

Green synthesis, characterization, antimicrobial studies of NiO nanoparticles and enhanced photocatalytic degradation of organic pollutant

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Abstract

Nanoparticles differ significantly from their bulk counterparts in terms of their characteristics, and they have a wide range of scientific uses. The use of green nanoparticles have received considerable attention. Recent advances in green nanomaterial production have made it possible to utilize these materials in catalysis. Many techniques have been applied to treat the textile wastewater. In the current study, Alizarin Red S dye is photocatalytically degraded utilizing green synthesized NiO nanoparticles derived from green tea extract. Utilizing techniques such as FT-IR, UV-Visible spectroscopy, EDAX, SEM, and XRD, the synthesized nanoparticles were examined. The morphology of the nanoparticle was studied using the SEM images. The XRD analysis was used to find the size of the crystal. The formula developed by Debye Scherer was used to determine the crystallite size. Using EDAX, the existence of Ni was verified. FT-IR analysis was used to find the functional groups present in the nanoparticle. According to morphological research, the nanoparticles are flake-shaped and have a larger surface area. Systematically the impact of many parameters on dye degradation, including catalyst dosage, dye concentration, and pH was examined. The findings showed that NiO can be used as a good nanocatalyst to degrade organic dyes. The kinetics of photo degradation were studied. Antibacterial and antifungal activities carried out on the synthesized nanoparticle and the precursor green tea shows that they have good activity over bacteria and fungi. The right selection of operating conditions allows to degrade the pollutant effectively.

Keywords: *dye degradation, organic dyes, SEM, Alizarin Red S, NiO nanoparticle*

INTRODUCTION

Nanoscience and nanotechnology is an emerging interdisciplinary field of research. Nanomaterial studies is progressive at present in scientific knowledge as well as in commercial applications [1÷4]. Nanomaterials have potential applications such as supercapacitors, sensors, solar cells, photocatalysis and electrochromic devices [5÷8]. Metal oxide nanoparticles have been produced physically and chemically for a long time. However biological reduction of the metals using plant extracts have been known since early 1900s [9].

Recently green synthesis of nanoparticles like gold, silver, copper etc. and their application is one of the important areas of research. Metal oxide nanomaterial exhibits significant chemical, mechanical, electronic, thermal, magnetic, catalytic properties & optical properties in comparison with their bulk concentrates and have extensively attracted applications [10]. These metal oxide nanoparticles exhibit advanced properties due to their increased surface area. In chemical technologies, ecofriendly, environmentally benign green synthesis of nanoparticles have greater advantages than the conventional method. This method of synthesis is simple, cost effective, stable, and highly reproducible and they can be easily scaled up for the larger synthesis. Plant based nanomaterials have numerous benefits over traditional chemical processes and they have wide range of application in

biology and medicine. Metal oxide Nanomaterial extensively attracted application in many fields due to their significant chemical, electronic, thermal, magnetic, catalytic optical properties in comparison with their bulk concentrates [11÷15]. NiO nanoparticles have applications in the manufacture of magnetic materials, p-type transparent conducting films, sensors, fuel cells [16÷22].

Due to the prosperity of the modern industries, especially textile dying, a huge amount of wastewater with different kinds of effluents are discharged resulting in pollution of water. Organic dye pollutants are the main effluents that cause serious hazards and they destroy the ecological balance. This leaves a negative impact on human beings, plants and animals. Nano metal oxides can degrade these dyes. In the present study, we synthesized NiO NPs (NPs- nanoparticles) using organic Tulsi green tea extract. They were characterized using various analytical techniques like FT-IR, UV-Visible spectroscopy, EDAX, SEM, and XRD. These synthesized nanoparticles were used to degrade Alizarin Red S dye under various conditions and degradation percentage were calculated. Biological studies like antibacterial activity and antifungal activities were also carried out.

MATERIALS AND METHODS

The photo degradation studies were carried out using double distilled water. Organic Tulsi green tea was purchased from market. The precursor NiSO₄, used for the synthesis of nanoparticle was of analytical grade and was procured from Sigma Aldrich Company. Alizarin red S dye (CAS No. 130-22-3) was procured from Merck.

Preparation of Green Tea extract

5 grams of the green tea was boiled with 100 mL of double distilled water in a 250 mL beaker for about 15 minutes and afterwards cooled to room temperature. The solution was filtered and the filtrate was stored for further use.

Synthesis of metal oxide nanoparticles

Preparation of NiO-NPs

Nickel oxide nanoparticles were synthesized using a modified protocol from the previous studies [7]. 0.01M solution of nickel sulphate solution was added to the Organic Tulsi green tea extract in 1:1 volume ratio. NiO-NPs were formed immediately by the reduction process. The mixture was stirred magnetically for 30 minutes and allowed to stand for about an hour at room temperature to get a colloidal suspension of the nanoparticles. The mixture was then centrifuged and washed with water several times and dried in an air oven at 100°C for about 2 hours. The dried nanoparticle was calcined at 400°C in a muffle furnace and stored in air tight container for further use.

Characterization of the synthesized NiO photocatalyst

The synthesized photocatalyst was characterized by UV-Visible spectroscopy, FT-IR, EDAX, SEM, XRD. UV absorption measurements were carried out using Systronics 2203 UV Visible Double Beam Spectrophotometer. FT-IR analysis were carried out using Shimatzu FR-IR spectrophotometer having the range of 400 - 4000cm⁻¹. For the X ray Diffraction analysis, the synthesized powdered sample of the NiO photocatalyst was used by a Cu K α- X-ray diffractometer (Model-D 5000 with consuming wavelength λ= 1.54 nm) for confirming the presence of NiO and analyze its structure. The crystallite size was calculated using Debye Scherer formula

$$D_{hkl} = k\lambda/\beta\cos\theta \quad (1)$$

where, λ is the wavelength (λ=1.542Å) (Cu Kα), β is the full width at half maximum (FWHM) of the line θ is the diffraction angle.

SEM analysis was carried out using TESCAN VEGA 3SBH with BRUCKER EASY EDS scanning electron microscope. The instrumental Parameter, accelerating voltage, SEM magnification & working distance are indicated on image. Emission spectral analysis was carried out using JASCO-FP-8200 spectrophotometer. The characterization studies were carried out to understand the structural, morphological, elemental composition, crystallite size, functional groups. The dye

degradation studies were carried out and they were analyzed using UV- visible spectroscopic Techniques. Sonication was done in presence of sunlight and the temperature was 31°C. The luminescence level was recorded using a luxmeter. The intensity of sunlight varied between 950 and 1000Wm⁻². The degradation studies were carried out in presence of induced light using 200W bulb. Studies were carried out by varying the pH of the dye solution between 2 to 10.

Kinetics of the photo-degradation can be studied by plotting of graph between $\ln C_0/C_t$ vs. irradiation time. A straight-line behavior is observed in all case. The rate constant for the photocatalytic degradation are obtained from the pseudo-first order rate equation

$$\ln C_0/C_t = Kt \quad (2)$$

where C_0 and C are the concentrations of the dye solution at time 0 and time t in minutes. K is the first order rate constant (min^{-1}) determined from the slope of the straight line.

The efficiency of degradation was determined using the formula

$$\text{Degradation efficiency \%} = \left(\frac{C_0 - C}{C_0} \right) \times 100 \quad (3)$$

where C_0 represents the absorbance before degradation and C refers to the absorbance of the dye after degradation.

RESULT AND DISCUSSION

Photo physical measurements

Figure 1 shows the colour change confirming the formation of nanoparticle. The precursors NiSO₄ solution has an absorption maximum at 395 nm and that of the green tea extract has an absorption at 355 nm. The NiO nanoparticle shows a maximum absorbance at 378 nm. The gradual colour change shows the formation of the nanoparticle. The nanoparticle shows an emission maximum at 708 nm.

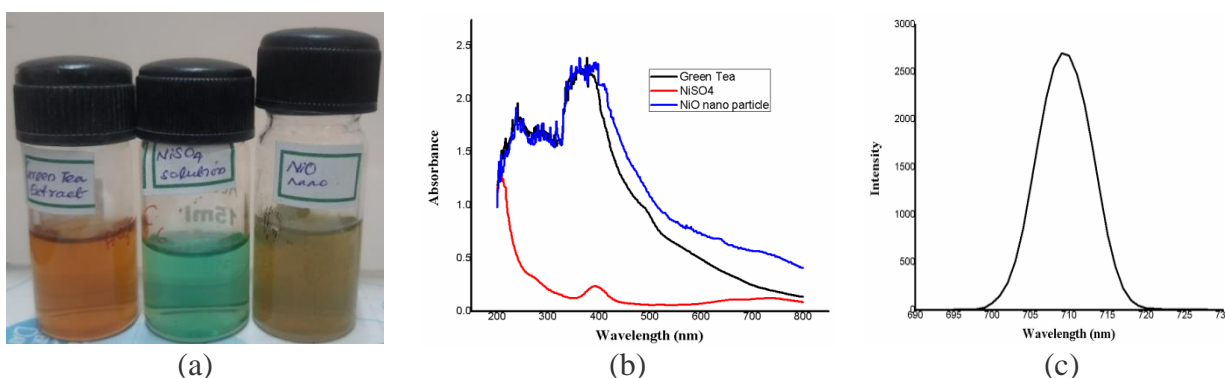


Fig.1. (a) Visible interpretation of colour change; (b) absorption spectrum of NiO nanoparticle with the precursors; (c) emission spectrum of NiO nanoparticle

SEM and EDAX analysis

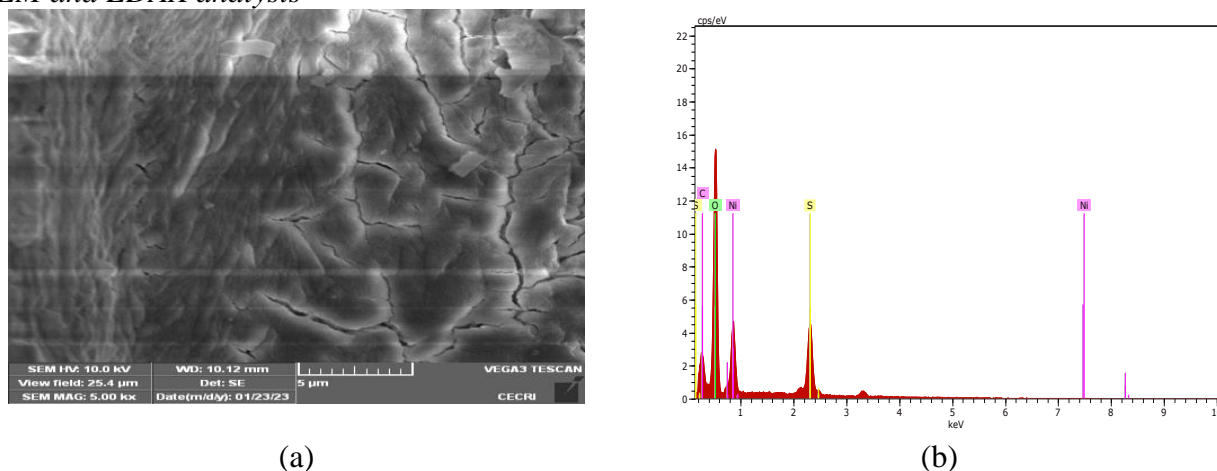


Fig. 2. (a) SEM image of NiO nanoparticle (NP); (b) EDAX spectrum of NiO-NPs

The SEM image of the nanoparticle was shown in Figure 2(a). Using the SEM image, the morphology of the nanoparticle was determined. The particles had the flattened shape like that of flakes. These particles have very high surface areas. This study shows that the average size was about 29.75 nm. The EDAX spectrum shown in Figure 2(b), confirms the presence of Ni and O. The main components of the photocatalyst are Oxygen and Nickel. This is seen from their high weight percentage as shown in table 1.

Table 1. Chemical composition of NiO nanoparticle based on EDAX

Element	Atomic Number	Series name	[weight, %]	[atomic, %]
O	8	K-series	35.89	58.55
Ni	28	L-series	13.88	6.17
C	6	K-series	12.80	27.81
S	16	K-series	9.18	7.47
Total			71.75	100

XRD Analysis

X ray diffraction pattern obtained for the NiO-NPs synthesized using green tea extract is shown in Figure 3. There exist strong diffraction peaks at 2θ values of 30.059, 34.538, 45.695, 53.379, 53.568. They correspond to the planes (204), (303), (306), (330) and (406). The crystallite size was found to be 29.75 nm (JCPDS card no 04-0835) which confirms the nanoscale nature of the formed product.

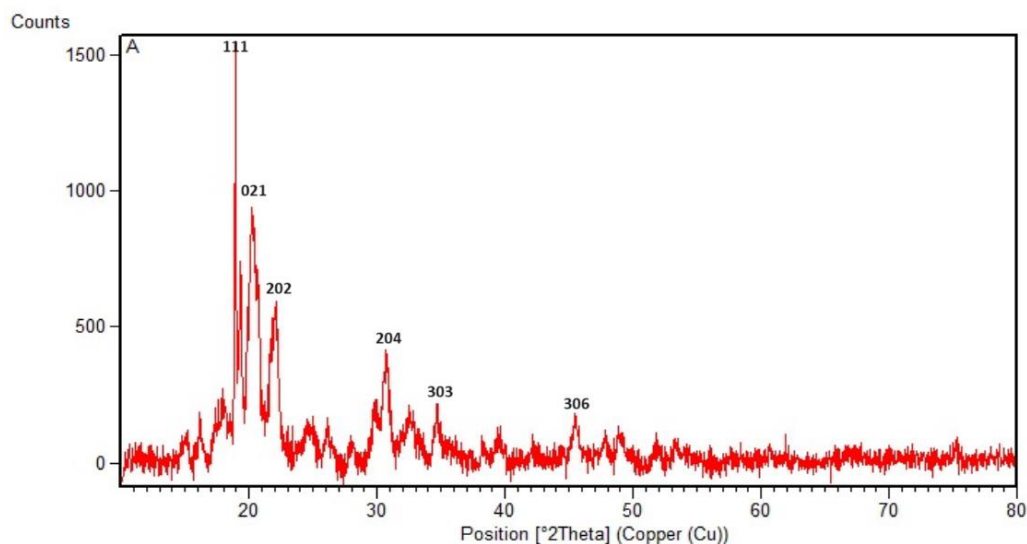


Fig. 3. XRD pattern of the synthesized NiO nanoparticles.

FT-IR analysis

FT-IR analysis of the photocatalyst (Figure 4) shows the stretching vibrations at 3388.83 cm^{-1} , 2900 cm^{-1} , 1606 cm^{-1} , 606 cm^{-1} within the region of $400\text{--}40000\text{ cm}^{-1}$. These peaks confirm the formation of NiO-NPs. The peak at 3388.83 cm^{-1} corresponds to the O-H bond stretching. This shows the aqueous phase as well as the reduction of NiSO_4 . The peak at 1606 cm^{-1} represent the C-O precursor. The strong peak at 606 cm^{-1} denotes the Ni-O-H stretching bond. 2900 cm^{-1} shows the C-H stretching mode.

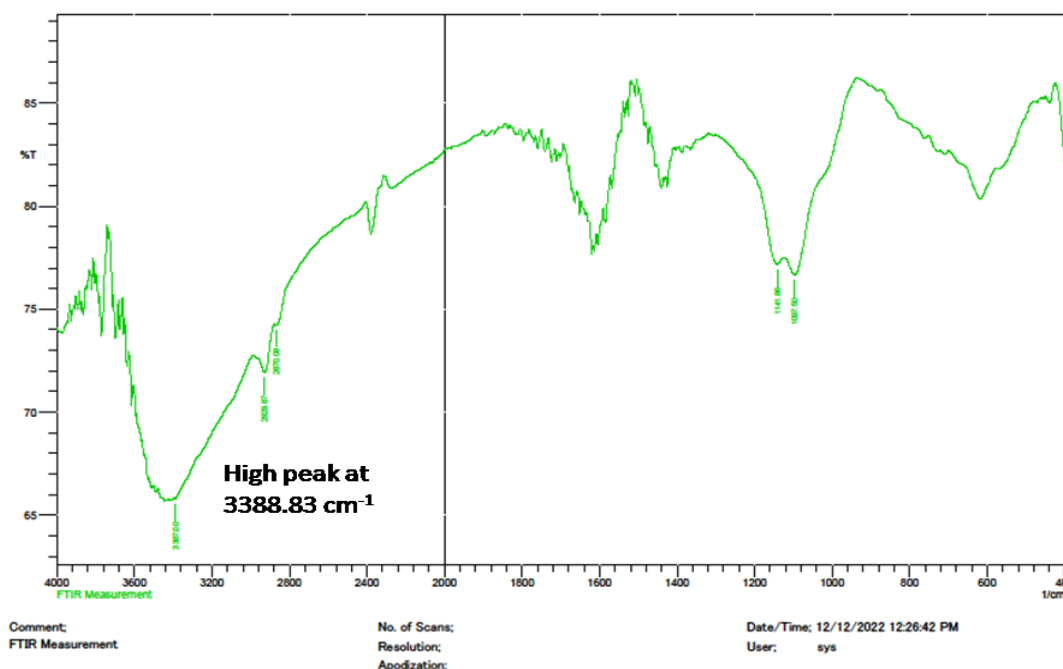


Fig. 4. FT-IR spectra of NiO nanoparticle synthesized from green tea extract

Degradation of Alizarin Red S dye in presence of NiO nanoparticle

Alizarin Red S is a water soluble dye with molecular formula $C_{14}H_7NaO_7S$. The dye has an absorption maximum of 545 nm and is displayed in Figure 5(a). The effect of the irradiation time on the photo-decolorization of the dye is shown in Figure 5(b). The rate of degradation increases with time.

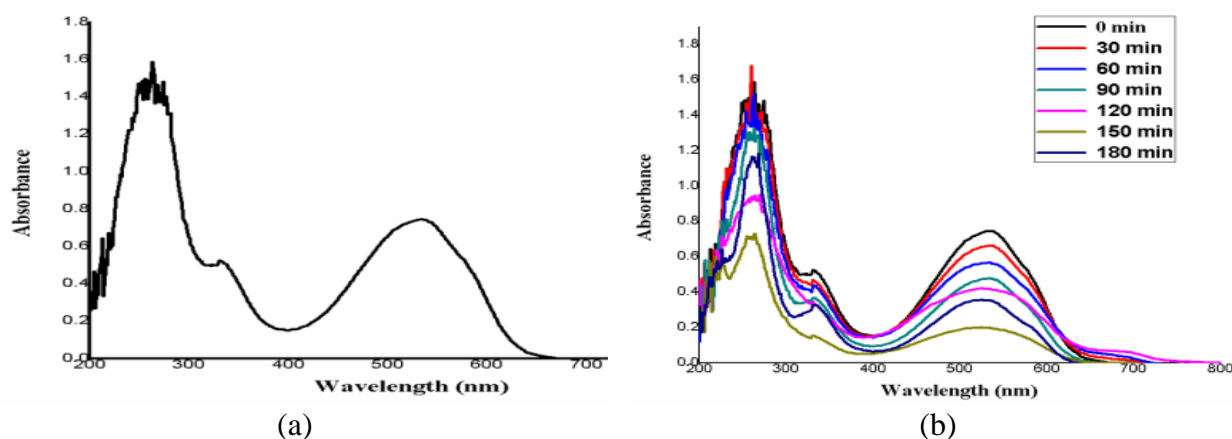


Fig. 5. Absorption spectrum of (a) Alizarin Red S dye (b) Degradation of Alizarin Red S dye in presence of NiO nanoparticle with time

Effect of pH

The dye solution concentration was fixed as 0.001M. 0.01g of the photocatalyst was used for the analysis. The pH of the solution also affects the photo degradation efficiency and it is shown in Figure 6. The surface charge of nanoparticle is altered when there is a change in solution pH. As a result the adsorption of dye on the catalyst surface is altered which imparts a change in the degradation rate. Maximum degradation occurs at pH 4. The degradation rate decreases, as there is an increase in pH. This may be due to the repulsion of the dye molecule and the nanoparticle.

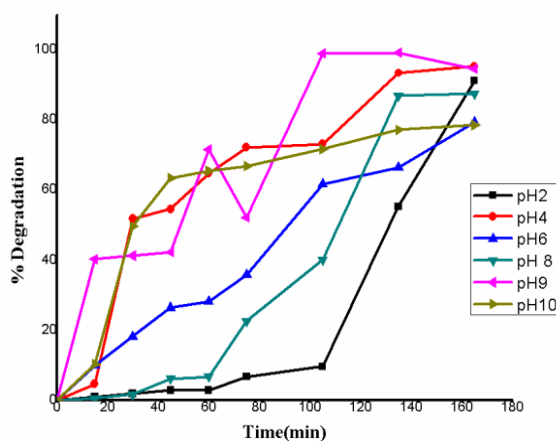


Fig. 6. Degradation of Alizarin Red S in presence of NiO photocatalyst at various pH

Kinetics of photocatalytic degradation of Alizarin Red S

The photo degradation of Alizarin Red S at room temperature is shown in Figure.7. The concentration of the dye solution was 0.001M. To 100 mL of the dye solution 0.01g of the NiO nanoparticle was added for the degradation studies. The regression coefficient R^2 of the experimental values was found to be 0.99. The K value is 0.00532. This confirms that the degradation of the dye molecules obeys the pseudo first order linear kinetics.

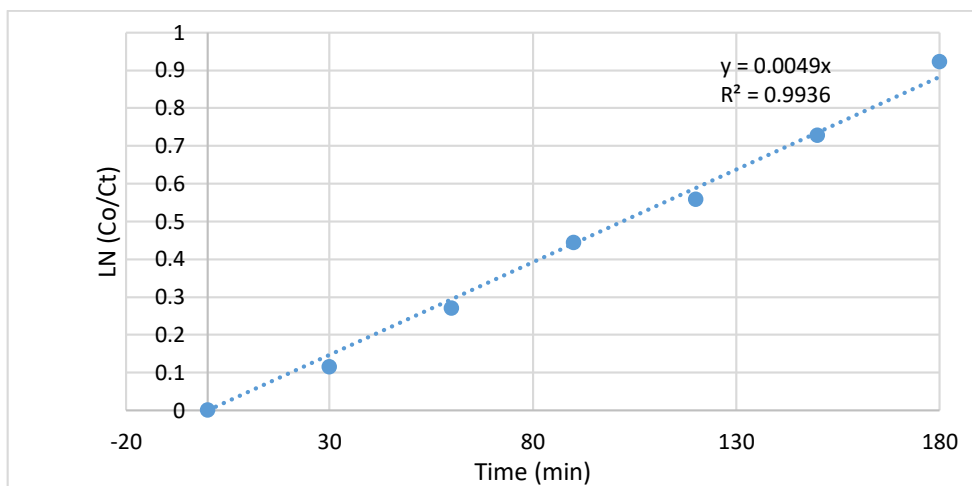


Fig. 7. Kinetics plot for the photo degradation of Alizarin Red S dye

The degradation efficiency is calculated and the same is displayed in Figure 8. The dye shows a maximum degradation efficiency of 72.86 % in 180 minutes in presence of sunlight.

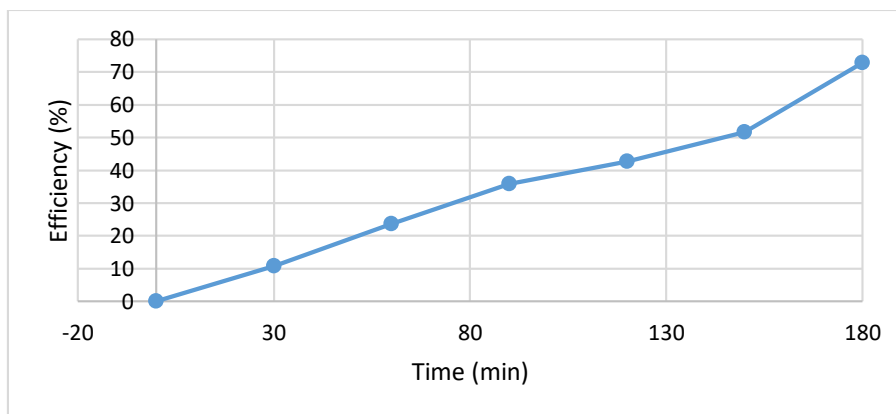


Fig. 8. Degradation efficiency of Alizarin Red S dye in presence of NiO photocatalyst under sunlight

Antibacterial Activity

The antibacterial activity of NiO nanoparticles were carried out using agar - well diffusion method. 25 mL of nutrient agar was poured into a sterile petri plate. The plates were allowed to solidify 100 μ L of pathogenic bacteria *Bacillus cereus* and *Escherichia coli* and they were transferred into the dish and made culture lawn by using a sterile L rod spreader. After five minutes of setting of the pathogenic microbes, a sterile cork borer was used to make a 5 mm well on the agar. The test samples were loaded into the wells. The solvent saline loaded well served as the negative control and ampicillin (30 μ g/mL) served as the positive control. The plates were incubated at 37°C for 24 hours. The petri plates showed the diameter of the zones. The antibacterial activity was determined by measuring the diameter of the zone of inhibition around the well (Table 2).

Table 2. Antibacterial activity of the metal oxide nanoparticles

Sample	Zone of inhibition (mm)		
	Gram-positive bacteria (<i>Bacillus cereus</i>)	Gram-negative bacteria (<i>Escherichia coli</i>)	Ampicillin (Control)
NiO	5	4	16
Green tea extract	7	5	19

All the strains used for the work were provided by Biomeltez Research and Development Pvt. Ltd., Tamilnadu. From the table 2, it is seen that the NiO nanoparticles show a zone of inhibition of 5 mm for gram positive bacteria *Bacillus cereus* and 4 mm zone of inhibition for *Escherichia coli*, a gram negative bacteria (Figures 9 and 10). The precursor Green tea extract itself shows a good zone of inhibition compared to the synthesized NiO nanoparticle. Ampicillin tablet was used as a control. The results show that NiO nanoparticle shows a good antibacterial activity against both *Bacillus cereus* and *Escherichia coli*.

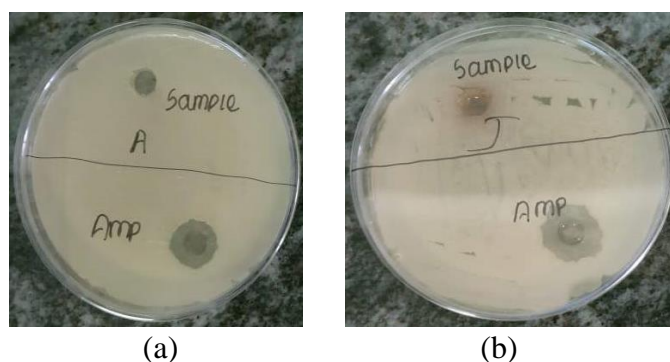


Fig. 9. Antibacterial activity: (a) Nickel oxide nanoparticles; (b) Green Tea extract against *Bacillus cereus* (Gram positive bacteria)

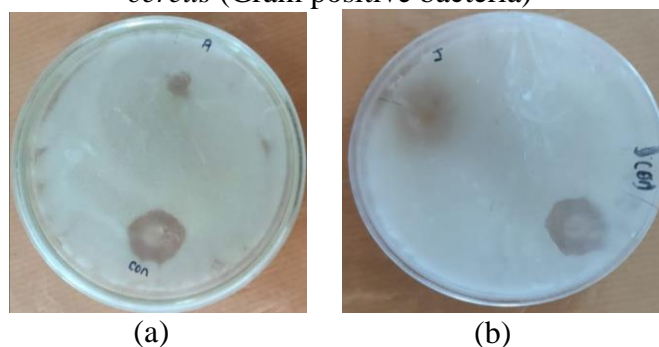


Fig. 10. Antibacterial activity: (a) Nickel oxide nanoparticles; (b) Green Tea extract against *Escherichia coli* (Gram negative bacteria)

Antifungal Activity

The antifungal activity was tested by the well diffusion assay. The potato dextrose agar medium was poured into a sterile petri dish. The plates were allowed to dry. Then, 100 μ L of fungi were transferred into the plate. After, five minutes, a sterile cork borer was used to make a 5mm well on the agar. The samples were loaded into the well and fluconazole (30 μ g/mL) served as the positive control. The plates were incubated at 37°C for 24 to 48 hours. The antifungal activity was determined by measuring the diameter of the zone of inhibition around the well (Figure 11).

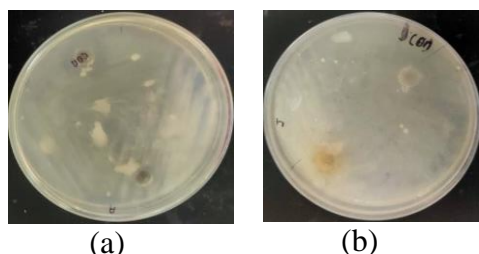


Fig. 11. Antifungal activity: (a) Nickel oxide nanoparticles; (b) Green Tea extract against fluconazole

Table 3. Antifungal activity of the metal oxide nanoparticles and green tea extract against fluconazole

Sample	Zone of inhibition (mm)	
	Test solution (30 μ g/mL)	Fluconazole (Control)
NiO	9	25
Green tea extract	12	24

Antifungal activity was examined using well diffusion method. Fluconazole was used as a control. *Fusarium oxysporum* was the fungi used for examination. NiO nanoparticle shows good antifungal activity. The precursor green tea shows good antifungal activity (Table 3). They have a larger zone of inhibition against the fungal stain. The bioactivities of the synthesized nanoparticles show that they can be used effectively in pharmaceutical fields.

CONCLUSION

NiO nanoparticles were successfully synthesized using green tea extract and NiSO₄ as precursor. The synthesized nanoparticles were characterized by XRD, SEM, FT-IR & EDAX Analysis. The SEM result shows that the nanoparticles have the shape of flakes and the EDAX confirm the presence of Nickel and oxygen. The dye degrades efficiently in presence of NiO nanoparticles.

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