Bismuth Oxide Nanoparticle Fabrication and Characterization for Photocatalytic Bromophenol Blue Degradation

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Abstract

Water is a critical resource for the survival of life on earth and the development of humanity. More than 4,000 years have passed since the beginning of the textile industry. Yet, textile dyes and the chemicals used in the manufacturing of clothing continue to be ignored, despite the fact that both humans and the environment can be negatively impacted by them. Not only are artificial dyes dangerous to our health, but they are also detrimental to ecosystems and the environment as a whole. They generate hazardous chemical waste, which winds up in rivers and other sources of water and causes havoc on the environment. Toxic pollutants released by the textile industry are a growing problem for water contamination and are linked to dangerous diseases all over the world. Efforts to treat textile industry effluents have been made, however these efforts are failing miserably. Thus, bismuth oxide is commonly employed because of its stability and proper band structure in photocatalytic processes. It functions as a photo catalyst to degrade organic dyes and has several edges as a catalyst. Although bismuth oxide occurs naturally in a variety of polymorphic forms, Bi_2O_3 has a relatively modest band gap. In this study, sodium hydroxide, bismuth nitrate, and nitric acid were used to hydrothermally produce Bi_2O_3. We first added bismuth nitrate to the water, then added a few drops of nitric acid while stirring the mixture for 45 minutes. To the bismuth nitrate solution, sodium hydroxides were gradually added. The mixture was then transferred to a Teflon-lined autoclave and heated for 24 hours at 160°C. At 450°C, the dried sample was calcined. FTIR, XRD, SEM, UV-Vis spectroscopy, and EDX were used to study morphology as well as size of the bismuth oxide

nanoparticles. Bismuth oxide exhibits a potent excitonic absorption band at 380 nm in UV-Vis spectroscopy. 3.26 eV of band gap energy is therefore provided. The Bi_2O_3 stretching peak was observed in the FTIR spectra at 700 - 400 cm^{-1}. The SEM images shown that synthesized material were agglomerated and round shape. XRD Sherrer's equation was used to determine the average crystalline structure, and the results showed that the average size of the Bismuth Oxide NPs was 25.54 nm. According to the EDX study, bismuth and oxygen, which together make up roughly 94.21% of the elemental composition of bismuth oxide, are particularly high. Moreover, there is 5.79% of the total amount of carbon present that may have come from citric acid. For the bromophenol blue photocatalytic degradation under solar light irradiation, bismuth oxide nanoparticles were examined. UV-visible spectroscopy was used to monitor the reaction's progress and calculate the percentage of photocatalytic degradation. In 120 minutes, Bi_2O_3 NPs effectively degraded almost 98.35% of the bromophenol blue dye.

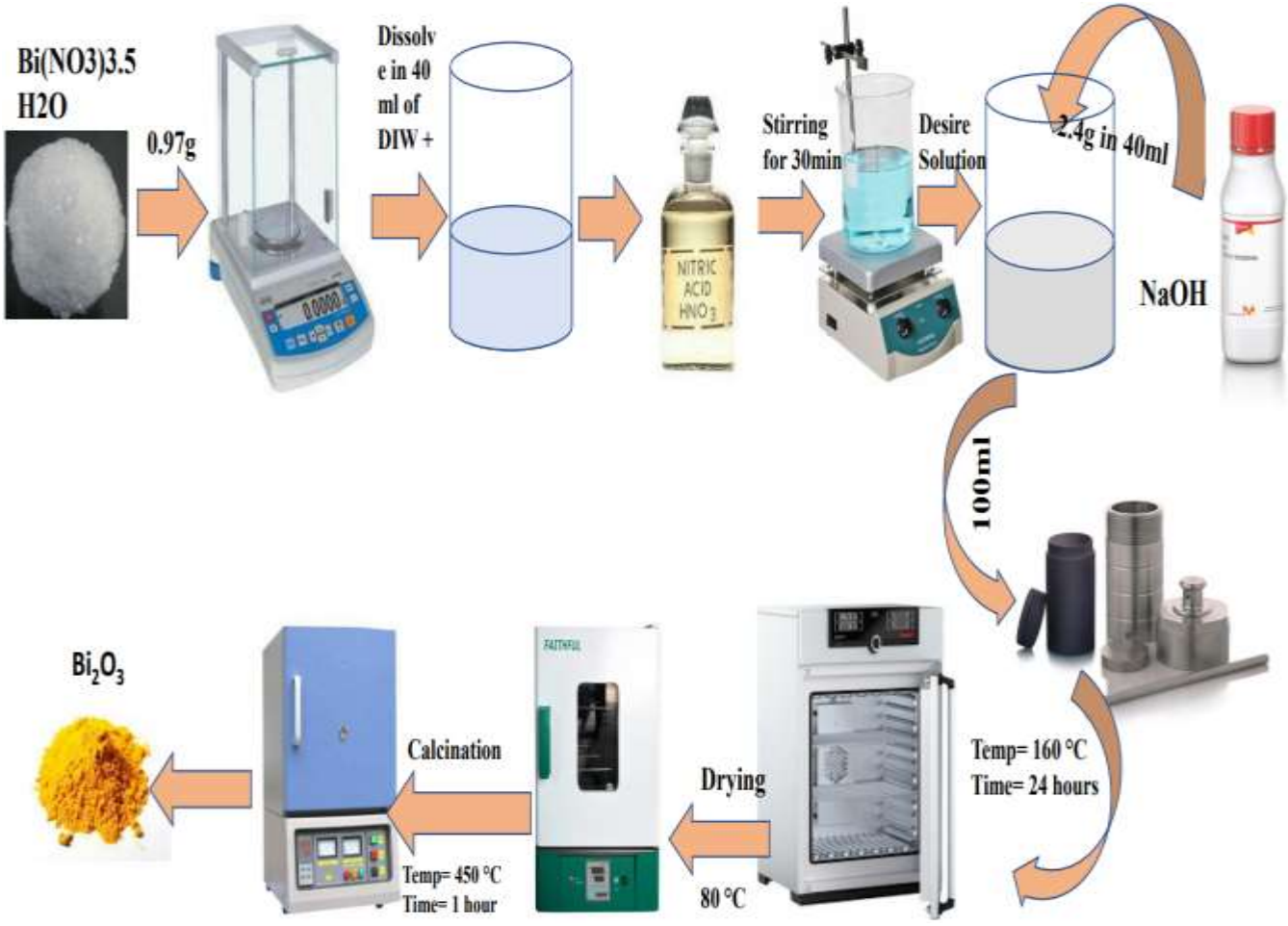


Figure 1. Graphical Abstract

1. Introduction

The study of materials containing sizes on the range of one 100nm or smaller is the focus of the branch of science and engineering known as "nanotechnology"[1-4]. While it's true that the term is still relatively new, it is being widely used to create more efficient technological advancements. Due to its uses in the areas of targeted drug delivery[5], pre-concentration of target observations, photo catalysis, magnetic separation, as well as Bi_2O_3 technology [6], electronic storage systems, vehicles for gene as well as drugs deliveries[7, 8] ,variety of industrial fields have started to embrace nanotechnology in recent times. Because of the diverse range of uses for which they might be used, these particles have the ability to have a significant influence on society. Despite being relatively new, the history of nano scale materials can be traced all the way back to 1959, where Richard P. Feynman, a physicist at Cal Tech, foretold the creation of NPs. He stated that the primary factor in determining the future technological as well as scientific development was should start low and scale down to nanoscale, saying in his class, "There is tons of ways at the bottom" [9]. As the field of nanotechnology has developed, newer nanomaterials have appeared with distinctive properties that set them apart from their larger analogs. The physiochemical characteristics of nanoparticles differ greatly from those of conventional materials because of their large surface-to-volume ratio [10]. Owing to their excellent properties, they are a fantastic choice for usage in Bi_2O_3 medical applications, which are becoming more and more significant as more and more Bi_2O_3 logical processes occur at Nano scale scales [11, 12].

A notable metal-oxide semiconductor with outstanding electrical and optical characteristics is bismuth oxide. High refractive index, wide bandgap, photoconductivity, as well as dielectric permittivity are some of these characteristics. The nineteenth century saw the discovery of bismuth oxide [13]. Because to this, it has various applications including photo-catalyst, solid oxide fuel cells, functional ceramics, materials of high temperature superconductor, gas sensors, and many more [14-18]. The three methods for making nano-bismuth oxide are the sol-gel approach, the hydrothermal technique, as well as the combustion technique [19-21]. The hydrothermal approach is a viable alternative synthetic method due to the low temperature needed for the process and the ease by which particle size could be controlled. In comparison to

other growth techniques, the hydrothermal approach has a number of benefits, such as the employment of less complex equipment, the lack of a catalyst throughout development, a cheaper cost, large-area uniform output, eco-benign, as well as a lower hazard. Because to the low reaction temperatures needed, this method is appealing for usage in microelectronics and plastic electronics. This method has also been extremely successful in the nanoscale synthesis of bismuth oxide as well as other bright compounds. By adjusting the reaction's temperature, its duration, as well as the concentration of the precursors, the hydrothermal process allows one to control the characteristics of the particles, including their size and shape [22].

The two biggest problems the world is currently experiencing are environmental damage and a lack of energy supplies. As a result, numerous investigations on semi-conductor photo catalysts have been conducted. These catalysts are thought to be a hydrothermal technology that is used to clean up the environment and convert solar energy by using sunlight [23]. TiO_2, is the most prevalent heterogeneous semiconductors in the area of photo catalysis. It is recognized as a top competitor and is used as a material of references. It is challenging to execute TiO_2's particle applications due to its large band gap (3.21 eV) as well as fast electron hole pair recombination rate. As a result, the development of a photo catalyst that is triggered by visible light faces a considerable challenge in the scientific community. In order to increase the effectiveness of solar energy use, a lot of study has recently been done into widening the absorption spectra of semiconductor photo catalysts further in visible area. Band gap engineering, that involves doping the semiconductor using various non-metals and metals or even linking it with other semiconductors, has been used to achieve this [24]. Other way to find the small band gap semiconductor photo catalysts that can work when exposed to visible light [25, 26]. Bismuth-based semiconductors are receiving greater attention these days because of their ability for usage as photo catalysts, which degrade organic pollutants whenever subjected to UV-visible light. Bi_2O_3 is becoming more and more popular because to the numerous potential applications it provides in ceramic glass production, solid oxide fuel cells, gas sensing, and optical coating [24]. furthermore, bismuth oxide is a type of semiconductor with a suitable band edge potential for water oxidation as well as a direct band gap of 2.81 eV. This may cause the emergence of some reactive species that can start oxidation reactions [27]. This results in a direct band gap for bismuth oxide of 2.81 eV. It has been observed in a range of dyes, including rhodamine B, could be degraded by bismuth oxide in its various forms, including micro as well as nanostructure [28,

29], methylene Blue [30, 31], CBBG-250 [31], methylene orange [32], malachite green [33], acetaldehyde [34], 4-chlorophenol [23], drugs [35], as well as gases [36].

In this paper, we describe the hydrothermal method used to synthesize bismuth oxide nanoparticles, which produced nanoparticles with a homogenous form and good structural stability. Conventional analytical methods including UV-visible, EDX, SEM, XRD, and FTIR spectroscopies were used to examine the produced materials. For the first time photo catalytic activity of the synthesized material was examined using the degradation of the bromophenol blue dye under visible light illumination.

2. Materials and methods

At the AWKUM Chemistry Department in KPK, Pakistan, everything that had to be done to get ready for the experimental tests has been done.

2.1. Chemicals

The main materials used in this experimental effort included ethanol, deionized water, nitric acid, citric acid, sodium hydroxide, bromophenol blue dye, as well as bismuth nitrate. Distilled water was used throughout the experiment.

2.2. Methodology

The study was performed in accordance with the relevant studies.

2.3. Synthesis of Bismuth oxide nanoparticles

Under this particular research project, the hydrothermal method was used to synthesize bismuth oxide (NPs). The next stage was adding 0.13 g of citric acid to the solution after dissolving 0.97 g of bismuth nitrate in nitric acid of 10 ml, at a concentration of 1M. The mixture was then agitated for 15 minutes. Subsequently, 2M NaOH was added while stirring continuously up to pH control "4". It was successful in producing a white colour precipitates. When the precipitate dissolved, a uniformly colored solution might be obtained. The homogeneous solution was then heated at 160 °C in an oven before being placed inside an autoclave for 24 hrs in order to precipitate on high temperature and pressure. Then centrifuged the precipitate after washing with

deionized water along with ethanol to get rid of un - reacted reactants after the autoclave's cooling procedure was finished. The precipitate that was produced was heated for 24 hours at 160 °C before being calcined for 1 hr at 450 °C to produce bismuth oxide NPs, as shown in the figure 2.

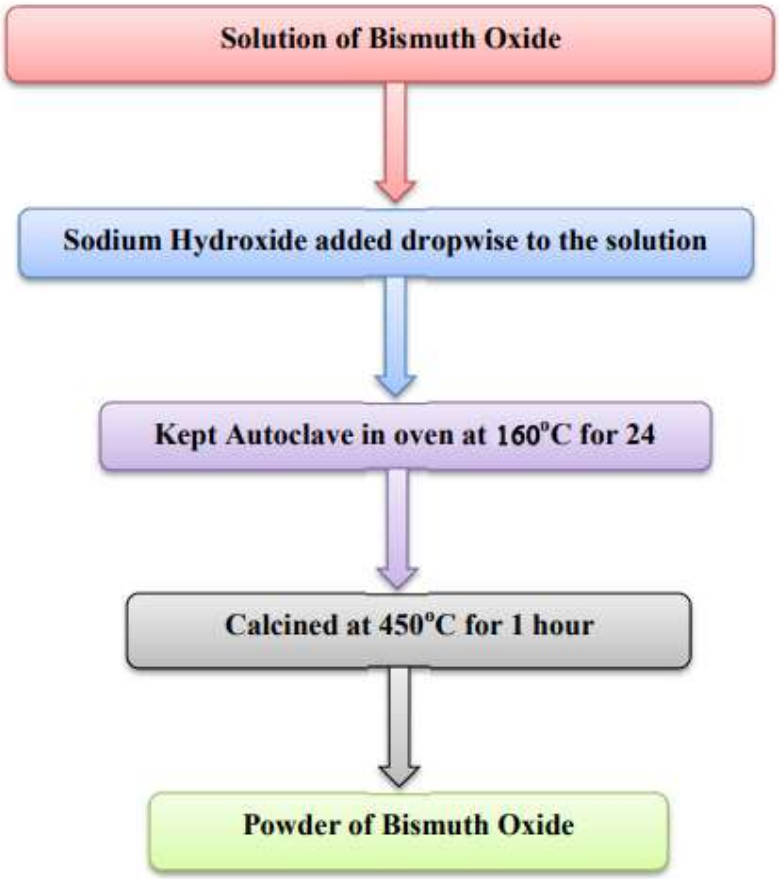


Figure 2. Bismuth oxide nanoparticles Synthesis

3. Characterizations

The synthesized NPs size, morphology, and shape were examined using the characterization technique. In order to investigate UV-Vis spectral behaviour, a computer-controlled JASCO V-650 was utilized. An FTIR analysis in the region of 4500–400 cm^{-1} was performed using a Nicolet 6700 FTIR analyzer to determine the functional groups that were found in the samples (USA). X-ray diffraction was utilized so that the crystallization and purity of the samples that

were produced could be evaluated. On the instrument, XRD analysis was performed (Bruker D8 Advance x-ray diffractometer). Surface image measurements and chemical characterization of a material were carried out with the help of a Hitachi S-3500N scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) spectroscopy.

4. Photocatalytic degradation of Bromophenol Blue dye

The photocatalytic activity for the produced nano-powder samples was assessed using the degradation of bromophenol blue dye in the sunlight. The photocatalytic reaction was effectively performed with the aid of a light source. 100 mL of BPB solution, including 20 ppm of BPB, was combined with a total of 0.2 g of photo catalysts. The suspension from the previous illustration was heated at room temperature for half hr in the dark in order to reach equilibrium between the processes of adsorption as well as desorption. The mixture was then forcefully stirred and simultaneously exposed to ionizing radiation. To ensure that the solid catalyst has been removed, around 5 mL of the solution was taken out and centrifuged on a regular basis. The catalyst's dye adsorption capacity and dye degradation efficiency were ultimately measured using an ultraviolet-visible spectrometer. By using the formula below to calculate the amount of dye that has already been removed:

$$\text{Degradation efficiency (\%)} = (C_o - C/C_{o)} \times 100$$

Figure 3. BPB dye degraded dramatically

5. Result and Discussion

In this study, a range of experimental approaches were used to assess the optical, morphological, as well as structural features of bismuth oxide NPs. After that, the photocatalytic degradation of the created photo catalysts was assessed by degrading the dye bromophenol blue under the influence of solar light.

5.1. UV-Visible spectroscopy

UV-Vis characterization of nanomaterials is a technique that is not only straightforward but also rapid and user-friendly. Figure 4 shows the powder sample's UV-visible spectrum, which ranges from 300 – 800 nanometers. Bi_2O_3 clearly exhibits a potent excitonic absorption band at 380 nm. This gives Bi_2O_3 a band gap energy of 3.26 eV. Because of bismuth oxide large band gap, this substance creates electron as well as hole pairs whenever exposed to a stream of photons having equivalent energy to or larger than its own. These electron-hole pairs produce free radicals, which carry out subsequent secondary reactions.

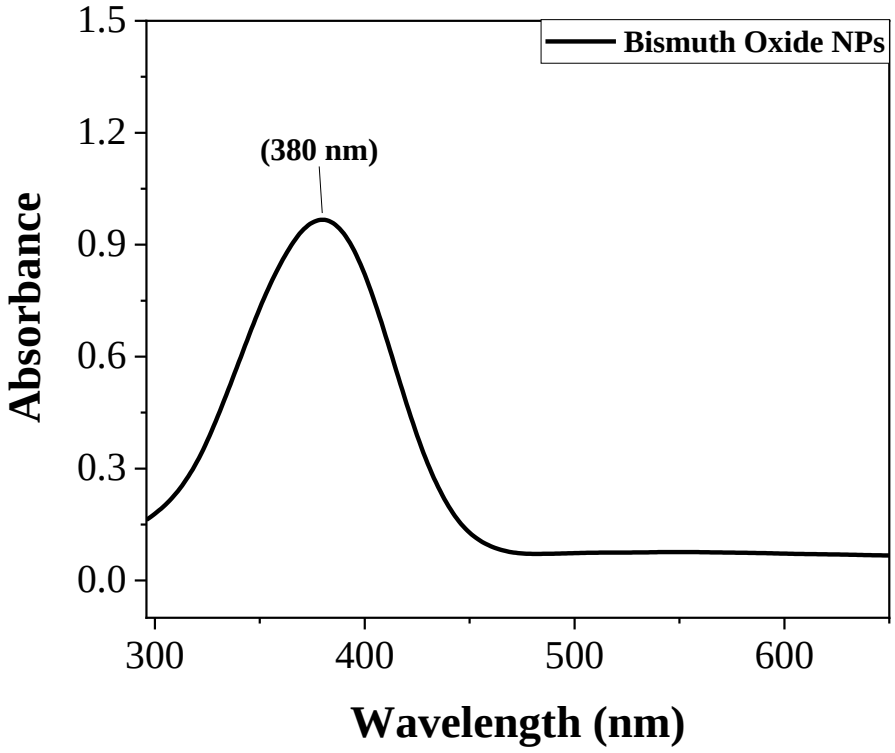


Figure 4. Bismuth Oxide Nanoparticles UV-Vis Spectra

5.2. Fourier-transform infrared (FTIR) spectroscopy

The Fourier transform infrared spectroscopy, is a method which may employed to establish the presence of chemical functional groups in sample. The findings of bismuth oxide nanoparticles, FTIR spectrum gathering between 4000– 500 cm^{-1} are displayed in the figure. The large peak from 700 to 400 cm^{-1} is due to the M-O bonding, and the vibration band at 1200-1700 cm^{-1} is a distinguishing property of the NO3- group (Bi_2O_3). The vibration of the C-O molecule is responsible for the IR bands between 3000 – 3280 cm^{-1}.

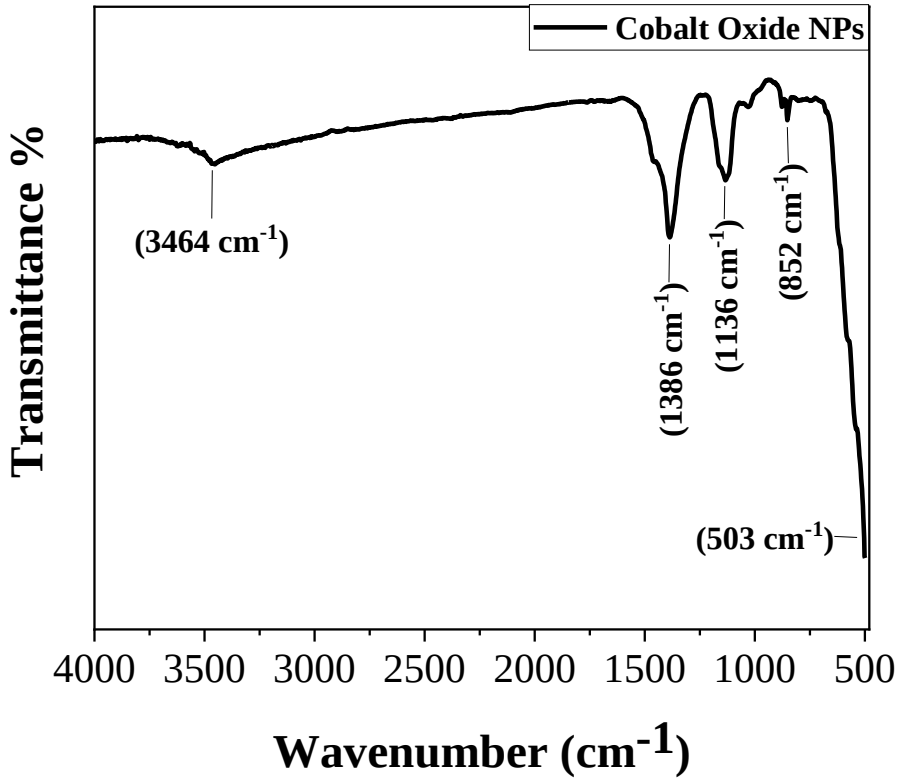


Figure 5. Bismuth Oxide Nanoparticles FTIR Spectra

5.3. X-Ray diffraction (XRD) Analysis

The non-destructive method of X-ray diffraction, sometimes known as XRD, is particularly useful in acquiring knowledge about crystalline materials. It is used to identify the best crystalline orientation, phases, structures, as well as other structural information including strain, crystalline nature, and flaws in crystals. Figure 6 shows the outcomes of the XRD examination of our sample. It is evident that Bi_2O_3 exhibits strong as well as distinct peaks at $2\theta = 26^o$, 27^o, 29^o, 32^o, 45^o, 47^o, 54^o, 56^o and 68^o, these are corresponding to the crystal planes of (111), (002), (220), (101), (110), (431), (422), (511) as well as (200) accordingly. The sample is a superb crystalline nano-material, as shown by the relatively narrow as well as sharp XRD peaks. This further reveals the high crystallinity of the Bi_2O_3 sample. The average crystallite diameter of Bi_2O_3 NPs, calculated employing Scherer's equation, is 25.54 nm, according to the study's findings.

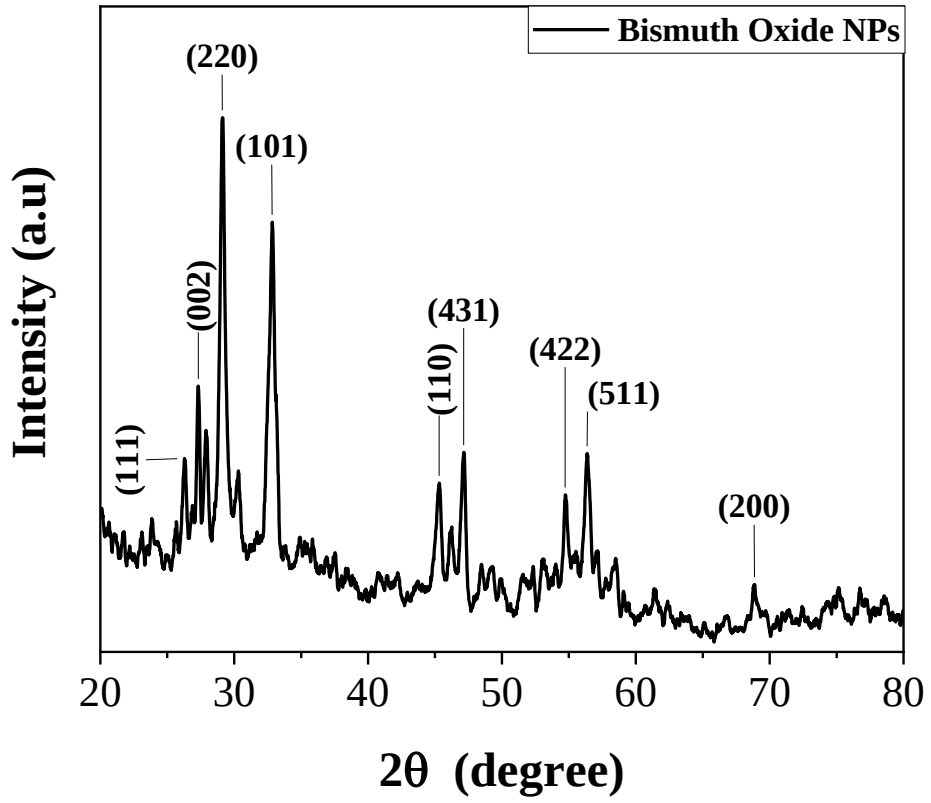


Figure 6. Bismuth oxide nanoparticles XRD

5.4. Scanning Electronic Microscopy

Figure 7 present scanning electron microscopic (SEM) images of bismuth oxide NPs at various magnifications. The SEM images shown that the prepared material have agglomerated and round shape morphologies. Evidently, there are visible particles of various sizes when agglomeration levels are high. Similar-sized particles are dispersed throughout and the overall morphology is dense [37].

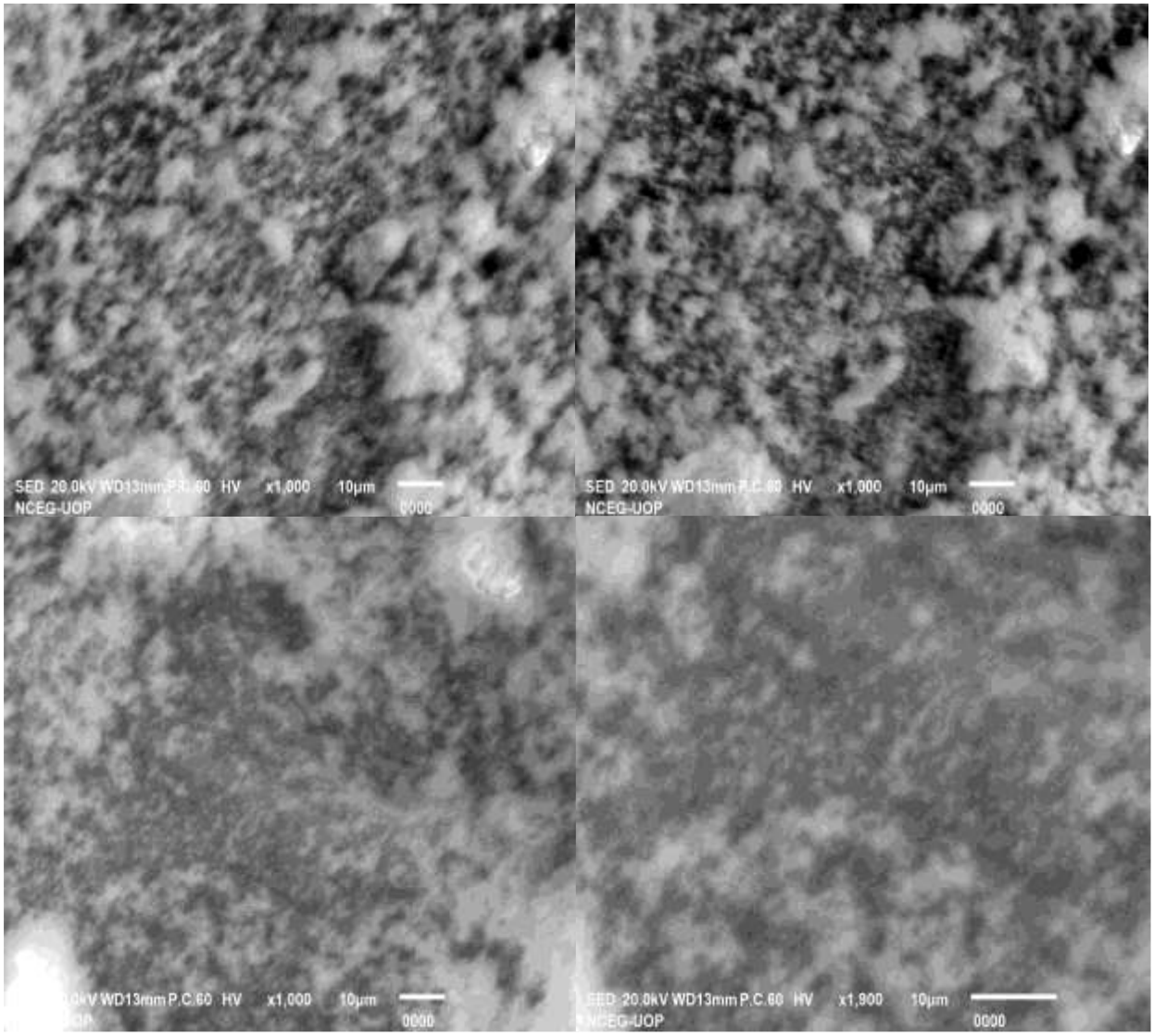
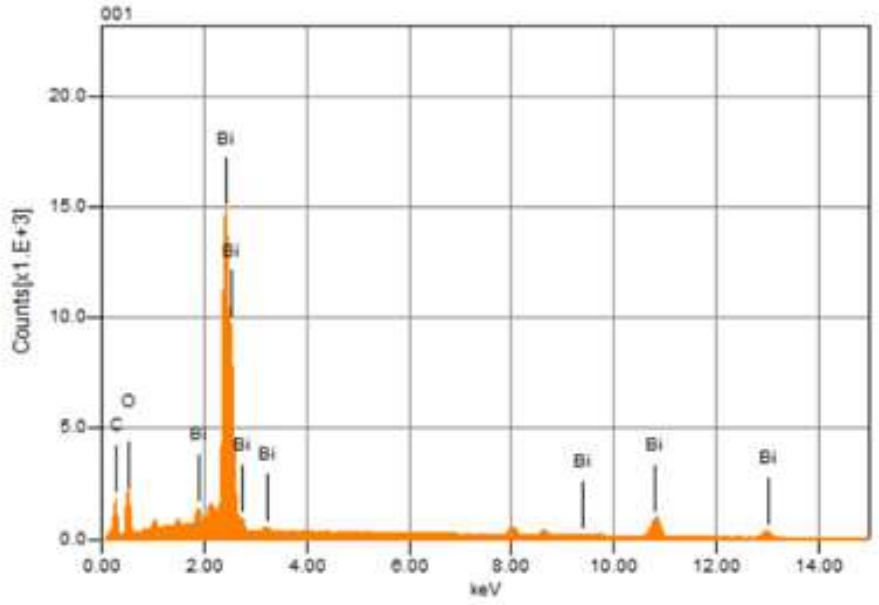


Figure 7. Bismuth oxide nanoparticles SEM images

5.5. Energy dispersive X-ray

By employing the widely used EDX technology, the elemental composition of a sample as small as a few cubic micrometers could determine as well as examined. Figure 8 shows the bismuth oxide sample's elemental composition in addition to the EDX result. It is readily obvious that the sample has every component that is required, demonstrating its outstanding purity. There is also a substantial amount of bismuth as well as oxygen, which together make up around 94.21% of the total. Moreover, there is 5.79% of the total amount of C present that may came from citric acid.



Formula	mass%	Atom%	Sigma	Net	K ratio	Line
C	5.79	29.98	0.01	40134	0.0071873	K
O	11.69	45.45	0.04	52770	0.0431843	K
Bi	82.53	24.57	0.17	1051525	0.5417387	M
Total	100.00	100.00				

Figure 8. Bismuth oxide NPs EDX image

5.6. Photocatalytic degradation

A semiconductor's photocatalytic activity will be triggered by the light energy absorption which is equivalent to or more than that of semiconductor's band gap energy, which subsequently cause excited electrons as well as holes to form. The electron-hole pair interacts with adsorbed reactants as they move to the surface, speeding up the reactions of oxidation and reduction. The photo catalytic activity of Bi_2O_3 NPs was assessed using BPB degradation under visible light irradiation at ambient temperature. Diluted the photo catalyst to a concentration of 0.2 g/100 mL before adding to a BPB solution with a 5 mg/L concentration. The solution was magnetically stir in the dark for half an hour to achieve a balance between the dye molecule states as well as the photo catalyst surface. The combination exposed to visible light irradiation from a filament light source of tungsten at a three-centimeter distance. An aliquot of 10 milliliters was taken every half an hour and centrifuged for 5 min at a speed of 3000 rpm, as illustrated in Figure 9, while the reaction mixture was continually stirred. Because of their large band gap and rapid charge

recombination, Bi_2O_3 photocatalytic activities are clearly good photo catalysts as well as degrade 98.35 percent of bromo phenol blue dye.

$$\text{Degradation efficiency (\%)} = \text{Co-C/Co} \times 100\%$$

5.6.1. Photodegradation Mechanism

The production of reactive species by the BPB dye in response to photon illumination led to the insertion of electrons back into the bismuth oxide NPs. This helped to produce superoxide radicals when there was available oxygen in the solution, which accelerated the photo degradation process. The photocatalytic degradation of the target dye is linked to the disintegration of the chromophoric group and the conversion of dye into low molecular weight byproducts. When dyes are exposed to visible light, electrons (e^-) and holes (h^+) are produced on the catalyst surface, which is the main factor in dye degradation. To create the OH radical, water molecules combine with holes (h^+). The O_2 molecule scavenges the electrons e and transfers them to OH using intermediates HOO and H_2O_2. The organic dye is non-selectively degraded into H_2O, CO_2, and inorganic ions by the potent oxidizing species known as OH. Three times the task was done under the exact identical experimental settings, and each time the standard deviation values were computed. Figure 10 shows the 98.35 percent degradation of the BPB dye under the 120-min radiation exposure. The kinetic study infers the pace of the order of the reaction, a positive slope and a rate constant of 0.03638 min^{-1} for bismuth oxide NPs. Bandgap, surface area, Light source, sizes, ion-releasing capability, dye concentration, pH, catalyst dose, and many other factors all affect the rate at which pollutants degrade.

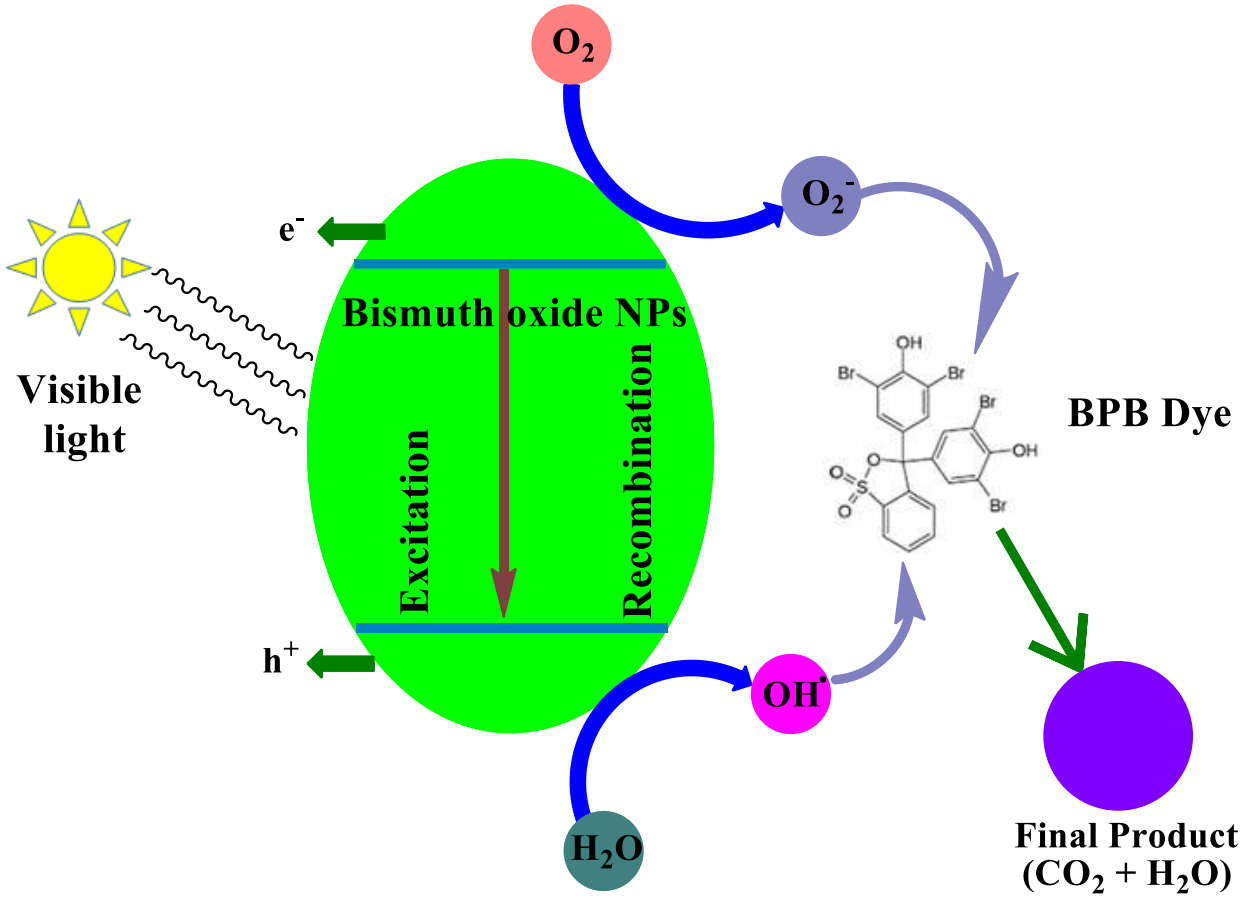


Figure 9. Photocatalytic BPB dye degradation mechanism of Bismuth oxide NPs.

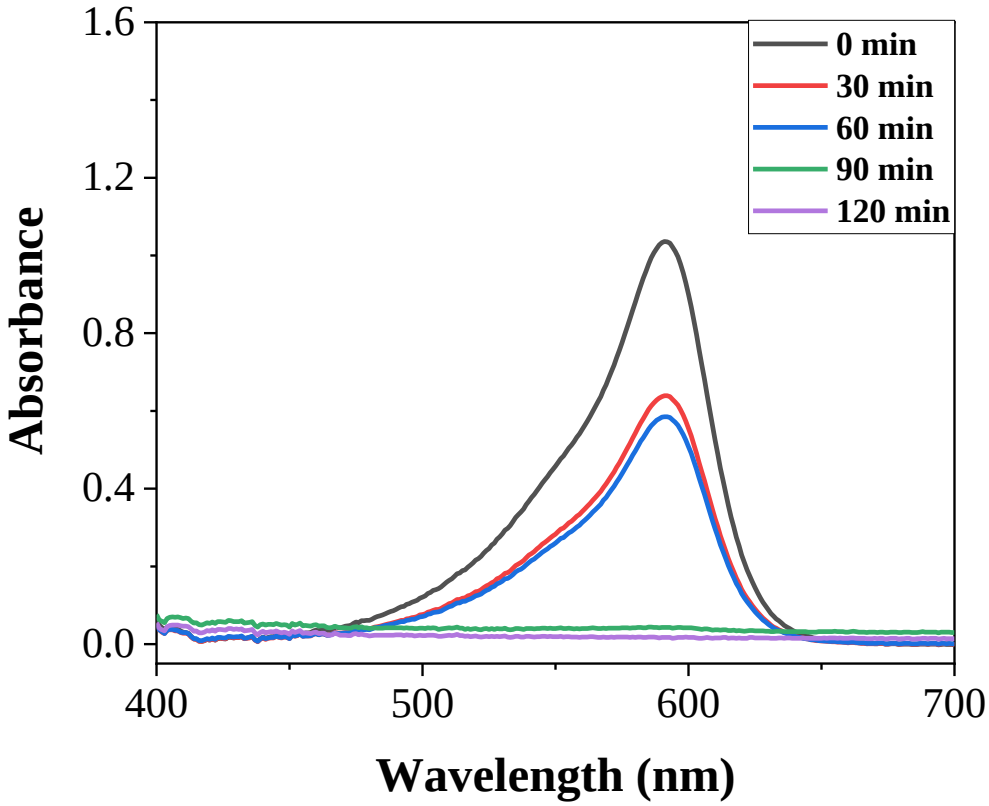


Figure 10. Bismuth Oxide nanoparticles photocatalytic degradation

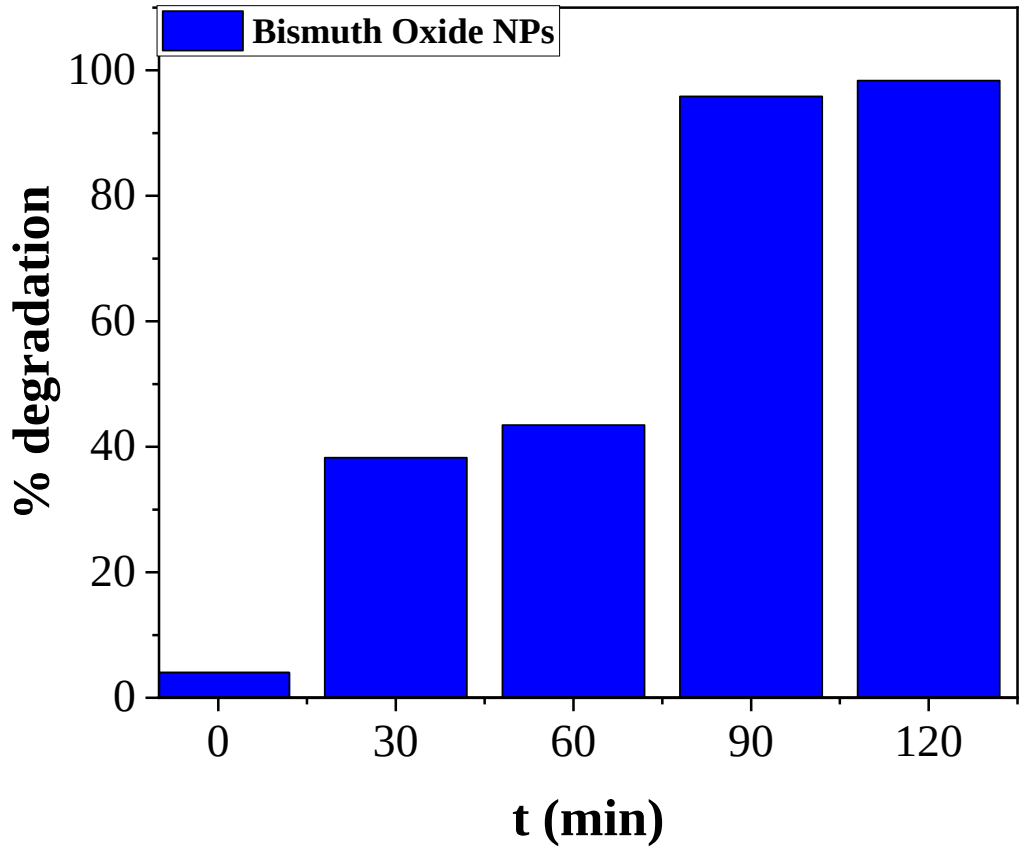


Figure 11. % Degradation of bismuth oxide nanoparticles

5.6.2. Effect of Catalyst dosage

The efficiency of photocatalytic destruction of pollutants is also greatly influenced by the mass of the photo catalyst. Up to a certain point, increasing the catalyst dose improves the efficiency of photocatalytic degradation of pollutants; but, beyond that point, increasing the catalyst dose slows down the rate of reaction. The rate of the reaction increases as more catalyst is used because more electron pairs are generated. Light can't reach the catalyst's surface as well when the catalyst dose is increased further because of the increased turbidity of the reaction mixture [38]. When the catalyst dose increases, the reaction rate slows. Increasing the catalyst dose from 50 mg to 200 mg resulted in a rise in photo degradation efficiency from 25% to 98.35%, but after that, raising the catalyst dose again had the opposite effect.

Dye bonding was broken, and the nanomaterial surfaces gained more active sites, thanks to the large surface area as well as OH radical productivities. High occupancy of the 300 mg of bismuth oxide NPs prevented light from moving in ways that would suppress the charge carrier multiplicity, limiting the effectiveness of electron mitigations from distinct bands. In order to enhance photocatalytic dye degradation, we produce 200 mg of bismuth oxide NPs.

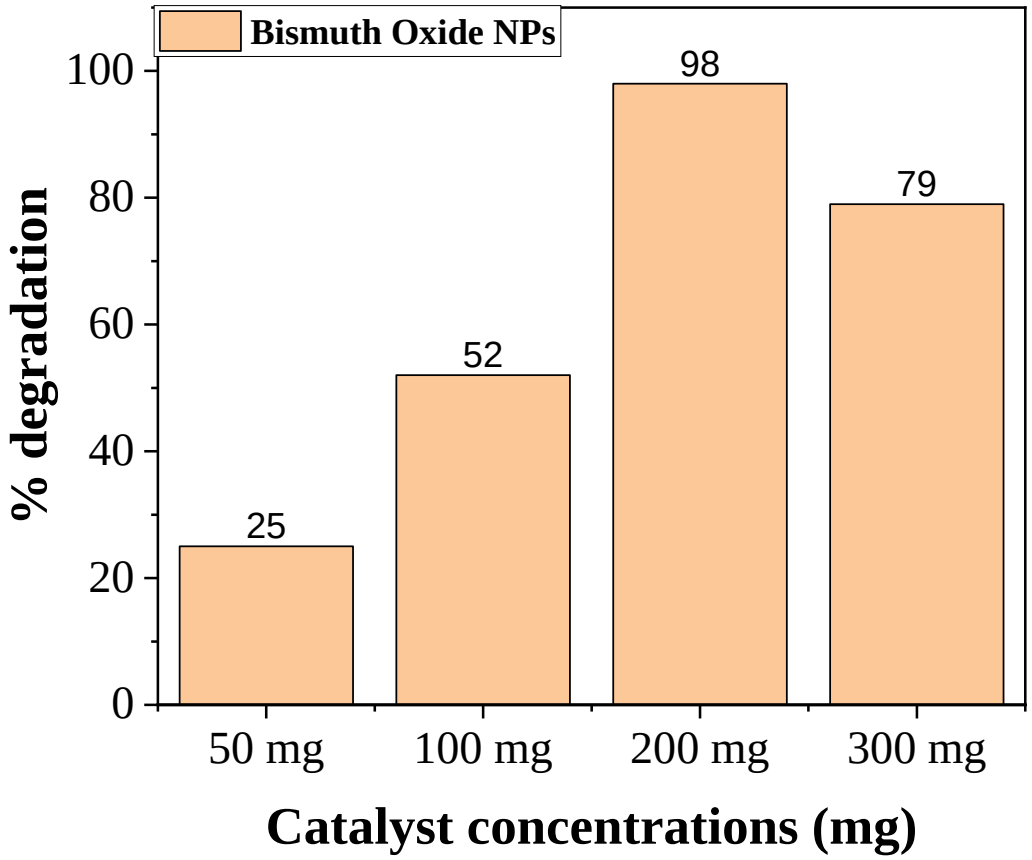


Figure 12. Effect of catalyst dosage on Bismuth oxide NPs.

5.6.3. Effect of Dye Concentrations

The adsorption of dyes on the surface of the photo catalyst is necessary for the process of photo catalysis to take place. In the process of photo catalysis, the quantity of dye that is adsorbed onto the surface of the photo catalyst is the only amount that contributes; the quantity that is present in the majority of the solution does not. The initial concentration of dye has a significant impact on

the amount of dye that can be adsorbed. In each particular photocatalytic process, the initial concentration of dye is an essential component that must be taken into consideration. In general, the percentage of degradation falls as the amount of dye concentration rises, provided that the amount of catalyst remains unchanged [39, 40].

This might be rationalized on the basis that as the dye concentration rises, a greater number of organic substances will be adsorbed on the surface of bismuth oxide NPs. On the other hand, a lower number of photons will be able to reach the catalyst surface, which will result in a lower formation of •OH and a lower degradation percentage. The photo degradation of bromophenol blue is illustrated in Figure 13 using a variety of photo catalysts. When there is a decrease in the concentration of dyes combined with the photo catalyst, the rate of photo degradation of the dyes increases.

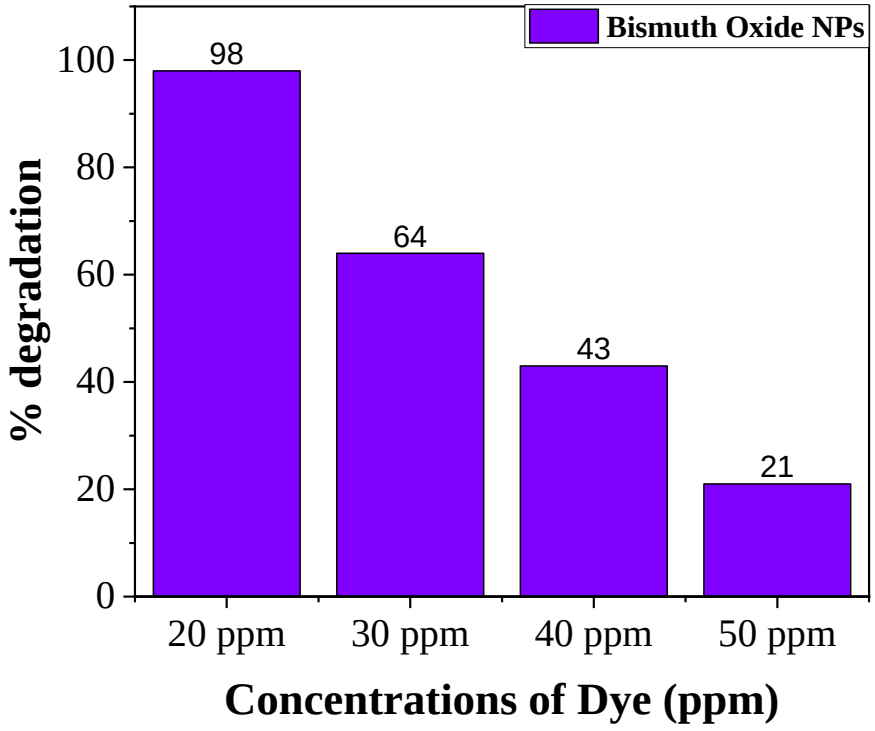


Figure 13. Effect of bromophenol blue dye concentrations on photo degradation.

6. Conclusion

The desired outcome of the synthesized bismuth oxide has been achieved by using a simple and effective hydrothermal method. The phase composition as well as crystallite size of the produced material are obviously influenced by the hydrothermal reaction's temperature and by the initial concentrations of bismuth nitrate, and the crystallite sizes of the bismuth oxide nanoparticles were also controlled by maintaining a range of 25.54 nm. A synthesized sample was examined using a number of methods, comprising UV-Vis, FTIR, XRD, EDX as well as SEM, in order to determine morphology, optical properties, as well as phase purity. The XRD analysis clearly demonstrated that the synthesized systems had a crystalline structure. The FTIR spectrum analysis identified the vibrations modes of Bismuth Oxide NPs. It was possible to investigate the optical properties of bismuth oxide by using UV-visible spectra. The ability of a photo-catalyst having bismuth oxide to remove bromophenol blue was tested. A photocatalyst made of bismuth oxide was what caused 98.35% of the BPB dye to degrade.

7. Future Perspectives

Since the scientific community has traditionally valued human life highly, attempts have been undertaken to develop conventional approaches to the evaluation and cure of a wide range of ailments. Despite the numerous efforts that have been taken, there are still numerous diseases that are hard to cure, including tumors, bacterial infections that are resistant to medication, heart conditions, various disorders of organ failure, which lead to a high annual mortality rate. Scientists working in the area of nanoscience are continually looking for potent particles which could result in the development of new medications and could aid in the primary detection as well as treatment of life-threatening illnesses as a viable remedy. Research is being conducted for these kinds of goals on a vast array of various organic and inorganic Nano carriers despite being in their development, bismuth oxide-containing NPs have recently attracted a lot of consideration as a scientific breakthrough for Bi_2O_3 medical applications. This is because (Bi_2O_3NPs) have outstanding features, such as strong diamagnetism, a large surface area, excellent stability, high electrical as well as magneto-resistance, desired catalytic activity, the simplicity of functionalization. In addition, in comparison to metals like silver, Bi_2O_3 is thought to be the least toxic as well as theoretically non-reactive heavy metals, which makes it further

suitable for in vivo applications. In experiments conducted in the lab, bismuth was found to stop the growth of malignant cells. The simplicity by which their particle shape as well as size could be regulated in the synthesis process is another benefit of Bi_2O_3 NPs. This benefit might create new opportunities for their possible medicinal uses in the future.

References

1. Salata, O.V., *Applications of nanoparticles in biology and medicine.* Journal of nanobiotechnology, 2004. **2**(1): p. 1-6.
2. Hamza, M., S. Muhammad, and S.J.A.S.A.P. Zahoor, *Biologically synthesized zinc oxide nanoparticles and its effect-a review.* 2022. **2**(9).
3. Zahoor, S., et al., *Biosynthesis and Anti-inflammatory Activity of Zinc Oxide Nanoparticles Using Leaf Extract of Senecio chrysanthemoides.* 2023. **2023**.
4. Hamza, M., et al., *Catalytic removal of alizarin red using chromium manganese oxide nanorods: degradation and kinetic studies.* 2020. **10**(10): p. 1150.
5. Kang, Y.S., et al., *Synthesis and characterization of nanometer-size Fe3O4 and γ-Fe2O3 particles.* Chemistry of Materials, 1996. **8**(9): p. 2209-2211.
6. Pankhurst, Q.A., et al., *Applications of magnetic nanoparticles in biomedicine.* Journal of physics D: Applied physics, 2003. **36**(13): p. R167.
7. Dobson, J., *Gene therapy progress and prospects: magnetic nanoparticle-based gene delivery.* Gene therapy, 2006. **13**(4): p. 283-287.
8. Rudge, S., et al., *Adsorption and desorption of chemotherapeutic drugs from a magnetically targeted carrier (MTC).* Journal of Controlled Release, 2001. **74**(1-3): p. 335-340.
9. Appenzeller, T., *The Man Who Dared to Think Small: In a visionary lecture 32 years ago, Richard Feynman predicted many of the advances that are the subject of this special section of Science—and foresaw their implications.* Science, 1991. **254**(5036): p. 1300-1300.
10. Wang, C., et al., *Electronic Transfer Enhanced Fishnet-Like Coxp Loaded Ru Nanoclusters as Efficient Catalyst for Hydrogen Generation Via Nabh4 Hydrolysis.*
11. Mody, V.V., et al., *Introduction to metallic nanoparticles.* Journal of Pharmacy and Bioallied Sciences, 2010. **2**(4): p. 282.

12. Yang, C.-W., et al. *Holey Bismuth for Selective Electrochmical CO2 Reduction*. in *Electrochemical Society Meeting Abstracts 235*. 2019. The Electrochemical Society, Inc.
13. Wang, Y., J. Zhao, and Z. Wang, *A simple low-temperature fabrication of oblique prism-like bismuth oxide via a one-step aqueous process.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2011. **377**(1-3): p. 409-413.
14. Monnereau, O., et al., *Synthesis of Bi2O3 by controlled transformation rate thermal analysis: a new route for this oxide?* Solid State Ionics, 2003. **157**(1-4): p. 163-169.
15. Gujar, T., et al., *Electrosynthesis of Bi2O3 thin films and their use in electrochemical supercapacitors.* Journal of power sources, 2006. **161**(2): p. 1479-1485.
16. Zhang, L., et al., *Sonochemical synthesis of nanocrystallite Bi2O3 as a visible-light-driven photocatalyst.* Applied Catalysis A: General, 2006. **308**: p. 105-110.
17. Skorodumova, N.V., et al., *Random conductivity of δ-Bi 2 O 3 films.* Applied Physics Letters, 2005. **86**(24): p. 241910.
18. Gotić, M., S. Popović, and S. Musić, *Influence of synthesis procedure on the morphology of bismuth oxide particles.* Materials letters, 2007. **61**(3): p. 709-714.
19. Anilkumar, M., R. Pasricha, and V. Ravi, *Synthesis of bismuth oxide nanoparticles by citrate gel method.* Ceramics international, 2005. **31**(6): p. 889-891.
20. Yang, Q., et al., *Hydrothermal synthesis of bismuth oxide needles.* Materials letters, 2002. **55**(1-2): p. 46-49.
21. De Sousa, V.C., M.R. Morelli, and R.H. Kiminami, *Combustion process in the synthesis of ZnO–Bi2O3.* Ceramics International, 2000. **26**(5): p. 561-564.
22. Madathil, A.N.P., K. Vanaja, and M. Jayaraj. *Synthesis of ZnO nanoparticles by hydrothermal method*. in *Nanophotonic materials IV*. 2007. SPIE.
23. Cheng, H., et al., *Synergistic effect of crystal and electronic structures on the visible-light-driven photocatalytic performances of Bi 2 O 3 polymorphs.* Physical Chemistry Chemical Physics, 2010. **12**(47): p. 15468-15475.
24. Hu, J., et al., *Enhanced photocatalytic activity of Bi2O3 under visible light irradiation by Cu (II) clusters modification.* Applied Catalysis B: Environmental, 2013. **142**: p. 598-603.
25. Kim, D.S. and Y.S. Park, *Photocatalytic decolorization of rhodamine B by immobilized TiO2 onto silicone sealant.* Chemical Engineering Journal, 2006. **116**(2): p. 133-137.

26. Habib, M.A., et al., *Synthesis and characterization of ZnO-TiO2 nanocomposites and their application as photocatalysts.* International Nano Letters, 2013. **3**(1): p. 1-8.
27. Xie, T., et al., *Novel heterojunction Bi2O3/SrFe12O19 magnetic photocatalyst with highly enhanced photocatalytic activity.* The Journal of Physical Chemistry C, 2013. **117**(46): p. 24601-24610.
28. Schlesinger, M., et al., *Metastable β-Bi2O3 nanoparticles with potential for photocatalytic water purification using visible light irradiation.* ChemistryOpen, 2013. **2**(4): p. 146-155.
29. Raza, W., et al., *Facile fabrication of visible light induced Bi2O3 nanorod using conventional heat treatment method.* Journal of Molecular Structure, 2016. **1107**: p. 39-46.
30. Liu, X., et al., *Visible light-induced photocatalytic activity of Bi2O3 prepared via microwave-assisted method.* Journal of Nanoscience and Nanotechnology, 2013. **13**(7): p. 5044-5047.
31. Raza, W., et al., *Synthesis, characterization and photocatalytic performance of visible light induced bismuth oxide nanoparticle.* Journal of Alloys and Compounds, 2015. **648**: p. 641-650.
32. Iyyapushpam, S., S. Nishanthi, and D.P. Padiyan, *Photocatalytic degradation of methyl orange using α-Bi2O3 prepared without surfactant.* Journal of Alloys and Compounds, 2013. **563**: p. 104-107.
33. Sivaraj, D., et al., *Graphene oxide reinforced bismuth titanate for photocatalytic degradation of azo dye (DB15) prepared by hydrothermal method.* Ceramics International, 2021. **47**(17): p. 25074-25080.
34. Amano, F., K. Nogami, and B. Ohtani, *Enhanced photocatalytic activity of bismuth-tungsten mixed oxides for oxidative decomposition of acetaldehyde under visible light irradiation.* Catalysis Communications, 2012. **20**: p. 12-16.
35. Xiao, X., et al., *Facile large-scale synthesis of β-Bi2O3 nanospheres as a highly efficient photocatalyst for the degradation of acetaminophen under visible light irradiation.* Applied Catalysis B: Environmental, 2013. **140**: p. 433-443.

36. Ai, Z., et al., *Monoclinic α-Bi2O3 photocatalyst for efficient removal of gaseous NO and HCHO under visible light irradiation.* Journal of Alloys and Compounds, 2011. **509**(5): p. 2044-2049.
37. Ismail, M., et al., *Green synthesis of zerovalent copper nanoparticles for efficient reduction of toxic azo dyes congo red and methyl orange.* Green processing and synthesis, 2019. **8**(1): p. 135-143.
38. Saeed, M., et al., *Photocatalysis: An effective tool for photodegradation of dyes—A review.* 2022: p. 1-19.
39. Azad, K. and P.J.C.S.J. Gajanan, *Photodegradation of methyl orange in aqueous solution by the visible light active Co: La: TiO2 nanocomposite.* 2017. **8**(3): p. 1000164-1000174.
40. Reza, K.M., A. Kurny, and F.J.A.W.S. Gulshan, *Parameters affecting the photocatalytic degradation of dyes using TiO 2: a review.* 2017. **7**: p. 1569-1578.