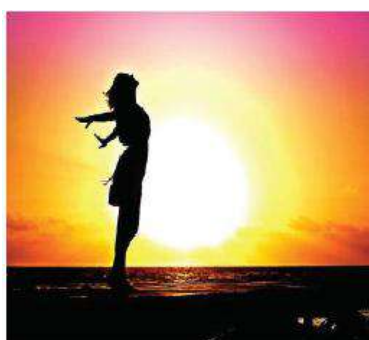
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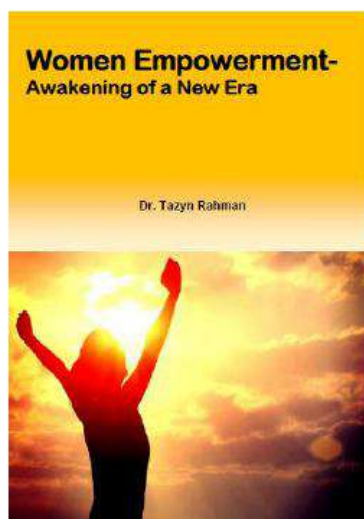
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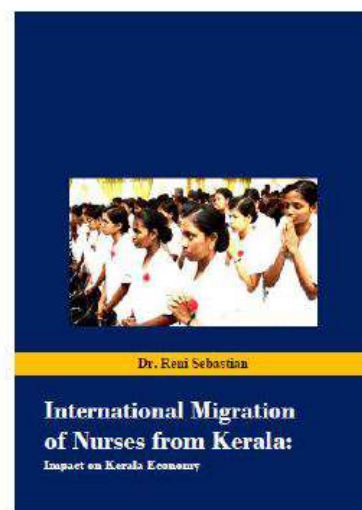
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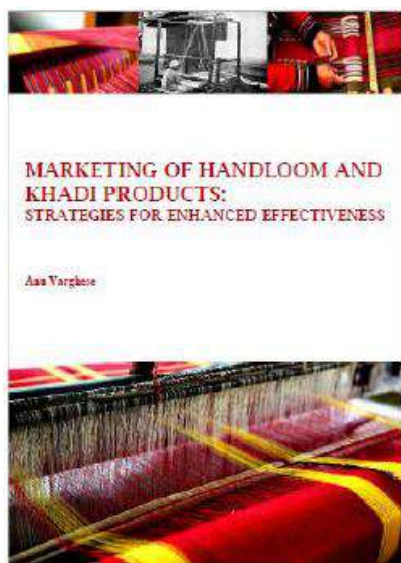
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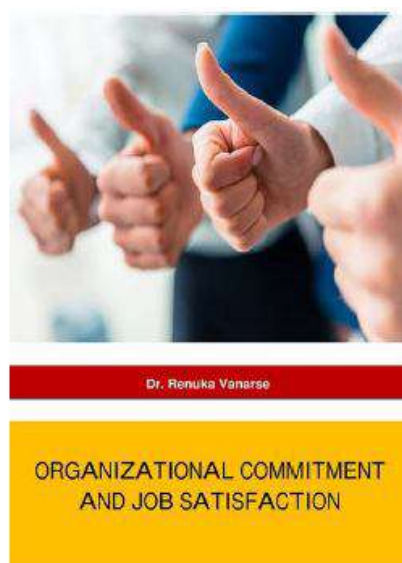**Dr. Vijay Prakash Gupta**
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