



GREEN SYNTHESIS OF NICKEL OXIDE NANOPARTICLES BY ELECTROCHEMICAL REDUCTION METHOD USING *SYGIZIUM CUMINI* LEAVES EXTRACT

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ABSTRACT:

In materials science, “green” synthesis has gained extensive attention as a reliable, sustainable, and eco-friendly protocol for synthesizing a wide range of nanomaterials including metal/metal oxides nanomaterials, hybrid materials, and bioinspired materials. As such, green synthesis is regarded as an important tool to reduce the destructive effects associated with the traditional methods of synthesis for nanoparticles commonly utilized in laboratory and industry. Nanoparticles are key components in the advancement of future energy technologies, thus, strategies for preparing nanoparticles enlarge volume by techniques that are cost-effective are required. Nickel oxide nanoparticles were synthesized by electrochemical reduction method using *Syngizium cumini* leaves extract as structure directing agent in an organic medium viz. The reduction process takes place over a period of 2 hrs. Such nanoparticles are prepared using simple electrolysis cell in which the sacrificial anode as a commercially available nickel metal sheet and platinum (inert) sheet act as a cathode. The parameters such as current density, solvent polarity and distance between electrodes are used to control the size of nanoparticles. The synthesized nickel oxide nanoparticles were characterized by using FT-IR, XRD, SEM, EDX, FE-TEM, SAED, etc.

Keywords: Electrochemical cell, Syngizium cumini leaves extract, nickel oxide nanoparticles, FE-SEM etc.

Introduction:

Green synthesis approach of nanoparticles is based on 12 green chemistry principles which include the development and design of nanoparticles using nontoxic chemicals, renewable material, environmentally benign solvents, and finally degradable waste product [1]. Three important steps in the preparation of nanoparticles from a green chemistry perception comprise of harmless solvent medium, nontoxic reducing agent, and environmentally benign stabilization agents [2]. Another significant factor is the selection of the capping agent

used to passivate the nanoparticles surface. The capping agent also shows a significant effect on the size ranges, morphologies, and targeted applications. Sustainability is at stake and continuation of the quality of life is under threat [3]. Nanoparticles exhibit novel properties that significantly differ from those of corresponding bulk solid state owing to the different effects in terms of small size effect, surface effect, quantum size effect, and macroscopic quantum tunnel effect [4,5]. Over the past decade there has been an increased emphasis on the topic of “green” chemistry and chemical processes. [6-10].

In the present work, we present green approach toward the synthesis and stabilization of metal nanoparticles. Size, shape, and surface morphology play pivotal roles in controlling the physical, chemical, optical, and electronic properties of these nanoscopic materials. Preparation of nanoparticles generally involves the reduction of metal ions in solutions or in high temperature gaseous environments. Metal and semiconductor nanoparticles are of importance due to their potential applications in emerging areas of nanoscience and technology [11-19]. Nickel nanoparticles synthesized from the aqueous extract of *Syngizium cumini* leaves in hot condition, have been reported in literature [20]. The nanomaterials having unique properties are used in various applications, such as photocatalysis, lithium-ion batteries, smart windows, field emission studies, antimicrobial activity, thermal conductivity, and anti-ferromagnetic films [21-24]. Because of the peculiar physiochemical properties, the nanoparticles change the properties of the materials like its thermal, optical, electrical, and mechanical properties [25]. The methods like electrochemical, co-precipitation, microemulsion, sol-gel method, electrospray synthesis, laser ablation and hydrothermal reaction are used for the synthesis of nanomaterials [26-27].

In recent research, nickel oxide nanoparticles have drawn a greater interest, because of its unique properties. It belongs to a wide band gap (3.6–4.0 eV) p-type semiconductor and is chemically stable with high electro-optical efficiency. Nickel oxide nanoparticles are widely applied in numerous fields as adsorbents, solar and fuel cells, catalytic agents, gas sensors, magnetic and antibacterial materials [28,29]. Since particle size, morphology and high crystallinity influence the physiochemical properties, it is of great importance to synthesize NiO nanoparticles with small particle size, preferably less than 50 nm, which could enhance the efficiency of their applications [30]. In the present study, synthesis of NiONPs in room temperature condition has been reported, reducing the nickel ions present on the nickel foil by the aqueous extract of *Syngizium cumini leaves* extract. In the past few decades, bionanotechnology is gaining momentum, as the scheme includes non-hazardous, environmental friendly biological systems like bacteria, fungi, leafs, vitamins and yeast for the synthesis of metal oxide nanoparticles [31]. Hence in the present work, NiO nanoparticles are prepared by a novel, simple, efficient, environment friendly and green route using *Syngizium cumini* extract, which plays the role of reducing and capping agent. It is also reported that using leaf extract, it is possible to control the shape and size of the particles. Being biotemplates, it also hinders agglomeration of nanoparticles [32].

Experimental:

Materials:

Syngizium cumini leaves were collected in fresh condition during the season of maturity June-July locally from University campus of Dr. Babasaheb Ambedkar Marathwada University Aurangabad, Maharashtra, India. The sacrificial anode in the form of nickel sheet and platinum sheet as inert cathode having thickness 0.25 mm and purity 99.99% were purchased from Alfa Aesar.

Preparation of *Syngizium cumini* leaves extract:

Syngizium cumini leaf extract was prepared by taking 5 g of the leaves and properly washed in deionized water. They were then cut into fine pieces and taken in a 250 ml Erlenmeyer flask with 100 ml of sterile distilled water. The mixture was boiled for 15 min and finally filtering it. The extract thus obtained was stored at normal temperature and used within a week. It has been reported that medicinally valuable angiosperms have the greatest potential for synthesis of metallic nanoparticles with respect to quality and quantity [33-35].

Phytochemical study of *Syzygium cumini* leaves extract:

Syzygium cumini commonly known as jambhul, black plum or Java plum is found throughout the India and is one of the most popular fruits. It is planted, and in many regions spontaneous. It is also a native of, Myanmar, Sri Lanka, Thailand, Australia, Colombia, Cuba, Mexico, Nepal, Kenya, United States of America, Zambia, and Zimbabwe. *Syzygium cumini* (L.) is belonging to the family Myrtaceae. Large trees cultivated throughout India for the edible fruits (Black Plum) and are reported to contain vitamin C, gallic acid, tannins, anthocyanins, includes cyanidin, petunidin, malvidin glucoside and other components.



Fig 1: Images of *syzygium cumini* (jambhul) leaves.

Leaves have been used in traditional medicine as a remedy for diabetes mellitus in many countries [36, 37]. The leaves are also used to strengthen the teeth and gums, to treat leucorrhoea, stomachalgia, fever, gastropathy, strangury, dermatopathy [38, 39]. It was observed that *S. cumini* leaves contained significant bioactive compounds that make the plant a potential antioxidant, anti-diabetic, anti-microbial, and among other therapeutic properties[40].

Synthesis of nickel nanoparticles:

Electrochemical reduction method was developed by Reetz in the 1990 [41,42]. The process makes the use of an inexpensive two electrode set up for 25-40 ml electrolyte solution. Including both oxidation of bulk metal and reduction of metal ions for size selective preparation of *Syzygium cumini* plant extract stabilized metal nanoparticles. In the initial experiment we have used a nickel metal sheet (1x1 cm) as anode and a platinum sheet (1x1 cm) as the cathode. These two electrodes were placed parallel to one another and were separated by 1cm. The electrolysis process was then carried out by applying current of 8 mA/cm² for 2 hrs. The agglomerated solid sample was separated from the solution by decantation and washed three to four times with double distilled water. The washed samples were then dried under vacuum condition in desiccators, calcinated at 500°C and stored for further characterization FT-IR, UV visible, XRD, SEM-EDS, FE-TEM etc. During the synthesis the bulk metal anode is oxidized and converted into metal cations. These cations migrate to the cathode and reduction takes place with the formation of metal in zero oxidation state.

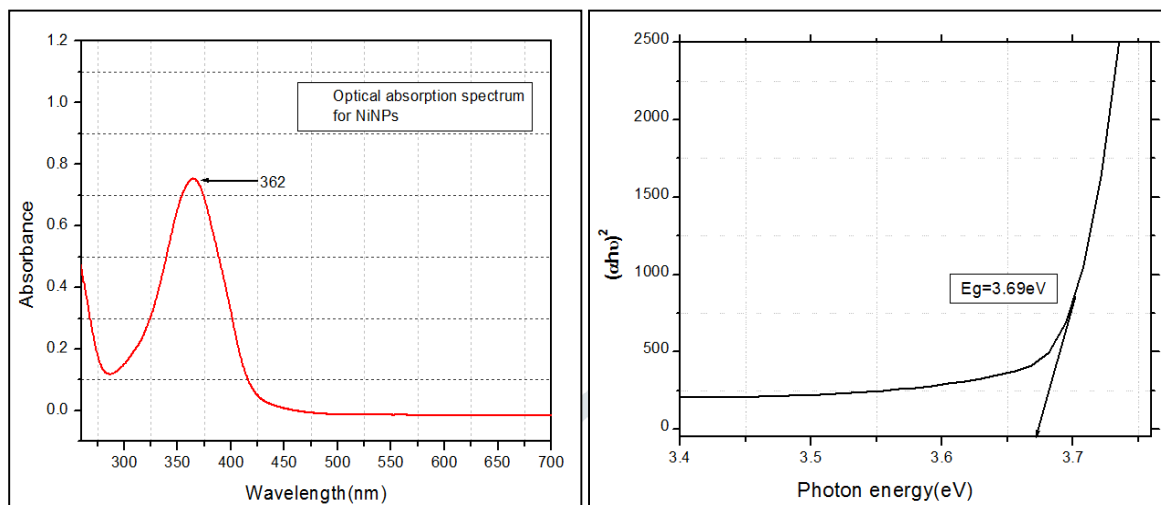
RESULTS AND DISCUSSION:**1] OPTICAL ABSORPTION SPECTRA:**

Fig 2: Optical Absorbtion spectra of NiO NPs and Tauc plot of NiO NPs.

2] FOURIER TRANSFORM INFRA-RED STUDIES (FTIR):

Fig.2. shows the FTIR spectra of NiO nanoparticles, which showed several significant absorption peaks. The broad absorption band in the region of $600\text{--}700\text{ cm}^{-1}$ is assigned to Ni–O stretching vibration mode; the broadness of the absorption band indicates that the NiO powders are nanocrystals. The size of samples used in this study was much less than the bulks form NiO, so that NiO nanoparticles had its IR peak of Ni–O stretching vibration. A strong band at 494.24 cm^{-1} is assigned to the Ni–O stretching band which is consistent with that reported elsewhere confirm the formation of NiO nanoparticles. Due to their quantum size effect, the FTIR absorption of NiO nanoparticles is compared to that of the bulk form. Besides the Ni–O vibration, it could be seen from Fig.2 that the broad absorption band centered at 3369.26 cm^{-1} attributable to the band O–H stretching vibrations.

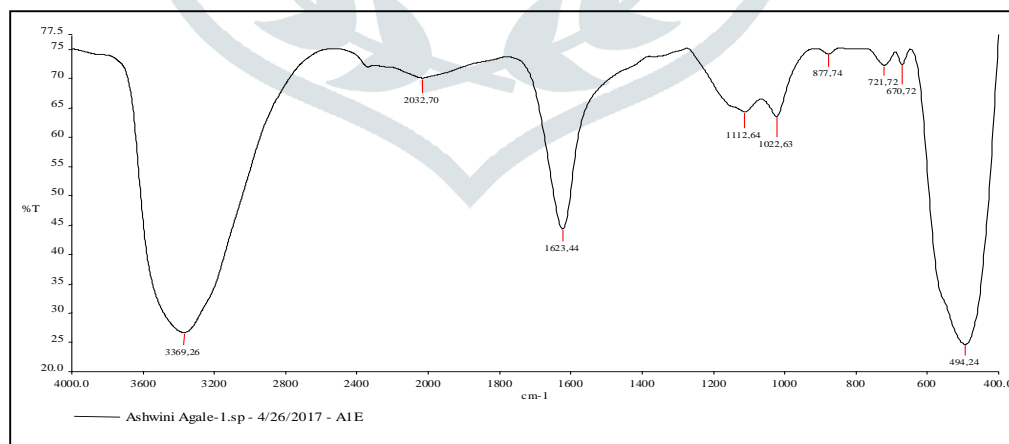


Fig: 2: FTIR spectrum of nickel Nps recorded between 400 cm^{-1} to 4000 cm^{-1}

The weak band near $1623,44\text{ cm}^{-1}$ is assigned to H–O–H bending vibrations mode were also presented due to the adsorption of water in air when FTIR sample disks were prepared in an open air. These observations provided the evidence to the effect of hydration in the structure. Meanwhile, it implied the presence of hydroxyl in the precursor, and the broad absorption around 721 cm^{-1} is assigned to the band C=O stretching vibrations. The serrated absorption bands in the region of $1000\text{--}1500\text{ cm}^{-1}$ are assigned to the O=C=O symmetric and asymmetric stretching vibrations. Due to adsorption of CO band at $1112,64\text{ cm}^{-1}$ symmetric stretching vibration,

but the intensity of the band has weakened, which indicated that the ultrafine powers tend to strong physically absorption to H₂O and CO₂.

3] STRUCTURAL INVESTIGATIONS OF NIO NANOPARTICLES:

X-ray diffraction (XRD) pattern of the prepared compound reveals the crystalline nature, phase purity and structure details. Figure 3(a) shows the powder XRD pattern recorded for as prepared nickel oxide. Five diffraction peaks (111), (200), (220), (311) and (222) were observed, not only their peak position but their intensity also Matches the standard pattern of FCC type NiO with (Joint Committee on Powder Diffraction Standards (JCPDS) file no. 04-0835) [43]. The powder X-ray diffraction (XRD) is performed using Philips Holland, XRD system PW 1710 with nickel filtered CuK α ($\lambda = 1.5405 \text{ \AA}$) radiation. The average crystallite size (t) has been calculated from the line broadening using the Scherrer's relation:

$$T = \frac{0.94\lambda}{\beta \cos \theta}$$

Where K is a constant (~ 1), β is full width at half maximum (FWHM) and θ is Bragg's angle.

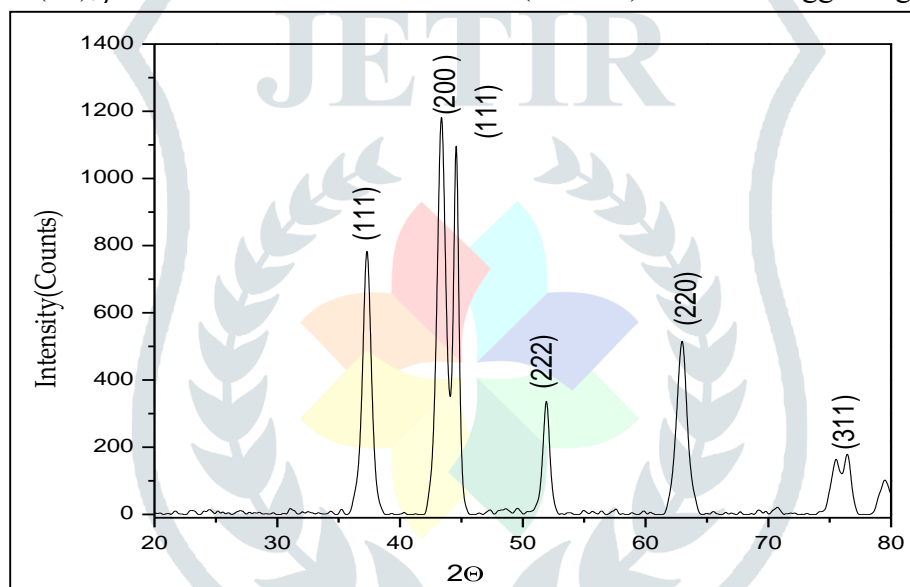


Fig 3: Shows X-ray diffraction pattern of prepared nickel nanoparticles.

The 2θ values for the planes (111), (200), (220), (311) and (222) are found to be 38.21° , 44.5° , 62.16° , 76.42° and 80.10° respectively. The XRD pattern shows cubic/Fcc structure. No distinct diffraction peak other than those from FCC-Ni is found in the sample. The lattice constant is $a = 3.4392 \text{ \AA}$ and unit cell volume is $V = 40.6757 \text{ \AA}^3$, matched with JCPDS file no. 04-850 as shown in figure 3 (a). Maximum intensity peak (111) was used to estimate the crystallite size and it is found to be 14-20 nm using Scherrer equation.

4] SCANNING ELECTRON MICROSCOPY:

Scanning electron microscopy (SEM) imaging technique was utilized to acquire information about the particle morphology on the nanoscale. Fig.3 a: shows magnification images of NiO. The shape of the Ni particles is rod shape. The formations of particle aggregates are observed due to strong interaction among of nickel oxide nanoparticles.

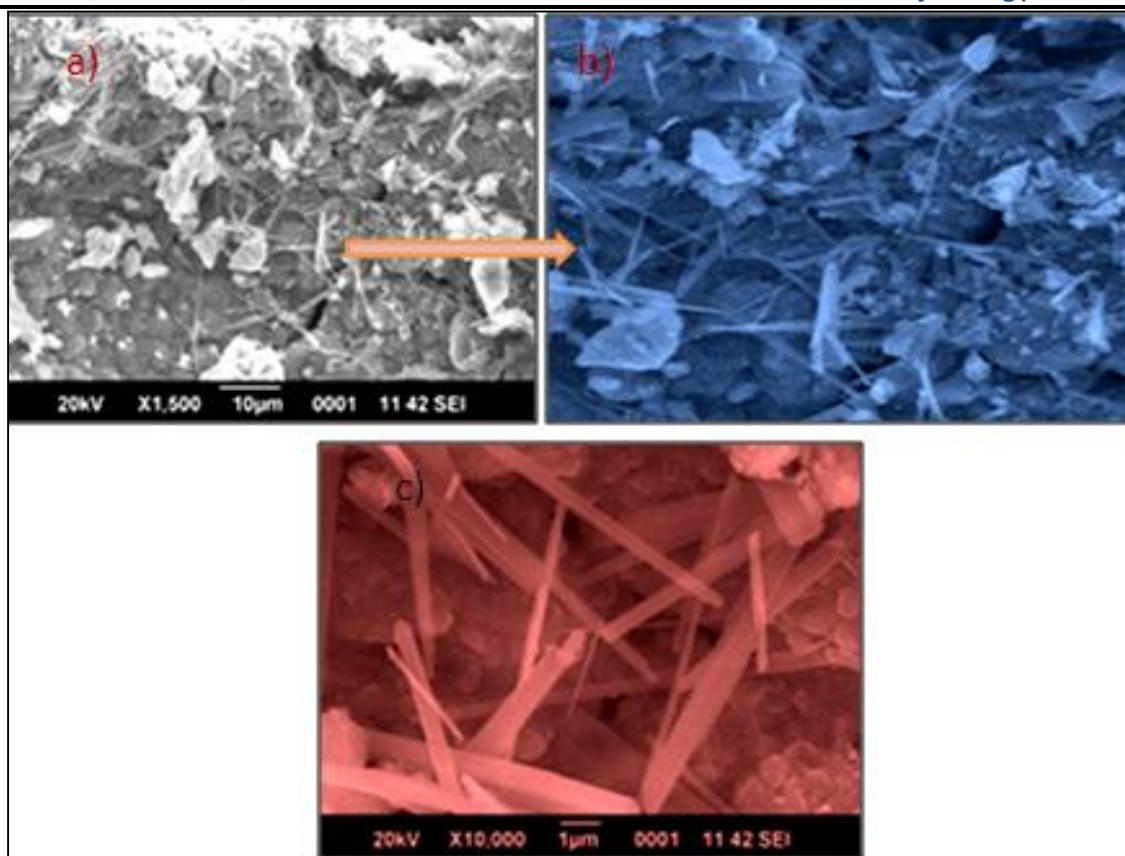


Fig 4: Shows SEM image of nickel nanoparticles with current density $8\text{mA}/\text{cm}^2$

5] FE-TEM:

The TEM images depicted in Fig 5 a-b are direct morphological observations of Ni NPs micrographs indicate that most particles were fine with various sizes, spherical, cubic and some clusters have also been observed. The average particles size was measured to be 20-50 nm for $8\text{mA}/\text{cm}^2$, which was in good agreement with calculated particles size by XRD analysis. The TEM image suggests the presence of (111) plane of FCC nickel and selected area electron diffraction pattern (SAED) shows a ring pattern corresponding to all planes of the FCC nickel. SAED pattern shows the areas for the electron diffraction pattern of the resultant nanoparticles. We observed five main fringe patterns.

Fig.5.c FEG-TEM image depicted that Ni-NPs rod shape and electron diffraction was also collected to determine phases of nickel nanoparticles. The electron diffraction pattern of the selected area of nanoparticles is shown in fig.4.e which verifies the formation of FCC nickel oxide for which five ring patterns with plane (111), (200), (220), (311) and (222) of NiO were identified. Fig.5.d lattice fringe image of Ni-NPs, Fig.5.f. shows histogram of NiO-NPs calculated from TEM images.

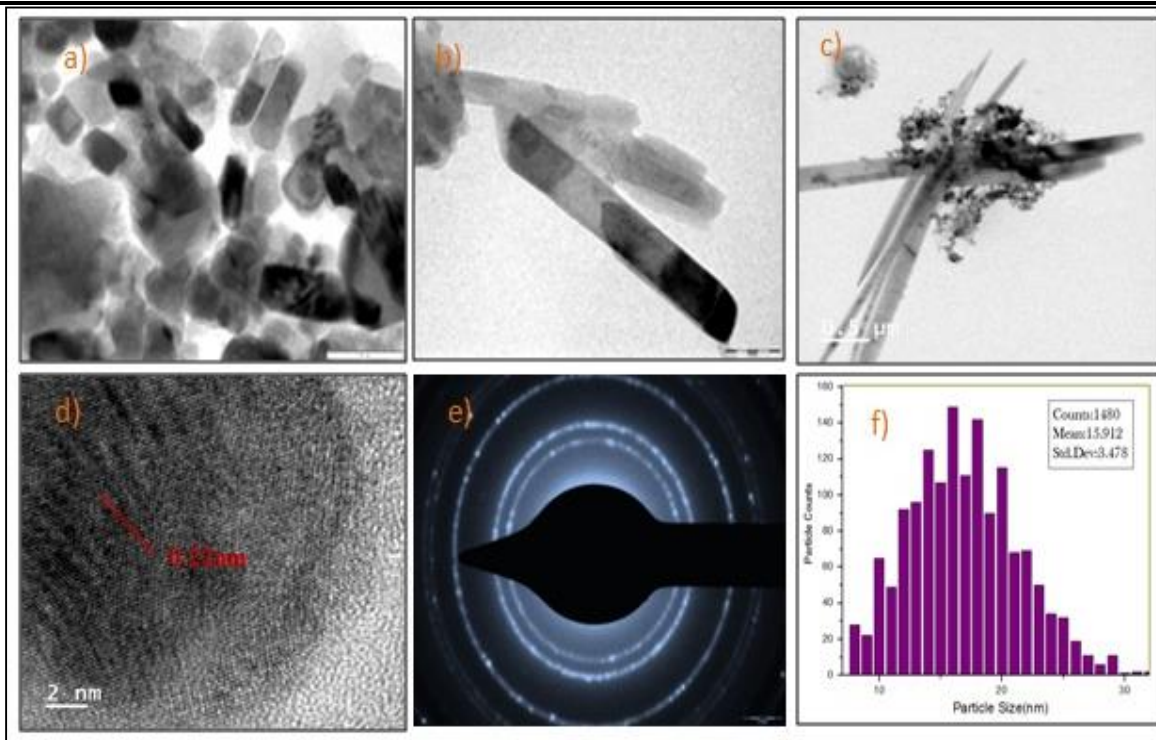


Fig 5: Shows TEM image of Ni-NPs at (a) images shows rod shape b) TEM image shows size of Ni-NPs c) FEG-TEM image of Ni-NPs d) Lattice fringe image of Ni-NPs e) SAED depicts five ring pattern f) Histogram of Ni-NPs.

4] ENERGY DISPERSIVE SPECTROSCOPY:

Energy-dispersive X-ray study confirmed the presence of nickel with energy bands centered on 7.5 and 8.3 keV (K lines) and at 0.8 keV (L lines). In detected is not a component of the capping agent attributed to partial oxidation of the nanoparticles during the handling of the sample due to atmospheric oxygen. Sodium, oxygen, carbon, silica contains observed in plant leaves.

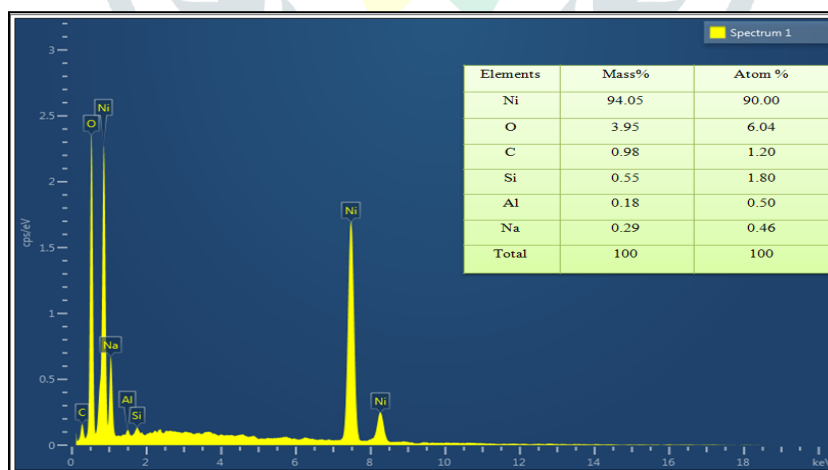


Fig 5: EDX spectrum of NiO nanoparticles

CONCLUSION:

We have demonstrated the synthesis of NiO nanoparticles by electrochemical reduction method. The synthesized nanoparticles were characterized by FT-IR, XRD, SEM-EDS and antibacterial activity. The FTIR spectroscopic study of the NiO nanoparticles confirmed the removal of the capping agent after calcinating the sample at 500°C. The XRD analysis showed the formation of NiO nanoparticles with face centered cubic (FCC) structure. The average particle size obtained from the XRD pattern was found 10-14nm at 8mA/cm² current density. The SEM analysis of NiO nanoparticles revealed the presence of rod shape nanoparticles that were

agglomerated irregularly. Energy Dispersive X-ray Spectroscopy analysis showed the formation of NiO nanoparticles. Composition of these particles also shows good yield.

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