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GREEN SYNTHESIS AND CHARACTERIZATION OF CO-DOPED ZnO NANOPARTICLES VIA THE ACCUMULATION OF COBALT ION ONTO PISTIA (*Pistia stratiotes* L.,) PLANT TISSUE AND ITS PHOTOCATALYTIC ACTIVITY TOWARD ORGANOSULFUR POLLUTANTS

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ABSTRACT

Water pollution has recently become a serious global problem and hence researchers were focusing to develop innovative methods for the purification of water and then getting access to purified water by reducing pollution. As a result, the current study concentrated on synthesizing cobalt-doped zinc oxide nanoparticles by accumulating cobalt ions on Pistia (*Pistiastratiotes L.*) plant tissue and combining them with zinc acetate precursor. Further, the synthesized particles were analyzed for their efficiency in photo-desulphurization of organo sulphur compounds such as Dibenzothiophene and 2,5-dimethyl thiophene. Various characterization studies proved that the nanoparticles were oval in shape and had particle sizes of 8-34 nm and the particles were distributed with less aggregation. The particles have 47 % of zinc element and 21% cobalt with hexagonal (wurtzite) crystalline structure. The synthesized Co-doped ZnO nanoparticles were utilized for the desulfurization of Sulphur containing pollutants such as dibenzothiophene and 2,5-dimethyl thiophene. The results proved that rapid desulfurization was observed during the initial time of the study. The % desulfurization of 14.36±0.136 and 19.63±0.201% was observed within 5 min of the study for dibenzothiophene and 2,5-dimethyl thiophene. Whereas the high % desulfurization was noticed within less time of 25 min wherein the % desulfurization was observed to be 95.61±0.279 and 93.66±0.137 for dibenzothiophene and 2,5-dimethyl thiophene respectively. The removal of harmful heavy metals utilizing the Pistia plant and recycling in the wastewater treatment process may therefore be inferred as being highly valued. Additionally, the Co-doped ZnO photocatalysts might improve photocatalytic activity owing to the catalysts' porosity and the hole recombination and electron suppression.

Keywords: Co-doped ZnO Nanoparticles, Pistia Plant, Photocatalytic Activity, Desulfurization, Dibenzothiophene, 2,5-Dimethyl Thiophene.

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INTRODUCTION

The area of technology known as nanotechnology is concerned with the understanding and control of matter that was in the dimension of 1 and 100 nanometers approximately and has unique phenomena that enable novel applications.[1] Nanoparticles are more preferentially referred to the materials that include particulate substances' having 5 to ~100 nm particle size that are feasibility to overcome various systemic barriers and was explained by Nanoparticles act as a bridge between atomic or molecular structures and bulk materials and hence are having excellent scientific interest.[2] Using toxic chemicals in chemical nanoparticle synthesis could exert potential hazards such as toxicity, carcinogenicity, and environmental toxicity.[3] The use of hazardous chemicals like organic solvents, stabilizers, and decreasing agents in nanoparticle synthesis may cause prominent toxicity problems. The presence of these toxic chemicals and solvents as a contaminant in the nanoparticles may limit the use of nanoparticles in various biomedical applications. Hence, trustworthy, biologically appropriate, and eco-friendly methods/procedures were

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required for nanoparticle synthesis. Therefore, the NPs synthesis with biological techniques was considered an attractive alternative for the synthesis of nanoparticles.[4] Plants are considered cost-efficient and eco-friendly chemical factories. Plants act as potential heavy metal detoxificant and were used to overcome the problems caused by various environmental pollutants and these pollutants were very toxic even at trace levels also.[5] The nanoparticle synthesis with plant extracts is considered a clean and environmentally accepted "green chemistry" concept.[6] Zinc oxide nanoparticle synthesis has got significant attention due to its broad variety of applications in areas including optics, electronics, and biomedical systems.[7] These nanoparticles were enlisted as "generally recognized as safe" by US FDA. Because of their large band gap (3.37eV) and strong exciton binding energy (60meV), these nanoparticles seem to exhibit exceptional semiconducting characteristics. These nanoparticles also have anti-inflammatory, wound healing, optic, UV filtering, and high catalytic activity. ZnO NPs have significant UV filtering activity and hence were widely used in preparing various cosmetics such as sunscreen lotions for protecting skin from UV light.[8] These nanoparticles have various applications as potential antibacterial agents, manufacturing rubber, and paints, removal of sulfur and arsenic from water, adsorption of protein, and dental applications.[7] Various researchers studied a variety of techniques to improve the photocatalytic activity of ZnO semiconductors.[9-11] Doping additional transition metals into the lattice of zinc oxide considerably increase the activity, according to several research findings.[12-13] Due to the development of oxygen vacancies, the co-doping and doping of metal or non-metal species may improve catalytic activities by accelerating the movement of photogenerated holes and electrons and widening the optical absorption range.[14] Investigations focused on the roles of cobalt doping in ZnO photocatalysts.[15] Additionally, it is well recognized that photocatalyst synthesis utilizing plant materials as a template is environmentally friendly, beneficial, and helpful in the technology of wastewater treatment.[16] Utilizing the undesirable plant Pistia (*Pistiastratiotes L*) as a template among natural resources is economical and useful. Taking into account the aforementioned factors, the current study concentrated on the production of cobalt (Co) doped ZnONPs. Further, the synthesized Co-doped ZnONPs were studied for their applicability to the desulfurization of Organo sulphur compounds such as Dibenzothiophene and 2,5-dimethyl thiophene. The sulfur-containing chemical type that is mostly found in heavier petroleum fractions is dibenzothiophene and 2,5-dimethyl thiophene. It is obvious that the final disposal of these contaminants poses a serious threat to the aquatic environment and is very poisonous to all living things.

EXPERIMENTAL

Reagent and Chemicals

The analytical grades chemicals like cobalt nitrate hexahydrate, zinc nitrate hexahydrate, sodium hydroxide, dibenzothiophene, and 2,5-dimethyl thiophene were utilized in the study and were procured from Sigma Aldrich - Merck, Bengaluru, Karnataka, India.

Instrumentation

The quantification of dibenzothiophene and 2,5-dimethyl thiophene was carried out using on Shimadzu gas chromatography (QP 2010, Japan) instrument equipped with AOC-20i auto-sampler, DB-5 fused silica capillary column (30m x 0.25mm; 0.25µm id) and flame ionized detector.

Collection of Plant Material

The fresh Pistia plant was collected in a water storage reservoir at Prakasam barrage, Krishna River, Vijayawada, Krishna district, Andhra Pradesh. The plant sample was collected following the institutional rules and necessary permissions taken from local legislation. It was verified and authenticated by Dr. Ch. Srinivasa Reddy, Assistant Professor, Department of Botany, SRR & CVR Government Degree College (A) Vijayawada, whose voucher specimen number SRR-CVR/2022/PI/11 was deposited at the Department of Botany. The collected plant material was cleaned using tissue paper and then the plant material was cut into small pieces then the pieces were dried under shade and the dried material was preserved in an amber color bottle.[17]

Co-doped ZnO Nanoparticles Synthesis

The powdered Pistia plant was subjected to immersion in a 1000ppm cobalt precursor solution for 12 and 24h in various sample containers. The cobalt-ion-accumulating plant tissue was then removed from the

solution. Using atomic absorption spectroscopy (AA), the number of cobalt ions in the solution was determined for each time under study. The number of cobalt ions that had accumulated on the plant tissue surface was then calculated using the data. Filtration was used to extract the plant powder from the cobalt solution, and a hot air oven was used to dry it. Then, 60mL of a 5M zinc acetate solution was added to the powdered dry plant material. Sodium hydroxide solution was used to raise the pH of the mixture to 10 while it was being heated at 80°C with constant stirring. The precipitate formed in the solution was separated using filtration. With distilled water and ethanol, the pellet was cleaned many times. Then, it was calcined for three hours at 600°C after being dried in an air oven.[1]

Characterization

The expected crystal structure of the Co-doped ZnO nanoparticles was verified by performing XRD (X-ray diffractometer - Rigaku Corporation, Japan) and the analysis was conducted in the diffraction angle (2θ) scan range of 20 to 80° with a scan speed of 2°/min. The zeta potential and particle size distribution of the produced nanoparticles were assessed by DLS (dynamic light scattering; Malvern Zetasizer Nano ZS90, UK). The size, surface morphology, and elemental nanoparticle composition were assessed using the FESEM (FE-SEM - Nova, Nanosem-450, FEI, United States) and energy-dispersive X-ray spectroscopy (EDX - RONTEC's, QuanTax 200, Germany). By using FTIR (FT-IR - Bruker, USA) analysis, the functional groups that were derived from the plant extract and that are included in the nanoparticle formation were assessed. The FI-IR study was conducted between 4000 and 500$cm^{-}1$.[19- 20]

Catalytic Applications of Nanoparticles

The Co-doped ZnO nanoparticles synthesized in the present study were evaluated for their ability to desulfurization of two organosulfur compounds viz., Dibenzothiophene and 2,5-dimethyl thiophene. The desulfurization study was conducted using synthesized Co-doped ZnO nanoparticles as catalysts and Dibenzothiophene and 2,5-dimethyl thiophene in methanol as substrate separately. The pH of the reaction mixture was set to 7, and a 20mL sample of wastewater containing 0.01g of manufactured nanocatalyst and 10 ppm of each organosulfur compound was added separately. The reaction mixture was then maintained in an orbital shaker rotating at 500 rpm while being exposed to UV light. The suspension is collected after every five minutes of UV light exposure, and the degradation process was examined using a gas chromatograph (GC). The desulfurization efficiency of the synthesized Co-doped ZnO nanoparticles was evaluated by comparing the standard results observed in GC analysis with the sample results observed in each time interval.[21]

Reusability

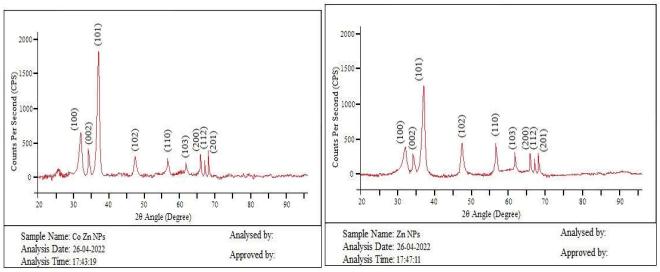
The reusability of the synthesized NPs for their catalytic application was evaluated for five cycles. After finishing the catalytic activity in each cycle, the nanoparticles were collected by filtering, repeatedly rinsed with distilled water, and then dried for three hours in an air oven at 120°C. These dried nanoparticles were studied for their catalytic ability for the removal of studied pollutants.

RESULTS AND DISCUSSION

By accumulating cobalt ions on the tissues of the pistia plant and fusing them with zinc precursor, a noble and efficient approach for the green production of Co-doped ZnO nanoparticles was developed. The cobalt accumulation up to 12 H and 24 H was studied for the synthesis of nanoparticles and the results proved that the cobalt accumulated up to 24 H shows a significantly high accumulation of cobalt and the % composition of the cobalt in the nanoparticles was high and hence the characterization and other studies were carried for the material synthesized using the plant material that accumulates cobalt up to 24H. Cobalt solution at a concentration of 1000 ppm was studied as the initial concentration of the cobalt metal for accumulation study. The amount of cobalt present in the aqueous solution during the accumulation study after 12 and 24 hours was studied using AAS and the concentration of cobalt solution was observed to be 921 ppm and 781 ppm respectively after 12 and 24 H of accumulation study. This confirms that after 12 H of study, a limited amount of cobalt only accumulated onto the plant whereas, after 24H of incubation, 21.9% of the cobalt metal was accumulated. Then, by adding the cobalt-accumulating plant material to the zinc precursor, nanoparticles were created.

Characterization of Nanoparticles

The prominent peak at 2θ of 32.1, 39.7, 42.1, 56.8, 61.2, 65.9, 67.5, and 68.2° corresponds to (100), (002), (101), (102), (110), (103), (200), (112), and (201) represents the hexagonal (wurtzite) composition of the nanoparticles, and the diffraction pattern was consistent with the standard hexagonal structure with JCPDS No. 36-1451. The XRD pattern of nanoparticles synthesized in the same procedure without the addition of the Cobalt (Fig.-1B) also shows the hexagonal wurtzite structure with similar diffraction peaks that were observed for the nanoparticles synthesized by doping cobalt (Fig.-1A). The results confirm that cobalt doping doesn't alter the diffraction pattern of ZnO. This might be because cobalt ions, which have an ionic radius of 0.72Å, have substituted zinc ions with an ionic radius of 0.74Å.[22] Additionally, the fact that the Co-doped ZnO nanoparticles' XRD pattern only displays a single phase indicates that the Cobalt was integrated into the lattice as a substitution atom.[23]

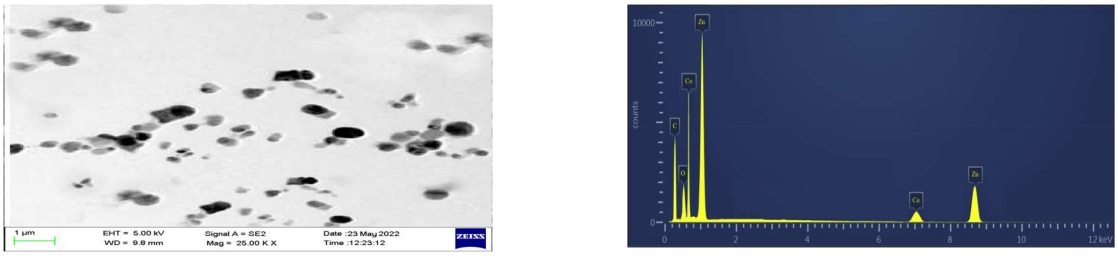


A B

(A) Co-doped ZnO nanoparticles XRD pattern (B) ZnO nanoparticles synthesized without the addition of Cobalt XRD pattern

Fig.-1: Synthesized Nanoparticles XRD Pattern

The elemental composition and surface morphology of the Co-doped ZnONPs formed were assessed using SEM as well as EDX analysis. Figure-2 shows the representative SEM image and EDX measurement results observed for the synthesized Co-doped ZnO nanoparticles. The SEM image clearly shows that the nanoparticles were oval in shape and the particles were isometric with a size range of 8-34 nm. The SEM analysis also confirms that the nanoparticles were separated and very less aggregation was identified. The quantitative elemental analysis of the synthesized nanoparticles was evaluated using EDX analysis. The EDX spectrum (Fig.-2B) shows the characteristic signal corresponds to cobalt and zinc was detected at 6.89 (Kα) and 0.73 (Lα) for cobalt and 8.64 (Kα) and 1.03 (Lα) for zinc. The characteristic signal corresponding to oxygen was also found in the EDX spectra confirming the oxide form of zinc ions. The % composition was observed to be 47% and 21% zinc and cobalt respectively. Based on the results observed in the EDX analysis, it was confirmed that the % composition of zinc was observed to be higher than cobalt. The EDX spectra don't show any additional peaks/detections throughout the scan range proving that the particles obtained in the study were highly pure that doesn't have any impurities.



(A) (B)

Fig.-2: Co-doped ZnOSEM (A) and EDX Spectra (B)

The particle size of the synthesized Co-doped ZnO was evaluated by performing DLS (Dynamic Light Scattering) technique. According to the findings, co-doped ZnO has distributed in particles smaller than 35nm. In the range of 10 to 25nm, the size distribution's highest abundance was noted. The average particle size for particles less than 10 nm and larger than 50 nm was only 18 nm, which is further validated by XRD examination. The zeta potential of the Co-doped ZnO was also evaluated using DLS

technology. The results show that the Co-doped ZnO particles were negatively changed and were observed at 29.8 mV (Fig.-3). As a result of the strong attraction between the particles caused by the high negative zeta potential,[24] the particles observed in the study were not having a high negative charge and hence were confirmed as stable.

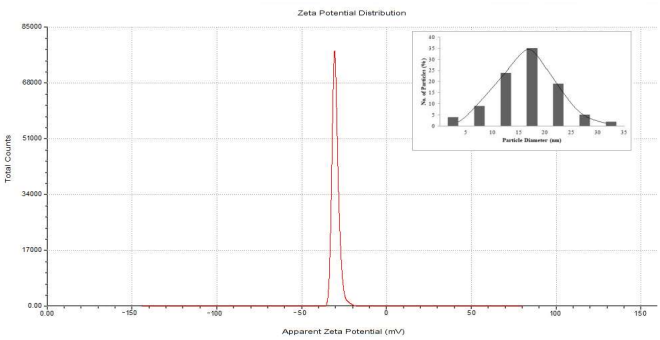
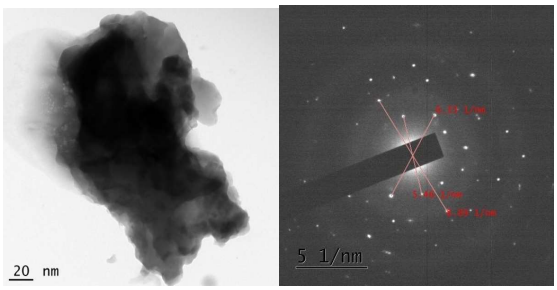


Fig.-3: Zeta Potential and Particle Size Co-doped ZnO Distribution

The surface morphology of the produced Co-doped ZnO particles was evaluated using TEM examination. The TEM analysis confirms that the particles were uniform in shape with fewer agglomerates identified. The shape of most of the particles was confirmed to be oval and very few particles were irregular in shape. The clear observation of the surfaces of the particles confirms that the particles have rough surfaces. The collected particles were determined to have an average size of 18nm by calculation and confirmation. The diffraction intensities of the particles were evaluated using TEM-SAED ("Selected area electron diffraction") analysis and the outcomes confirm that the particles exhibited quite low diffraction intensities. One explanation for the relatively low diffraction intensities was the deposition of tiny particles on the carbon film and the nanoparticle diffractions being hidden by the amorphous carbon background. The TEM bright-field image and SAED diffractogram were depicted in Fig.-4A and 4B.



(A) Bright-field image (B) SAED diffraction pattern

Fig.-4: TEM Analysis Results

The possible biomolecules responsible for capping and efficient stabilization of the particles synthesized in the study were evaluated using FT-IR analysis. In this FT-IR spectrum, the peak located at 3333 cm^{-1} indicated the presence of intermolecular bonded alcohol groups. The peaks located at 2945 cm^{-1} and 2832 cm^{-1} represent C-H stretching vibrations in alkanes and aldehydes respectively.

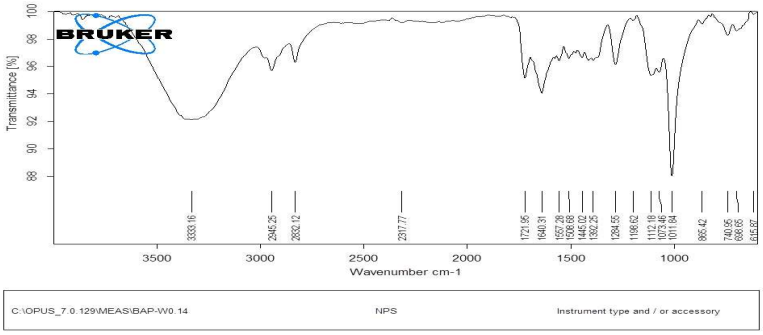
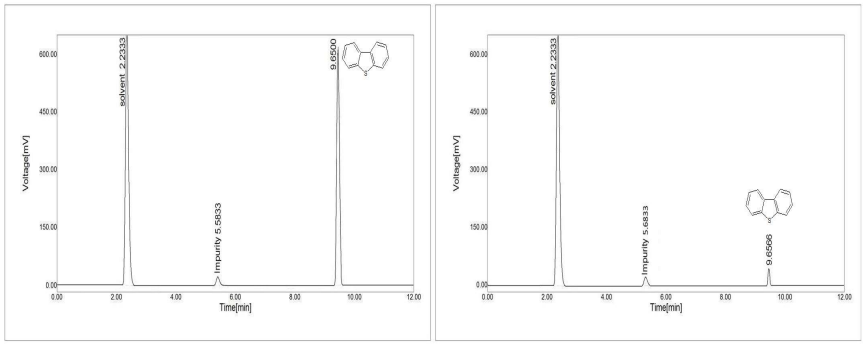


Fig.-5: FTIR Spectra of NPs

The presence of aldehyde was further verified with the existence of a band located at 1721 cm^{-1}. The presence of aromatic compounds in the synthesized particles was confirmed by observing C-O stretching, C-H bending, and C=C stretching vibrations at 1284 cm^{-1}, 1640 cm^{-1}, and 1557 cm^{-1}. The spectra of the Co-doped ZnONPs synthesized in the study were given in Fig.-5.

Photocatalytic Activity

The photocatalytic efficiency of the synthesized Co-doped ZnO nanoparticles was investigated using two organosulfur pollutants viz., dibenzothiophene and 2,5-dimethyl thiophene. The photocatalytic desulfurization experiment was performed in triplicates and using GC, the desulfurization progress at various time points was assessed by contrasting the sample's retention duration with a standard that had been generated in a lab. The gas chromatography analysis of the standard dibenzothiophene solution shows a clear separation of analytes with the solvent and the analyte was detected at a retention time of 2.2 min. The calibration curve obtained for the standard solution was for evaluating the analyte in the photocatalytic activity study. Every 5 min of the time interval, the sample was withdrawn from the reaction mixture and the % dibenzothiophene content and the % degradation was calculated. Figure-6 shows the GC chromatograms observed in the desulfurization of dibenzothiophene using the Co-doped ZnO nanoparticles. The chromatogram clearly shows the decrease in the peak area intensity of dibenzothiophene with the increase in the time of the study.



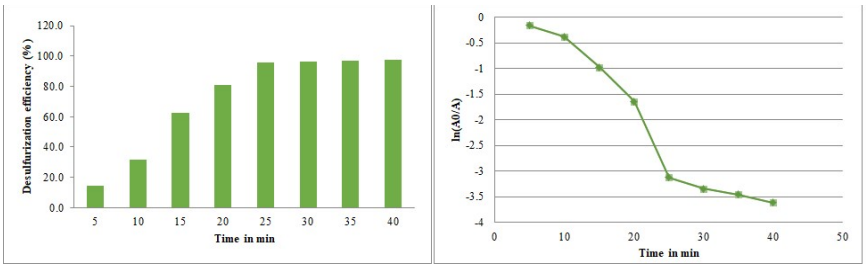
(A) (B)

(A) Desulfurization Chromatogram at Time 0 min, (B) Desulfurization Chromatogram at Time 30 min of Desulfurization Study

Fig.-6: GC Chromatograms Observed During the Desulfurization Study of Dibenzothiophene using Synthesized Co-Doped ZnO Nanoparticles

Based on the results it was proved that the desulfurization efficiency was calculated to be high at the initial time of study due to the vacant surface of the particles. The rapid desulfurization was noticed in the initial time of reaction and 62.25±0.066% of desulfurization was observed within 15 min of study. The desulfurization assay was seen to increase with a rise in study time and a % desulfurization of 80.66±0.201%, 95.61±0.279%, and 96.47±0.299% for 20, 25, and 30 min respectively. The desulfurization study results obtained from the study was shown in Fig.-7A. The desulfurization reaction rate and rate constant of the reaction were evaluated by adopting pseudo-first-order correlation i.e., $Kt = -\ln(Ct/C0)$, where K is the rate constant, C_0 and C_t are desulfurization strength at initial and at time t respectively. The plot of ln(Ct/C0) as a reaction time function for the desulfurization reaction of dibenzothiophene by synthesized nanoparticles shows a linear correlation (Fig.-7B). The rate constants were calculated as 0.1148 and hence it can be confirmed that the nanoparticles show the highest catalytic efficiency.

The synthesized Co-doped ZnO nanoparticles were also studied for their desulfurization efficiency of 22,5-dimethyl thiophene in the gas chromatography analysis, clear separation of 2,5-dimethyl thiophene from solvent was observed and 2,5-dimethyl thiophene was identified at a retention time of 7.9 min whereas the solvent was identified at 2.1 min. During the study, an increase in the time desulfurization time, the peak height, and the peak area response of 2,5-dimethyl thiophene decreased on increase in the time of the study. This confirms that the desulfurization of 2,5-dimethyl thiophene increased with increasing time and hence the peak area response was decreased.



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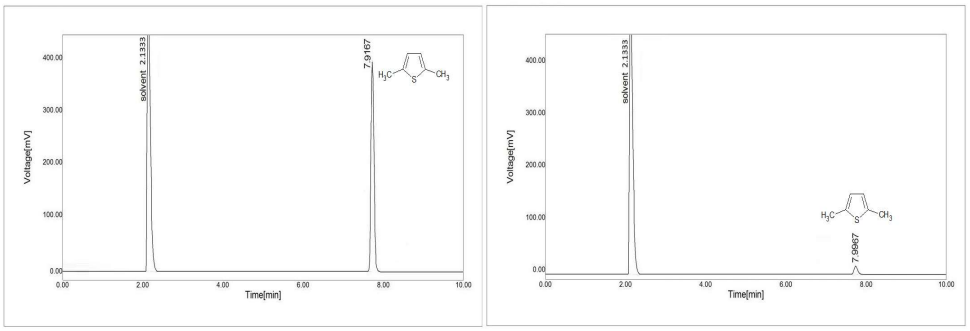
(A) Dibenzothiophene desulfurization efficiency of Co-doped ZnO; (B) ln(A0/A) graph obtained in the study

Fig.-7: Dibenzothiophene Desulfurization Efficiency Results of Co-doped ZnO Nanoparticles

The representative chromatogram observed at 0 min and 30 min of desulfurization study of 2,5-dimethyl thiophene were shown in Fig.-8. The desulfurization efficiency of nanoparticles was observed as 19.63±0.201 % within the time of 5 min of the study. The % desulfurization of 2,5-dimethyl thiophene was increased to 37.56±0.287, 63.75±0.135 and 81.59±0.228 % for 10 min, 15 min, 20 min, and 25 min of desulfurization study respectively. This confirms that a maximum of 81% desulfurization was completed within less time of 25 min., whereas in the studied high time of 40 min, the desulfurization was observed to be 97.33±0.301%. The desulfurization study results obtained from the study was shown in Fig.-9A. The pseudo-first-order correlation was utilized for the calculation of the constant rate and the rate constant was calculated as 0.1116 and linear relation was followed in the desulfurization study (Fig.-9B).



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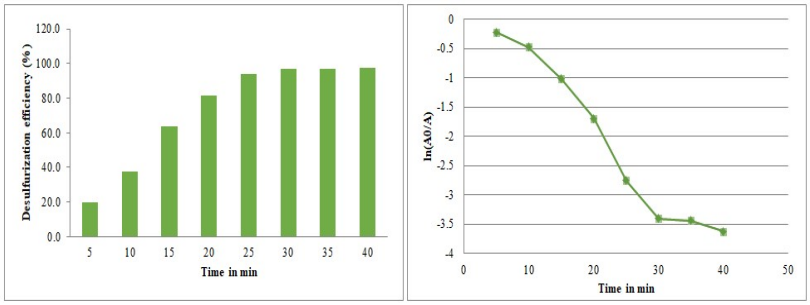
(A) Chromatogram at time 0 min of desulfurization study, (B) chromatogram at time 30 min of desulfurization study

Fig.-8: GC chromatograms Observed During the Desulfurization Study of 2,5-dimethyl thiophene Using Synthesized Nanoparticles



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(A) 2,5-dimethyl thiophene desulfurization efficiency of ZnO-CuO nanoparticles; (B) ln(A0/A) graph obtained in the study

Fig.-9: Desulfurization Efficiency Results of 2,5-dimethyl thiophene using Synthesized Co-doped ZnO Nanoparticles

The possible mechanism for the formation of nanoparticles and their desulfurization mechanism was shown in Fig.-10.

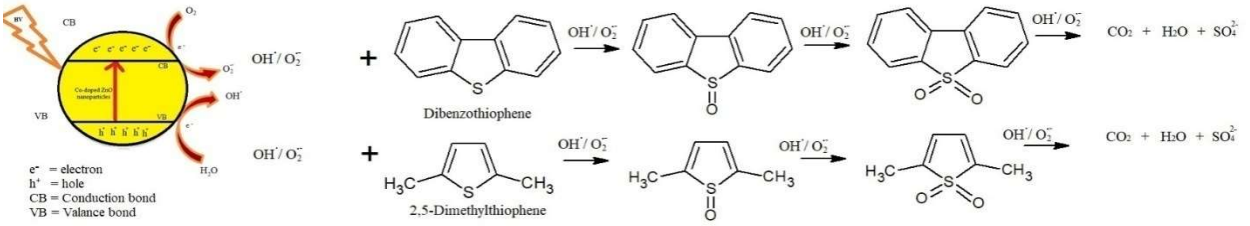

Fig.-10: Proposed Formation Mechanism and its Photo-Desulfurization Pathway of the Co-doped ZnO Nanoparticles Synthesized in the Study

The nanoparticles were evaluated for their reusability for their catalytic application and proved that more than 98 % results were achieved after the 5th cycle of reusability study for both the pollutants in the study. The results achieved in the reusability study confirmed that the nanoparticles were stable up to five cycles and hence can be reusable for their catalytic applications.

CONCLUSION

In conclusion, we have shown that the environmentally friendly synthesis of Co-doped ZnO nanoparticles with the accumulation of Cobalt ions onto Pistia plant tissue and coupled with Zinc Precursor is an innovative and efficient technique. The synthesized nanoparticles were stable with high purity with a circular shape having an average particle size of 8-34 nm with a hexagonal (wurtzite) structure crystalline structure. The synthesized Co-doped ZnO nanoparticles were investigated for desulfurization efficiency. The nanoparticles can effectively degrade dibenzothiophene and 2,5-dimethyl thiophene by desulfurization mechanism and the degradation is completed within very less time. The rapid desulfurization efficiency of the synthesized Co-doped ZnO nanoparticles proved as the best alternative source for the preparation of noble photocatalyst materials that can be used for the treatment of organosulfur compounds.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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