# B. TECH. PROJECT REPORT

On

# Synthesis of Nickel Oxide for its Application in Dye Degradation

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DISCIPLINE OF METALLURGY ENGINEERING AND MATERIAL SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE December 2019

# Synthesis of Nickel Oxide for its Application in Dye Degradation

### A PROJECT REPORT

Submitted in partial fulfilment of the requirements for the award of the degrees

of BACHELOR OF TECHNOLOGY

in METALLURGY ENGINEERING AND MATERIAL SCIENCE

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*Guided by:* **Dr. Rupesh Devan, Associate Professor** 



INDIAN INSTITUTE OF TECHNOLOGY INDORE December 2019

### **CANDIDATE'S DECLARATION**

We hereby declare that the project entitled "Synthesis of Nickel Oxide for its Application in Dye Degradation" submitted in partial fulfilment for the award of the degree of Bachelor of Technology in 'Metallurgy Engineering and Material Science' completed under the supervision of Dr. Rupesh Devan, Associate Professor, Discipline of Metallurgy Engineering and Material Science, IIT Indore is an authentic work.

Further, I declare that I have not submitted this work for the award of any other degree elsewhere.

Signature and name of the student with date

(Ramteke Mrunmay Sunil)

### **CERTIFICATE by BTP Guide**

It is certified that the above statement made by the students is correct to the best of my/our knowledge.

Signature of BTP Guide with dates and their designation

(Dr. Rupesh Devan, Associate Professor)

### **Preface**

This report on "Synthesis of Nickel Oxide for its Application in Dye Degradation" is prepared under the guidance of Dr. Rupesh Devan.

Nowadays, clean consumable water has become a luxury as many people around the world do not have access to it due to the rising consumption of water. Many methods have been researched to treat wastewater, for these methods must be economically feasible, geographically suitable etc. Through this report, we have tried to determine the degradation ability of nickel oxide nanobelts to degrade dyes such as rhodamine B, crystal violet, methylene blue and methyl orange. The nanobelts were synthesised by hydrothermal method followed by characterization techniques such as XRD, FESEM, EDS and UV-Vis spectroscopy.

Ramteke Mrunmay Sunil B.Tech. IV Year Discipline of Metallurgy Engineering and Material Science IIT Indore

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### **Ramteke Mrunmay Sunil**

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### **Abstract**

Nickel Oxide Nanobelts was synthesised by facile hydrothermal method. Using precursor (NiSO<sub>4</sub>.6H<sub>2</sub>O), ammonia (NH<sub>3</sub>) and ethanol ( $C_2H_5OH$ ) as a solvent, the nanobelts were developed on the ITO substrate. The final product was characterised using X-Ray Diffraction, Energy Dispersive X-Ray spectroscopy, UV-Vis, and Field Emission Scanning Electron Microscope Analysis techniques. The XRD pattern showed that NiO phases were formed. The Bandgap was 4.11 eV, obtained through UV-Vis spectra. Morphology was determined to be Nanobelts from the FESEM. Nickel oxide nanobelts showed the highest degradation efficiency for rhodamine B followed by crystal violet, methylene blue and methyl orange. The effect of catalyst loading on rhodamine B showed that increasing the concentration of photocatalyst, increased degradation efficiency.

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TABLE.1.1.1 Different dyes.

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## **CHAPTER 1: INTRODUCTION**

### **1.1 OVERVIEW**

Water is one of the basic needs required for survival. Good quality of water is essential for human health, industries and the ecosystem while ensuring there are enough supplies for the growing population, increasing industries and continuing survival of different ecosystems. (Humans can go without water only for certain days) Competition over freshwater will increase in coming years due to growing population, rising incomes, increasing demand by industrial and urban users. [1] The water crisis has been determined as a global risk in terms of potential impact for people and economies by the World Economic Forum. [2] Mesfin M. Mekonnen and Arjen Y. Hoekstra has reported that  $2/3^{rd}$  of the world's population live in areas suffering from severe water scarcity at least one month a year, with half of this population residing in China and India. [3] According to UNESCAP 2010, 80% -90 % of wastewater in Asia and Pacific region was released untreated.



FIGURE.1.1.1 Freshwater withdrawal distribution

In 2017, The Food and Agriculture Organization (FAO) AQUASTAT database estimated that the global freshwater withdrawal was  $3,298 \ km^3/year$ . Around 44% of the freshwater is consumed and the remaining 56% or  $2,212 \ km^3/year$  is released into the ecosystem with 24% contribution by industrial and municipal effluents and 32% contribution by agricultural drainage water. Esther Forgacs, Tibor Cserha'ti and Gyula Oros estimate that around

10,000 tons of dyes are produced annually and 1-2 % in production and 1-10 % in use was lost. [4]

Name of dye	Chemical Formula	Structural Formula
Rhodamine B Molecular Weight- 479 g/mol	C <sub>28</sub> H <sub>31</sub> ClN <sub>2</sub> O <sub>3</sub>	C - C - C



TABLE.1.1.1 Different dyes.

Known for its fluorescence properties, Rhodamine B is a synthetic dye used in the textile and food industries. It is used for staining purposes in biology and as a tracer dye in the water. It is used as a food colourant in chilli powder and is found to be carcinogenic. [5] Methyl Orange is frequently used as a pH indicator used in titrations, showing red colour in acidic medium and yellow colour in basic medium. Crystal Violet is dye having applications in varied fields such as forensics to develop fingerprints, textiles to dye cloth and used as an antiseptic, but reported to promote tumour growth. [6] Even though having side effects such as vomiting, high blood pressure, headache, etc, Methylene Blue was used as a medicine to treat urinary tract infections. It was also used for biological staining purposes.

## **1.2 DYE REMOVAL METHODS**



FIGURE.1.2.1 Main methods of dye removal

Various techniques for the removal of dye effluents have been employed over the years. These techniques are classified into main types such as Physical, Chemical and Advanced Oxidation Processes, etc. These methods are as follows: [7]

- Physical Method
  - Adsorption: In the absorption process, absorbents are made from materials having a high absorption capacity to absorb dye molecules. Around 29% removal efficiency of Methylene Blue was shown by activated carbon. [8] Another absorbent is metal hydroxide sludge which is an industrial waste containing hydroxide ions of metal and its salts. [9]
  - Ion exchange: Ions in dye wastewater swap themselves with similar ions attached to a stationary solid surface. It is a reversible process. Maximum efficiency for acid orange 7 is 87 %. [10] A Major disadvantage of this process is that no of dyes affected by this process is low. [11]
- Chemical Method
  - 1. Ozonation: Known as a powerful oxidant having oxidation potential greater than chlorine and hydrogen peroxide, a major advantage is that there is no sludge formation

and application is in gaseous form. Disadvantage faced by ozonation is high application cost and half-life of ozone (20 mins). The removal efficiency of 98 % for rhodamine B was shown by ozonation method. [12]

- Hypochlorite Ion (NaOCl/Ca(OCl)<sub>2</sub>): In this process, the dye molecules are attacked by Cl<sup>+</sup> ions. Increasing Chlorine concentration increases the dye removal and decolourization.
- Advanced Oxidation Process
  - Fenton's reagent (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>): It is hydrogen peroxide and ferrous ion. This method completely degrades contaminants into carbon dioxide, water and inorganic salts. This method is a low-cost process with no production of toxic products, the downside being the generation of ferric hydroxide sludge generation. [13] For acid orange 24, the dye removal efficiency of 95 % was reported with the use of Fenton's reagent. [14]
  - Photocatalysis: In photocatalysis, oxidation of dye takes place by hydroxyl radical. Hydroxyl radicals are produced by UV light with semiconductor, hydrogen peroxide or ozone.

## **1.3 PHOTOCATALYTIC DYE REMOVAL BY SEMICONDUCTORS**

Various semiconductors have shown photocatalytic properties such as Titanium dioxide [15], Calcium oxide [16], Zinc oxide [15], Nickel oxide [17] etc. The dye removal process is carried out in the presence of UV light. A p-type semiconductor, Nickel oxide has been used for its dye degradation capabilities. Various nickel oxide structures have been reported.

### **ADVANTAGES:**

- 1. Effective dye removal method with a success rate of 99 %.
- 2. There is no sludge formation
- 3. There is no foul odour production.
- 4. The photocatalyst semiconductors can be reused.

#### **DISADVANTAGES:**

- 1. Process is expensive.
- 2. This process forms number of by-products.

### **1.4 BASIC MECHANISM**



FIGURE.1.4.1 Oxidation of Pollutant using semiconductor illuminated by UV light. [18]

The basic mechanism of photocatalytic degradation is

as follows: [18] [19]

- 1. Light of wavelength less than 1240/Enm falls on the semiconductor.
- 2. Absorption of energy promotes conduction band electron into valence band, forming conduction band electron and valence band hole pair.

Semiconductor + 
$$h\nu \rightarrow$$
 Semiconductor ( $e^- + h^+$ )

 The Oxygen molecule O<sub>2</sub> uses the negative electron e<sup>-</sup> from conduction band forming superoxide radical O<sub>2</sub><sup>-</sup>. This superoxide molecule will further react with proton H<sup>+</sup> forming hydroperoxide radical HO<sub>2</sub><sup>\*-</sup>.

> Semiconductor ( $e^-$ ) +  $O_2 \rightarrow$  Semiconductor +  $O_2^{*-}$  $O_2^{*-} + H^+ \rightarrow HO_2^{*}$

4. The positive hole will reduce water forming hydroxyl radical HO<sup>\*</sup> and proton H<sup>+</sup>.

Semiconductor  $(h^+) + H_2 0 \rightarrow$  Semiconductor  $+ H^+ + 0H^*$ 

5. The HO<sup>\*</sup>, O<sub>2</sub><sup>-</sup> and HO<sub>2</sub><sup>\*-</sup> will repeatedly attack the pollutant degrading it into carbon dioxide and water.

### **1.5 OBJECTIVES**



FIGURE.1.5.1 Project work plan.

There are two main objectives for this project work:

- 1. To prepare samples from hydrothermal process.
- 2. To study dye degradation properties of synthesised samples.

In the first phase of project work, literature survey of the previous work was done. The optimization of parameters was done in the following step. In the next step, the samples were prepared using hydrothermal method. The different characterization techniques were done to determine properties and structure of the structures. Degradation efficacy of samples was determined using different dyes in the last step.

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S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO<sub>2</sub>, Solar Energy Materials & Solar Cells 77 (2003) 65–82.

Here, Acid brown 14 dye was used for performance analysis of TiO<sub>2</sub> and ZnO photocatalyst. The effect of the initial concentration of dye, catalyst loading, irradiation time etc was studied. The source of energy was sunlight. The effect of dye concentration was studied by varying concentration from 2 x10<sup>-4</sup> mol/L to 6 x10<sup>-4</sup> mol/L with a catalyst loading of 2.5 g/L. Rate of degradation increased up to 5 x10<sup>-4</sup> mol/L, after this point, it decreased in both cases of TiO<sub>2</sub> and ZnO. The catalyst loading was varied from 0.5 g/L to 3.0 g/L while initial concentration kept constant at 5 x10<sup>-4</sup> mol/L. Rate of degradation increased up to 2.5 g/L, after this point, it decreased in both cases of TiO<sub>2</sub> and ZnO. It took 2.5 g/L ZnO 360 mins irradiation time while 2.5 g/L TiO<sub>2</sub> 420 mins to degrade 5 x10<sup>-4</sup> mol/L acid brown 14. [15]

G. Jayakumar, A. Albert Irudayaraj, A. Dhayal Raj, Photocatalytic Degradation of Methylene Blue by Nickel Oxide Nanoparticles, Materials Today: Proceedings 4 (2017) 11690–11695.

Nickel Oxide nanoparticles were synthesised using a chemical precipitation method. Nanoparticles were reported with an average size of 64 nm having no

impurity. Methylene blue was degraded using 0.031 gm of NiO nanoparticles in 100 ml distilled water under sunlight. [17]

*Faezeh Farzaneh, Sara Haghshenas, Facile Synthesis and Characterization of Nanoporous NiO with Folic Acid as Photodegredation Catalyst for Congo Red, Materials Sciences and Applications, 2012, 3, 697-703.* 

Nano porous NiO was synthesised using the sol-gel process followed by calcination at 400 °C. Particles of the size of 21-22 nm were obtained. 0.05 g nanoparticles of NiO were poured into 100 mL aqueous solution of 3 ppm Congo red dye and under 30 W UV-C lamps, 90 % of Congo red dye was degraded in 1 hr compared to 20 % with NiO catalyst. [20]

Khizar Hayat, M.A. Gondal, Mazen M. Khaled, Shakeel Ahmed, Effect of operational key parameters on photocatalytic degradation of phenol using nano nickel oxide synthesized by sol-gel method, Journal of Molecular Catalysis A: Chemical 336 (2011) 64–71.

NiO nanoparticles were synthesised by the sol-gel method. Here, phenol was taken as a pollutant for degradation properties. Spherical nanoparticles with a smooth surface and uniform surface were obtained. Effect of catalyst weight and the concentration of phenol are discussed. As the catalyst weight was increased from 1.0 g/L to 6.0 g/L, the rate dropped as the weight amounted to 6.0 g/L. The initial concentration of phenol was changed from 0.532 mM to 2.66 mM, with the degradation rate increases up to a certain level and saturation limit is reached. 97 % photocatalytic degradation of phenol was achieved in a short span of time. [21]

Raja Vahini, Puvaneswaran Senthil Kumar, Swaminathan Karuthapandian, Bandgap-tailored NiO nanospheres: an efficient photocatalyst for the degradation of crystal violet dye solution, Appl. Phys. A (2016) 122:744.

Nanospheres were synthesised using the precipitation

method. The Bandgap was observed to be 3.31 eV. the average size of nanosphere was 500 nm, with a porous surface. Crystal violet dye was degraded under UV light. Rhodamine B and Methylene Blue dye were significantly degraded within 35 mins by 50 mg of NiO nanospheres, while crystal violet was degraded within 50 mins. As-synthesised NiO nanospheres were compared to TiO<sub>2</sub> P25 and commercial NiO, with degradation percentile 98, 81 and 61 for NiO nanospheres, TiO<sub>2</sub> P25 and commercial NiO respectively. [22]

Zhang Qing, Liu Haixia, Li Huali, Liu Yu, Zhang Huayong, Li Tianduo, Solvothermal synthesis and photocatalytic properties of NiO ultrathin nanosheets with porous structure, Applied Surface Science 328 (2015) 525–530.

hydrothermal method, followed by calcination. A hierarchical structure with ultrathin sheets as second grade and nanoparticle as the third grade was shown by NiO flower-like nanosphere. The nanosheets were of 10 nm thickness and nanoparticles of 5-10 nm size. For degradation under xenon arc lamp, 0.1 g of NiO was dispersed in 100 mL methylene blue solution having a concentration of 20 mg/L. In 140 mins, total methylene blue dye was degraded by nanospheres compared to commercial NiO where only 28 % of methylene blue was degraded. [23]

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## CHAPTER 3: SYNTHESIS AND CHARACTERIZATION

### **3.1 SYNTHESIS METHODS**

Various methods have been employed for NiO structure synthesis such as Sol-gel method [24], Thermal decomposition [25], Precipitation method [17], Solvothermal method [23] etc. Synthesis of nickel oxide was done by hydrothermal methods is due to control over process parameters such as temperature, solvent concentration, etc.

### **3.2 HYDROTHERMAL SYNTHESIS**

Hydrothermal Synthesis is defined as '*any heterogeneous or homogeneous chemical reaction in the presence of a solvent (whether aqueous or nonaqueous) above room temperature and at a pressure greater than 1 atm in a closed system*' by M. Yoshimura and K. Byrappa. [26] Inside the autoclave, various reactions are expected to occur such as: P a g e | 13

- 1. Synthesis of new phases or stabilization of new complexes.
- 2. Crystal growth of several inorganic compounds.
- 3. Decomposition, corrosion and etching.

### **ADVANTAGES:**

- 1. Compounds with elements in oxidation states that are difficult to obtain, especially important for transitional metal compounds, can be obtained in a closed system by the hydrothermal method (e.g., ferromagnetic chromium (IV) oxide).
- 2. The hydrothermal method is useful for the so-called low-temperature phases, e.g.,  $\alpha$ -quartz,  $\alpha$ -berlinite, and others.
- 3. For the synthesis of metastable compounds, such as subiodides of tellurium, Te<sub>2</sub>I.

#### **DISADVANTAGES:**

- 1. The autoclaves are expensive.
- 2. The reaction taking place cannot be observed.

### **3.3 SYNTHESIS**



FIGURE.3.3.1 Process step of synthesis of NiO

The chemicals were of analytical grade and used as received without any further purification. In a typical synthesis, 1 M nickel sulphate hexahydrate P a g e | 14

(NiSO<sub>4</sub>.6H<sub>2</sub>O) was dissolved in 5 mL deionised water (H<sub>2</sub>O) and 3 mL ammonia (NH<sub>3</sub>) was added drop by drop while stirring till the colour changed. Subsequently, the solution was added drop by drop to 15 mL of ethanol solvent (C<sub>2</sub>H<sub>5</sub>OH) and stirred for 15 min. After stirring, the solution was transferred into a 23 mL Teflon lined stainless steel autoclave. A 2cm x 2cm ITO substrate was kept inside the autoclave, with the conducting side facing up. The system was heated to 180 °C in an electric oven for 12 hours. Afterwards, the autoclave was cooled naturally to room temperature. The ITO substrate was taken out, cleaned with DI water several times and dried at room temperature. For characterization and further analysis, the nanostructures were scraped off the ITO substrate.

### **3.4 CHARACTERIZATION TECHNIQUES**

### **3.4.1 X-RAY DIFFRACTION**

X-ray diffraction is a non-destructible technique for characterizing crystalline material, providing information on structures, phases, average grain size etc. X-rays are high energy electromagnetic waves having a wavelength between  $10^{-3}$  and 10 nm. X-rays are generated when electrons accelerated through a high potential field are directed at a target.



FIGURE.3.4.1 Bragg's diffraction.

When x-rays having a wavelength ' $\lambda$ ' is incident at  $\Theta^{\circ}$  degrees on a crystal having interplanar distance 'd', the rays get scattered by the atoms and for

constructive interference to occur in accordance to Bragg's law, the path difference must be equal to integral value 'n' on the wavelength of the incident x-ray.

 $Path \ difference = AB + BC$   $Path \ difference = dsin\theta + dsin\theta$   $Path \ difference = 2dsin\theta$ 

So, Bragg's law is expressed as  $2dsin\theta = n\lambda$ .

An X-ray diffractometer consists of

- 1. X-ray generator
- 2. Sample stage
- 3. Detector

The X-rays generated are directed at the sample mounted on the stage at an angle  $\Theta$ , while the intensity of the diffracted rays is detected by the detector which is 2 $\Theta$  away from the source. The intensity of diffracted rays is measured as the detector is rotated. A diffraction peak occurs as the crystal geometry satisfies Bragg's law.

### **3.4.2 FIELD EMISSION SCANNING ELECTRON MICROSCOPY**

When the electron beam hits the sample various signals such as secondary electrons, backscattered electrons, X-rays, transmitted electrons etc are generated. Field Emission Scanning Electron Microscopy (FESEM) is a type of characterization technique used to determine the morphology of the sample by secondary electrons.



As the electron beam can interact with the atmosphere, the sample is placed in a vacuum. The electrons pass through a series of solenoids, which are used to focus the beam on the sample scanned line by line. Secondary electrons are generated when electrons from the electron beam are absorbed by the sample, making the atom unstable causing the ejection of electrons. Backscattered electrons are generated when the electrons bounce offs from the nuclei of the sample atoms. The secondary electrons are used to form the image which is then displayed on the monitor. For non-conductive sample, a gold coating is done in order to keep the sample intact.

### 3.4.3 ENERGY DISPERSIVE X-RAY SPECTROSCOPY

Energy Dispersive X-ray Spectroscopy (EDS) is a nondestructive characterization technique used to analyse the composition of the sample. EDS characterization can be done in using the same equipment as FESEM. The difference between EDS and FESEM is that the latter uses secondary electrons to determine the morphology while the former uses x-rays generated to determine the composition.



FIGURE.3.4.3 Principle of EDS.

When the electron from the electron beam strikes the inner shell of the atom, removing an electron from an inner shell. To reduce the energy of the atom, an electron from the outer shell will jump to the inner shell. This produces x-ray photons due to the energy difference between shells. From this process, the types of atom in the sample can be determined by their binding energy. The concentration of the elements is measured by counts of the photons. However, the concentration of lighter elements such as Oxygen (O), Nitrogen (N) etc cannot be determined accurately.

### 3.4.4 UV VISIBLE SPECTROSCOPY

Light can undergo various phenomena such as absorption, reflection or transmission while interacting with materials. The wavelength range 190 nm to 1100 nm corresponds to different electronic transitions.



FIGURE.3.4.4 Energy level diagram representing electronic transitions.

- 1.  $\sigma$ - $\sigma$ \* transition: This transition requires the largest amount of energy as it may result in breaking down of bonds. This type of transition requires wavelength below 190 nm.
- 2.  $\pi$ - $\pi$ \* transition: This transition requires a moderate amount of energy. Wavelength in UV Visible range causes the electron to be excited from pie bond to pie\* bond.
- 3.  $n-\pi^*$  and  $n-\sigma^*$  transition: Molecules have lone electrons which do not take part in any bonds. These electrons can absorb energy and excite to pie\* bond or sigma\* state. The  $n-\pi^*$  transition requires more energy compared to  $n-\sigma^*$  transition.



UV visible spectroscopy is a characterization technique in which absorption or reflectance of in ultraviolet-visible spectra is measured as a function of wavelength. The UV wavelength range is from ~10 nm to ~400 nm, while the visible wavelength range is from ~400 nm to ~700 nm. UV Vis spectroscopy is based on Lambert-Beer law. According to Lambert-Beer law,  $A = \mathcal{E} * b * C$  where A is the absorbance, b is the cell length in cm,  $\varepsilon$  is molar absorptivity in L/cm/mol, C is the concentration in mol/L.

A Spectrophotometer consists of:

- 1. Source
- 2. Monochromator
- 3. Reference Cell
- 4. Sample Cell
- 5. Detector

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### **4.1 X-RAY DIFFRACTION RESULTS**

The crystal structure and phase were examined by XRD. The pattern was recorded using Bruker D2 phaser diffractometer with Cu-K $\alpha$  radiation ( $\lambda$  = 1.54 Å) in angle range 20° to 80°. The diffraction pattern of the sample is shown in figure.4.1. Apart from NiO peaks, no other peaks were found suggesting that the precursor was completely converted into nickel oxide. The obtained pattern was well indexed with JCPDS file for pure NiO product having JCPDS File No. 47-1049. The diffraction peaks indicated an FCC structure, showing well-crystallized nickel oxide. The characteristic peaks were found in the sample at 37.26°, 43.29°, 62.88°, 75.42° and 79.41°, which can be indexed to the (111), (200), (220), (311), (222) respectively.



FIGURE.4.1.1 XRD Pattern of the as-prepared sample.

## 4.2 FIELD EMISSION SCANNING ELECTRON MICROSCOPE RESULT

The Field Emission Scanning Electron Microscope (FESEM) acts like a microscope that uses electrons instead of light. It is used for characterization of morphology off as prepared NiO sample. The morphology was determined using JEOL FESEM with a constant voltage of 5.0 kV. Different pictures were taken under different magnification. Figure (a) in Fig.4.2.1 show nanostructure formed were clustered. Further magnification as shown in Figure (b) of Fig.4.4 revealed the morphology of nanostructure to be nanobelts. In Figures (c, d) of Fig.4.2.1, nanobelts shown to have a uniform thickness, with an average of 88 nm. The nanobelts were also long and having smooth morphology.









FIGURE.4.2.1 FESEM images of NiO sample.

## 4.3 ENERGY-DISPERSIVE X-RAY SPECTROSCOPY RESULT

The composition and purity of the as-prepared product were determined by Energy-Dispersive X-Ray Spectroscopy (EDS). Used in conjunction with FESEM where electrons are used, EDS uses X-rays emitted during the bombardment of the electron beam on the sample. Fig.4.3.1 show EDS pattern of the as-prepared sample. Only nickel and oxygen peaks are observed, implicating that only NiO was obtained without any impurity. For the as-prepared sample, the elemental composition was found to be Ni:O = 47:52.5.



FIGURE.4.3.1 EDS of the as-prepared sample.

### 4.4 UV VISIBLE SPECTROSCOPY RESULT

UV Visible Spectroscopy was performed to calculate the bandgap of the as-prepared sample. The UV Visible spectra were obtained from Shimadzu UV-2600 spectrophotometer. The characterization was performed in absorbance mode, with the wavelength range from 275 nm to 800 nm. The optical band gap was calculated using the following formula,  $(\alpha hv)^2 = A(hv - E_g)$  where  $\alpha$  is the absorption coefficient in cm<sup>-1</sup>, A is the material constant, hv is the energy in eV. The bandgap was calculated extrapolating linear portion of  $(\alpha hv)^2$ verses hv to zero. Generally, NiO has bandgap around 3.5- 4.5 eV. [22] The value of asprepared nickel oxide was determined to be 4.11 eV, confirming potential application as photocatalyst.



FIGURE.4.4.1 UV-Visible Spectra (a) and Tauc plot (b) of as-prepared NiO sample

### **4.5 PHOTOCATALYSIS RESULT**

The Photocatalytic properties of nickel oxide nanobelts were measured using rhodamine B degradation. Rhodamine B is degraded using 3 different concentrations (25 mg, 40 mg, 60 mg) of nickel oxide nanobelts while keeping dye concentration constant at 10 ppm. 10 ppm of rhodamine B in 100 ml solution was prepared and different concentrations of nickel oxide were mixed using a magnetic stirrer for an hour. Afterwards, 100 mL solution was kept under Xenon lamp. The dye was degraded under UV illumination and every 20 mins for 140 mins, 5 mL solution was taken for UV Visible spectroscopy for estimating changes in UV absorption spectra. The initial UV absorption was taken before the photocatalyst and the dye was mixed.

The degradation rate was calculated using the formula,  $Degradation rate (\%) = (C_o - C_t)/C_o = (A_o - A_t)/A_o$  where C<sub>o</sub> and C<sub>t</sub> are the initial and variable concentration and A<sub>o</sub> and A<sub>t</sub> are the initial and variable absorbances. The degradation rate indicated how much of dye had degraded in that time period. It helps in determining the efficiency of the NiO nanobelts for its application as photocatalyst in dye degradation.

In the 25 mg and 40 mg NiO solution, the characteristic peak of Rhodamine B was observed at 553 nm while in 60 mg, it was observed at 554 nm. As evident from all 3 figures fig.4.5.1, fig.4.5.2 and fig.4.5.3, The absorbance at characteristic peaks of UV spectra decreased indicating that degradation of Rhodamine B is increasing as the illumination time under Xenon lamp increases.

The degradation percentage of rhodamine B increases linearly with time. On comparing Fig.4.5.1. (b), Fig.4.5.2. (b) and Fig.4.5.3. (b), it is evident that 60 mg of NiO nanobelts can degrade Rhodamine B faster as compared to 25 mg and 40 mg NiO nanobelts. In 140 mins, 60 mg NiO nanobelts show the highest degradation followed by 40 mg and 25 mg, indicating that increasing the photocatalyst, increased the degradation capabilities.

As the 60 mg concentration of NiO is shown highest degradation capabilities on 10 ppm of rhodamine B, its effect on other dyes such as methyl orange, crystal violet, and methylene blue are found out by repeating the experiment without changing any concentration of dyes, only the type of dye.

Fig.4.5.4. (a, b, c) shows absorbance spectra of methyl orange, crystal violet and methylene blue respectively. The methyl orange, crystal violet and methylene blue showed the characteristic peak at 462 nm, 590 nm and 664 nm respectively. The

absorbance at the characteristic peak in all three figures Fig.4.5.4 (a, b, c) decreased at the time under xenon lamp increased indicating that NiO nanobelts were able to degrade dyes.

Fig.4.5.5. shows the degradation rates of the four dyes methyl orange, crystal violet, methylene blue and rhodamine B. As evident from the figure, the NiO nanobelts were most effective on rhodamine dye, followed by crystal violet, methylene blue and least effective on methyl orange. After an hour of stirring, 16.9 % of rhodamine B, 15.2 % of crystal violet, 11.7 % of methylene blue and 7.3 % of methyl orange has degraded. While in 140 min, 89 % of rhodamine B, 82.8 % of crystal violet, 76.7 % of methylene blue and 79.1 % of methyl orange has degraded.



FIGURE.4.5.1. Absorption Spectra (a) and Degradation rate (b) of 10 ppm Rhodamine B in the presence of 25 mg NiO nanobelts.

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FIGURE.4.5.2. Absorption Spectra (a) and Degradation rate (b) of 10 ppm Rhodamine B in the presence of 40 mg NiO nanobelts.



FIGURE.4.5.3. Absorption Spectra (a) and Degradation rate (b) of 10 ppm Rhodamine B in the presence of 60 mg NiO nanobelts.







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FIGURE.4.5.4. Absorption Spectra of dyes Methyl Orange (a), Crystal Violet (b), and Methylene Blue (c) in the presence of 60 mg NiO nanobelts.



FIGURE.4.5.5 The degradation rates of dyes Methyl Orange, Crystal Violet and Methylene Blue in the presence of 60 mg NiO nanobelts.

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## **CHAPTER 5: SUMMARY**

Nickel Oxide nanobelts were successfully synthesised by a simple hydrothermal method and characterized using XRD, EDS, UV, and FESEM. The XRD patterns showed that the Nickel Oxide phases were formed having FCC crystal structure. The XRD and EDS show that the nickel oxide formed was of high purity. The synthesised NiO showed nanobelt morphology with an average thickness of 88 nm. The degradation properties of nickel oxide nanobelts were determined against four dyes: Rhodamine B, Crystal Violet, Methyl Orange, and Methylene Blue. The effect of catalyst loading was determined with rhodamine B, with 60 mg nanobelts showing highest degradation efficiency for 10 ppm concentration. Among the dyes, the degradation efficiency of 89 % was highest for rhodamine B followed by 82.8 % for crystal violet, 76.7 % methylene blue and 79.1 % for methyl orange.

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