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GREEN SYNTHESIS, CHARACTERIZATIONSAND PHOTOCATALYTIC APPLICATIONS OFCERIUM DOPED NICKEL OXIDE NANOPARTICLES ASSISTED BYALTERNANTHERASESSILIS

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Abstract-Ceriumion doped Nickel oxide nanoparticles were successfully prepared using aqueous extract ofAlternantheraSessilis leaves. Ammonium ceric sulphateand NickelSulphatesolutions were used as precursors.The crystalline structure and optical properties of Ce ion doped NiO nanoparticles were characterized by UV, FTIR, SEM and TEM spectroscopy. The morphological studies (SEM and TEM) of the nanoparticles revealed triangle and rod like morphological structures. The energy dispersive analysis confirmed the presence of Ce ion in the doped NiO lattice. The morphology of the nanoparticle was studied with AFM Spectoscopy.The effects of initial concentration of p-nitrophenol and nanoparticle concentrations on the photocatalytic activity have been studied and the results demonstrated that the photodegradation follows pseudo-first-order kinetics. The observed maximum degradation efficiency ofp-nitrophenol is about58.5% for Ce ion doped NiO nanoparticles.
Keywords: NiO, nanoparticles, SEM, photodegradation.

1.INTRODUCTION

Nanoparticle having one or more dimensions of the order of 100nm or less- have attracted considerable attraction due to their unusual and fascinating properties, with various applications, over their bulk counterparts [1,2]. Currently, a large number of physical, chemical, biological, and hybrid methods are available to synthesize different types of nanoparticles [3-6].Though physical and chemical methods are more popular for nanoparticle synthesis, the use of toxic compounds limits their applications. The development of safe eco-friendly methods for biogenetic production is now of more interest due to simplicity of the procedures and versatility [7, 8]. Traditionally nanoparticles were produced only by physical and chemical methods. Some of the commonly used physical and chemical methods are ion sputtering, solvothermal synthesis, reduction and sol gel technique. Basically there are two approaches for nanoparticles synthesis namely the Bottom up approach and the Top down approach.Current research in biosynthesis of nanoparticles using plant extracts has opened a new era in fast and nontoxic methods for production of nanoparticles. Utilising plant extracts in the synthesis of nanoparticles has drawn more interest of researchers since it is single step biosynthesis. Plants are a superior option for synthesis of nanoparticle since natural capping agents are readily supplied by the plants .The production of gold and silver nanoparticles using *Geranium*extract [9], *Aloe vera* plant extracts [10], sundried *Cinnamomum camphora* and *Azadiracta indica* leaf extract has been explained [11-13].Oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites.A decrease in the average size of an oxide particle does in fact change the magnitude of the band gap [14] with strong influence in the conductivity and chemical reactivity [15].

Alternanthera sessilis is belonging to the Amaranthacea family. Alternanthera sessilis is commonly known as sessile joy weed a well known herb with fleshy leaves. The herb is mainly used as cholagogue, galactogue, intellect promoting, strength, diarrhea, constipation, leprosy, skin disease and dyspepsia(Surendra Kumar.M et al). Alternanthera sessilis which posseses anatomical studies, Phytochemistry ,Anti- Inflammatory Activity, antidiabetic activity, antioxidant and antimicrobial activities from medicinal plants (Alonso-Paz et al., 1995; Nascimento et al., 1990).

Here, we have used simple nontoxic, ecofriendly method for the synthesis of undoped and doped Nickel oxide nanoparticles from Nickel sulphate and ceric ammonium sulphate using the leaf extracts of Alternanthera sessilis (Amaranthaceae). The leaf extracts act as stabilizing and capping agents in the synthesis of Nickel oxide nanoparticles.

2. MATERIALS AND METHODS

2.1MATERIALS

2.1.1.CHEMICALS :

AR grade Nickel sulphate hexahydrate $[(NiSO_4)(H_2O)_6]$, Ammonium Ceric sulphate $[(NH_4)_4Ce(SO_4)_4]$ and p-nitrophenol were purchased from Himedia Chemicals and used without further purification. Double distilled water was used throughout the experiment.

2.1.2. PLANT MATERIALS :

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The leaves of Alternanthera Sessilis were procured from the market of Thoothukudi district, Tamilnadu. It was washed well with water, shade dried, powdered and sieved. The fine powder thus obtained was used for extract preparation.

2.2 PREPARATION OF LEAF EXTRACT :

About 10g each of the powder of the dried leaf of *Alternanthera Sessilis* was added to 100mL of double distilled water separately, heated for 20 min and filtered through Whattman No.41 filter paper. These extract was stored in a refrigerator for further synthesis.

2.3 SYNTHESIS OF UNDOPED NIO NANOPARTICLES AND CE ION DOPED NIO NANOPARTICLESS USING ALTERNANTHERA SESSILISLEAF EXTRACT USING ALTERNANTHERA SESSILISLEAF EXTRACT *:*

10 mL of 0.1M Nickel sulphate solution was made upto 100 mL.10 mL of 0.1M Nickel sulphate solution was taken and made upto 100 mL and stirred in a magnetic stirrer to obtain a homogenous solution .To these solutions 10mL of Alternanthera Sessilis leaf extract was added and stirred for about 30 min. The stirred solution was heated at 80^0C for 2 h till the supernatant liquid got evaporated.The black color residue thus obtained was collected in a previously cleaned, washed and dried silica crucible. It was heated to 600ºC for 2 h in a muffle furnace. The black colored Nickel oxide nanoparticles thus obtained was collected, preserved and used for further characterization and applications.Similar method as adopted for the synthesis of Ce ion doped NiO nanoparticless using ceric ammonium sulphate as precursor.

3.RESULT AND DISCUSSION

3.1UV-Vis analysis

The UV-Vis spectrum of undoped NiO nanoparticles synthesized using leaf Alternanthera Sessilis extract was shown in (Fig.1). An absorption band is observed at 331nm which is effectively blue shifted compared to the wavelength of bulk NiO which appeared at 362 nm .The absorption wavelengths are seen to be slightly shifted towards lower wavelength. This blue shift is attributed to the smaller size of nanoparticles. This indicates the formation of smaller particles.

Fig.2 shows the UV-Vis absorption spectra of Ce ion doped NiO nanoparticles synthesized using Alternanthera Sessilis leaf extract. Here the absorption band is observed at 254 nm. The blue shift in this case is more compared to the undoped NiO nanoparticles, which in turn is considerably blue-shifted when compared to the bulk phase NiO.

The blue shifted absorption peak is attributed to the quantum size effect .The blue shift of the absorption peak of undoped and doped nanoparticles result from certain unique effects of nanomaterial, such as nanoscale effect yang, zhu et al [16].

3.2.FTIRSTUDIES

Fig.3 shows the FTIR spectrum of Ce ion doped NiO nanoparticles synthesized using aqueous leaf extract of Alternanthera Sessilis. The broad peak located at 3386.73cm^{-1} can be assigned to the O–H stretching vibrations, indicating the presence of hydroxyl groups[17]. The peak at 1636.57cm^{-1} corresponds to H-O-H stretching vibration of water molecule [18].The peak at 1384.13cm^{-1} can be attributed to the carbonyl group C=O and the band at 1150.43cm^{-1} is due to –C–H– stretching vibration.The band at 1100.38cm^{-1} can be attributed to the C–O stretching[17]. The peak located at 984.51 cm^{-1}corresponds to C–N stretching vibrations of the amine. The peaks observed at 745.72 cm^{-1} and 631.46 cm^{-1} indicating the formation of stretching mode of Ce ion doped NiO nanoparticles**.**The peaks corresponding to Ni-O bonds are shifted towards lower wavenumber for Ce ion doped NiO nanoparticles, indicating the incorporation of Ce ions in the NiO lattice.The band obtained at 612.92 cm^{-1} was assigned to Ni-O-H stretching vibration present into the Alternanthera Sessilis leaf extract[19].The band at 593.73 cm^{-1} was produced by CeO_2,which is assigned to the Ce–O stretching [20].

3.3SEM ANALYSIS:

Fig.4. shows the SEM image of Ce ion doped nickel oxide nanoparticles synthesized using Alternanthera Sessilisleaf extract and it exhibited distinct pyramidal structure. This exhibited moderately crystalline like structure.

3.4.TEM

The TEM monograph (Fig.5.) clearly shows the distribution of rod shaped Ce ion doped NiO nanoparticles synthesized using aqueous leaf extract of Alternanthera Sessilis.The size of Ce ion doped nickel oxide nanoparticles synthesized using aqueous leaf extracts of Alternanthera Sessilis was found to be 45.77 nm.

3.5. PHOTOCATALYTIC STUDIES

The UV visible absorbance values of pure p-nitrophenol solution shows maximum wavelength at 318 nm as shown in the Fig.6. The spectra reveal that there was no formation of new intermediates or products. The characteristic absorption peak at 318 nm was used to track the photocatalytic degradation process. The absorption of the above peak decreased in intensitywith increasing irradiation time. The rapid disappearance of the 318 nm absorption band suggests that the chromophore structure responsible for the characteristic yellow colour is breaking down. Thus, the opening of benzene ring caused speedy decolourization [21].

It can be clearly noticed from the recorded values that there is no significant changes of the concentration of p-nitrophenol after 3 h irradiation, which indicated that p-nitrophenol solution cannot be easily degraded by UV light as shown in Fig.7.

Fig.8 and Fig.9. shows the change in the absorbance spectra and the fluorescence quenching efficiency of p-nitrophenol in the presence of the undoped and Ce ion doped NiO nanoparticles synthesized using Alternanthera Sessilis leaf extract as photocatalyst. The yellow colour almost disappeared after UV irradiation for 60 min.From the absorbance spectra, it was observed that the maximum degradation efficiency of the p-nitrophenol solution within 60 min irradiation time was about 28.5% for undoped NiOnanoparticles and 58.5% for Ce ion doped nanoparticles. The results showed that Ce ion deposited on the surface of NiO increases efficiency of degradation. Thus, Ce ion doped NiO nanoparticles possess much higher photocatalytic activity than undoped NiO nanoparticles.

Fig.10.compares the photocatalytic degradation efficiency of p-nitrophenol using undoped and Ce ion doped NiO naoparticles as photocatalysts. The Ce ion doped nickel oxide nanoparticles degrade the dye solution more effectively than the undoped nanoparticles. The Ce ion doped nanoparticles degrade the p-nitrophenol solution more efficiently from the beginning than the undoped nanoparticles, thus leading to the decoloration of p-nitrophenol solution.

4.CONCLUSION

The blue shifted UV-Vis absorption peak at 331 nm confirmed the nano-size of the synthesized NiO nanoparticles synthesized using Alternanthera Sessilis. The FT-IR studies showed an absorption peak at 984 cm^{-1} (Ni-O linkage) which indicated the formation of nickel oxide nanoparticles. XRD behaviour exhibits the size of doped and undoped NiO nanoparticles. The surface morphology of the undoped NiO, Ce ion doped NiO and Cu ion doped NiO nanoparticles is characterized by SEM analysis and suggested different morphological structures. TEM micrographs also confirmed the particle size of the doped samples are in the nanoscale range and the size of the doped samples was found to be in the range of 30 nm to 45 nm. Photocatalytic degradation was also investigated with Sudan blue dye and Alizarin red dye under UV-irradiation source. NiO nanoparticles showed significant photocatalytic degradative ability with and without dye. The degradation efficiency of undoped NiO nanoparticles was higher than the Ce ion doped NiO nanoparticles for Sudan blue organic dye. The Ce:NiO nanoparticles nanoparticles exhibited enhanced photocatalytic activity and can be efficiently used as photocatalysts in the process of removal of organic dyes and thus it can be used for environmental cleaning and water purification.

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College,Thoothukudi-8.

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FIGURES

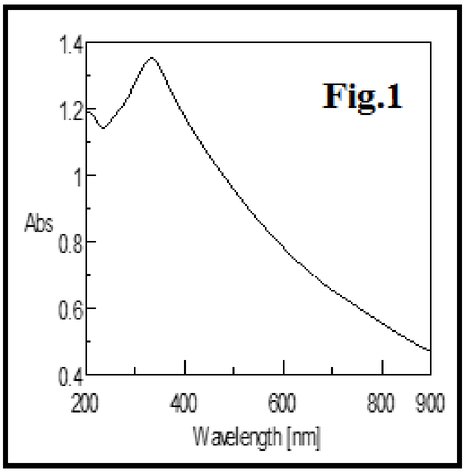


Fig.1
Abs
1.4
1.2
1
0.8
0.6
0.4
200
400
600
800
900
Wavelength [nm]

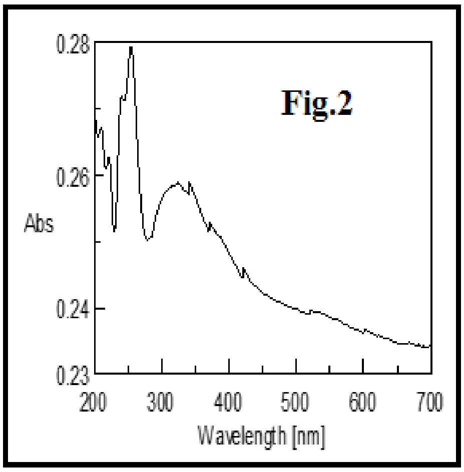
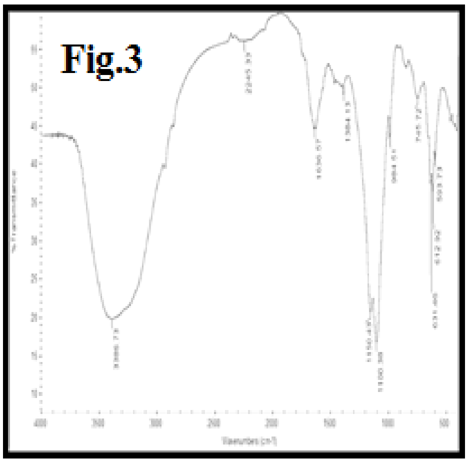


Fig.2
Abs
0.28
0.26
0.24
0.23
200
300
400
500
600
700
Wavelength [nm]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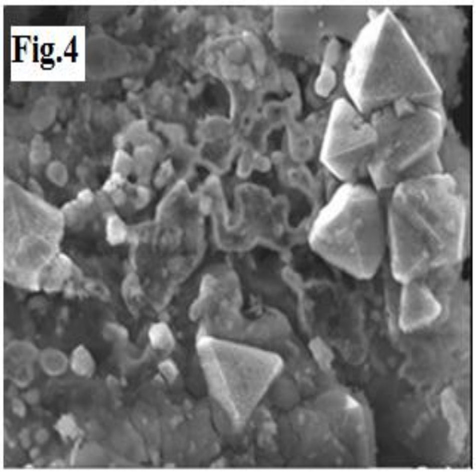


Fig.4

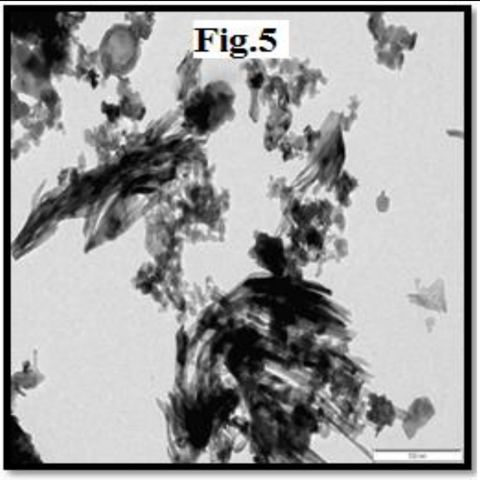


Fig.5

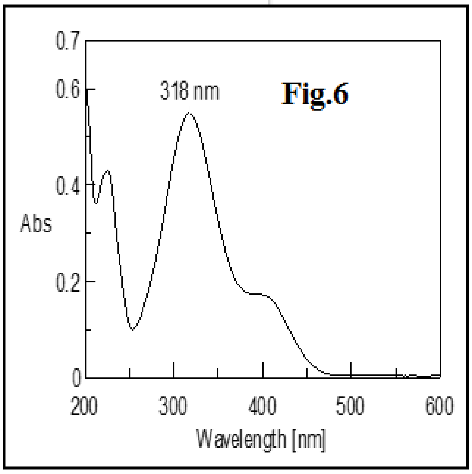


Fig.6
318 nm
Abs
0.7
0.6
0.4
0.2
0
200
300
400
500
600
Wavelength [nm]

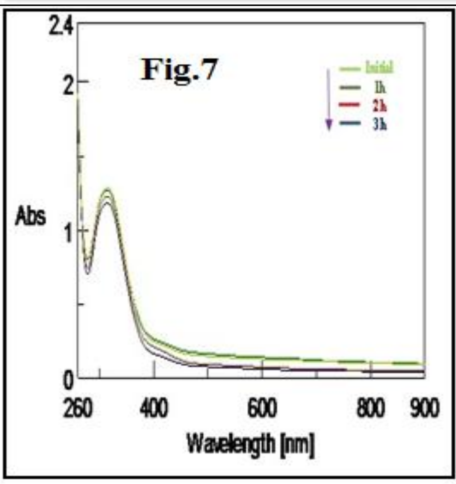


Fig.7
Initial
1h
2h
3h
Abs
2.4
2
1
0
260
400
600
800
900
Wavelength [nm]

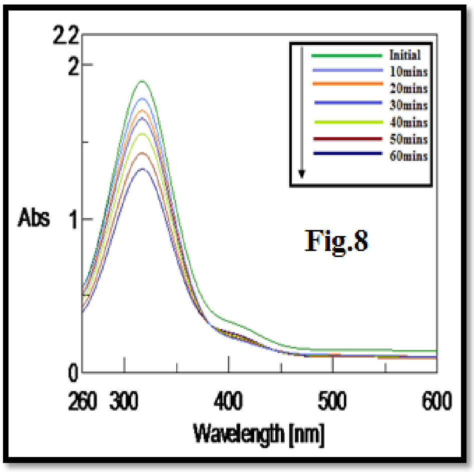
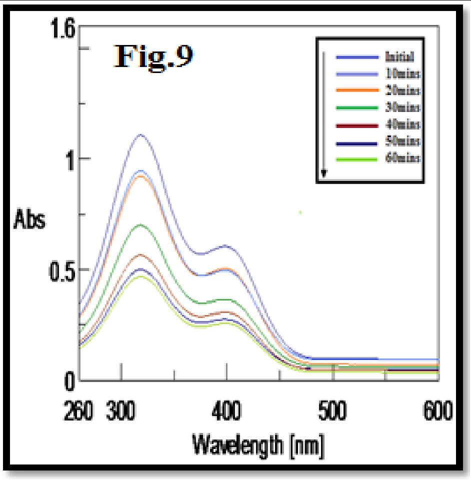


Fig.8
Initial
10mins
20mins
30mins
40mins
50mins
60mins
Abs
2.2
2
1
0
260
300
400
500
600
Wavelength [nm]



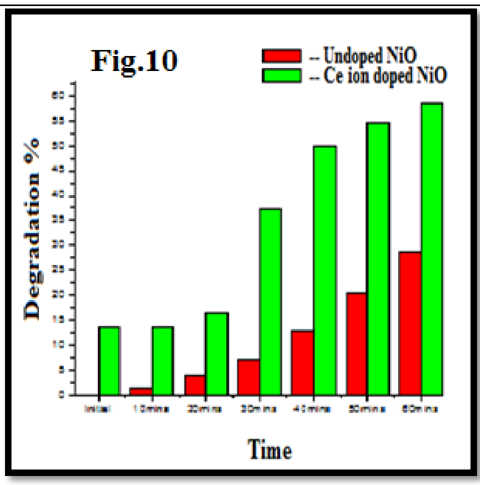


FIGURE CAPTIONS

Fig.1.UV-Vis absorption spectra of undoped NiO nanoparticlessynthesized using Alternanthera Sessilisleaf extract

Fig.2.UV-Vis absorption spectra of Ce ion dopedNiO nanoparticles synthesized using Alternanthera Sessilisleaf extract.

Fig.3.FTIR spectrum of Ce ion doped NiO nanoparticles synthesizedusing Alternanthera Sessilis leaf extract

Fig.4.SEM image of Ce ion doped NiO nanoparticles synthesized using Alternanthera Sessilisleaf extract

Fig.5.TEM image of Ce ion doped NiO nanoparticles synthesized using Alternanthera Sessilis leaf extract

Fig.6.UV-Visible absorption spectra of p-nitrophenol

Fig.7.UV-Visible absorption spectra of p-nitrophenol upon exposure to sunlight for 3h.

Fig.8.UV-Visible absorption spectra of p-nitrophenol in the presence of undoped NiOnanoparticles synthesized using Alternanthera Sessilis leafextract

Fig.9.UV-Visible absorption spectra of p-nitrophenol in the presence of Ce ion doped NiO nanoparticles synthesized using Alternanthera Sessilis leafextractFig.10.Degradation efficiency of p-nitrophenol in the presence of Undoped and Ce ion doped NiO nanoparticles synthesized using Alternanthera Sessilis leafextract