ZIBELINE INTERNATIONAL PUBLISHING

**ISSN: 2576-6724 (Print)**
**ISSN: 2576-6732 (Online)**
**CODEN: ACMCCG**

## Acta Chemica Malaysia (ACMY)

*DOI: http://doi.org/10.26480/acmy.02.2023.83.88*

CrossMark

*RESEARCH ARTICLE*

# NANOSIZED NICKEL SULFIDE PHOTOCATALYST FOR REMOVAL OF ORGANIC DYES FROM TEXTILE WASTEWATER

**Usman Mureed[a*], Zohaib Saddique[a,b] , Fakhra Asad[c], Kiran Asad[a]**

[a]Department of Chemistry, University of Education, Lahore, Pakistan
[b]School of Chemistry, University of the Punjab, Lahore, Pakistan
[c]Department of Environmental Sciences, Bahauddin Zakariya University, Multan, Pakistan
[*]Corresponding Author Email: usmankhosa77@gmail.com



**ARTICLE DETAILS**

*Article History:*

Received 14 August 2023
Revised 18 September 2023
Accepted 21 October 2023
Available online 11 November 2023

**ABSTRACT**

Nanotechnology is interdisciplinary concept involving different field of life and providing tailored solution in each problem. Environmental pollution in the form of textile wastewater dyes is one of them. Herein, we report cost effective and cheap hydrothermal synthesis of nanosized NiS NPs and their employment for degradation of MB and MO. Microscopic analysis informed us about size of Nanoparticles which is in the range of 25-30 nm and offer a lot of active surface area. Formation of NPs is confirmed by UV-Vis spectra by presence of narrow absorbance peak around 220 nm and DRS informed us its band gap energy about 3.63 eV. Synthesized photocatalyst degraded 88% of MB and 84 % of MO under photocatalytic chamber and comparable degradation under sunlight. Further tuning of band gap can lead to higher performance of photocatalyst for industrial scale application. Nevertheless, these materials possess promising potential for future applications like wastewater treatment and self-cleaning textiles.

**KEYWORDS**

Photocatalysis, NiS, Environmental Remediation, Wastewater, MB, MO

## 1. INTRODUCTION

Nanoscience is interdisciplinary science involving concepts of physics and chemistry in particular and biology, biotechnology, and structural science in general (G.L. Hornyak et al., 2008) Chemists and chemistry are playing leading role in Nanoscience and nanotechnology by producing new material by joining atom from diverse group to create novel materials for advance technologies. Bucky balls, quantum dots, phase-separated polymers and self-assembled mono-allays are few example of nanomaterial that are produce as result of chemical process done by a chemist (Whiteside, 2005).

Nanomaterial are the materials having at least one dimension in the range of nanometer (1 nm= $10^{-9}$ m). There structural properties are between those of atoms and bulk materials of given element. Morphology of Nanomaterials has important rule in their function. Classifying them on the base of dimension is very useful in understanding their functionality. Nanoparticles are particles having at least one dimension in <100nm range (Biswas et al., 2005). Properties of Nanoparticles are significantly different than their bulk materials even some times completely opposite properties are exhibited (Batista et al., 2015). Nanoparticle's physical and chemical properties are not only dependent of chemical composition of materials. Properties also depend upon size, shape and structure of Nanoparticles. Some metal sulfides nanoparticles are explaining below.

Zinc sulfide nanoparticles are important semiconductors with band gap of 3.7 eV. They are versatile nanoparticles being used in diverse industries such as optoelectronic industry. They are widely used in laser technologies and light emitting diode technologies (Moore et al., 2006). Copper sulfide Nanoparticles are important semiconductors. They are being used in lithium ion batteries. Optical material constitutes major part from copper sulfide nanoparticles

Nickel sulfide nanoparticles are important hydrodesulphurization catalyst due their useful stability. They are used in semiconductor industry because they are excellent transformation and toughening agent and can be used as coatings of semiconductors. Nickel sulfide is important part of photo galvanic cell and act as cathode in lithium ion batteries. Nickel Sulfide Nanoparticle is a good metallic conductor with a room temperature resistivity of about 1.8 x$10^5$ μcm leading to ease in transportation for lithium ions and electrons. They are also used for hydrogen storage (Cao et al., 2010; Zhang et al., 2010).

Synthesis of Nanoparticles refer to creation of NPs by applying different techniques. There are several strategies to synthesize NPs and these techniques are broadly classified into three kinds that are (1) physical, (2) chemical and (3) biosynthesis. Attrition and pyrolysis are usually acknowledged strategies used for synthesis of nanoparticles. There are problems and limitations in all synthesis strategies. The limitations of physical synthesis are expensive methods, a lot of energy and time input and slow methods. Chemical synthesis used for preparation Nanomaterials include sol-gel method, wet chemical strategies and their limitation includes toxicity to the environment and less success probability for living organisms. To cope with these limitation and harmful effects scientists worked for developing several biological strategies for speedy, less harmful and cost economical synthesis of Nanoparticles. These methods are way forward to more secure and effective cost managing methods and chemical techniques. In biological systems such as flowers, microorganisms and algae can produce important and useful nanoparticles by means of producing beneficial secondary metabolites.

| Quick Response Code | Access this article online | |
|---|---|---|
| | **Website:** www.actachemicamalaysia.com | **DOI:** 10.26480/acmy.02.2023.83.88 |

Cite the Article: Usman Mureed, Zohaib Saddique, Fakhra Asad, Kiran Asad (2023). Nanosized Nickel Sulfide Photocatalyst for Removal of Organic Dyes from Textile Wastewater. *Acta Chemica Malaysia, 7(2): 83-88.*

Molecules produced by microorganisms and algae helps in stabilizing and synthesizing Nanoparticles. For exquisite and exceptional characteristics possessing nanoparticles, cellular extract from living organism is useful foundation material. Biological synthesizing techniques outline a variety of ecofriendly methods with low manufacturing cost and minimal time consumption (Thakkar, 2010).

Being result of an interdisciplinary science Nanoparticles are applied and being tested in various field of life. Scientist are expecting such contribution from them that can solve today's challenges to the humanity. A few applications are presented here.

There are a lot of industries that are using nanoparticles in improvement of their product by cost and performance such as use in sunscreen for better transparency and long lasting quality, skin penetrating cosmetics are being made from Nanoparticles that act effectively with less harm. Cosmetics companies are pursuing research on nanoparticles for improvement of their products for skin, environment and by cost. Nanoparticles surface filler and surface smoothing agent are being made and introduced in paint and finishing industry to give better look and attraction to substrate. Due to behavior shown by NPs while interacting with energy, matters and radiation, NPs are of good used in optical instrument production industry, energy producing areas such as solar cells and in diagnostic for different medical tests.

Metal sulfides nanoparticles have novel electronic properties and due to these interesting properties, they have potential to be used for more advance technological applications, this whole family have interesting features (An, 2006). Nickel sulfide is member of this family of metal sulfide and this member is getting much attention due to its potential application for transformation toughening agent in materials for semiconductor, catalyst and cathode of lithium-ion batteries (Fazli et al., 2016; Han et al., 2003). Various method has been used to produce different shapes of nickel sulfide Nanoparticles such as Nanospheres, Nanorods, Nanoprism, Nanoneedles, Hollowspheres, flower-like architectures, urchin-like Nanocrystallines, layer-rolled structures till now (Zhang, 2012). This form of nanoparticles can be obtained by using different methods such as hydrothermal synthesis, solvothermal synthesis, molecular process and precipitation routes (Salavati-Niasari, et al., 2013).

Various method has been used to prepare Nanoparticles of nickel sulfide and few are briefed here.

In solvo-thermal method sulfur (S) and nickel (Ni) are added in Teflon lined stainless steel autoclave and this autoclave is filled with ethane to 80% of its total capacity and then stirred for 15 min. Then this autoclave is sealed and maintained at 200$^{o}$C for 28 hours. After 28 hours, autoclave is gradually cooled to room temperature and precipitates having color black are collected from the bottom of autoclave and these precipitates are washed repeatedly with deionized water and alcohol to remove any organic or inorganic impurity. After purification, product is maintained in 50$^{o}$C for 6 hours and final product is obtained. For confirmation of desired product, characterization tests are run using different electroscopic and X-ray techniques. This method is commonly used to produce flower like nanoparticles of NiS (Yang, 2009).

Flower like alpha- NiS Nanoparticle are also prepared by hydrothermal method. In this method allyl thiourea ($C_4H_8N_2S$) and Nickel sulfate ($NiSO_4$) are mixed with deionized water, stirred vigorously. Then this solution is shifted to Teflon-lined stainless-steel autoclave of suitable capacity. Then system is kept at 170$^{o}$C for 10 h. then precipitates are obtained from the bottom of autoclave and washed with deionized water and ethanol repeatedly to remove any type organic and inorganic impurities in product. Final product is kept at 60$^{o}$C for 3 hour (Tang, 2011).

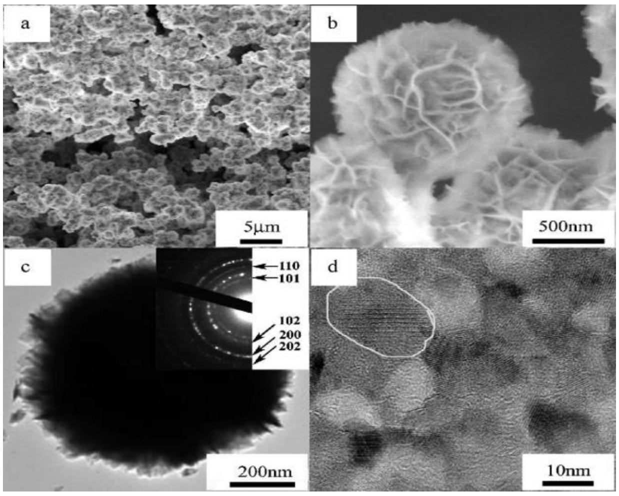


**Figure 1:** (a), (b) Typical SEM images of the -NiS flowers at different magnifications, (c) TEM images of a -NiS flower and the corresponding SAED and (d) HRTEM image of nanoflake (Tang, 2011).

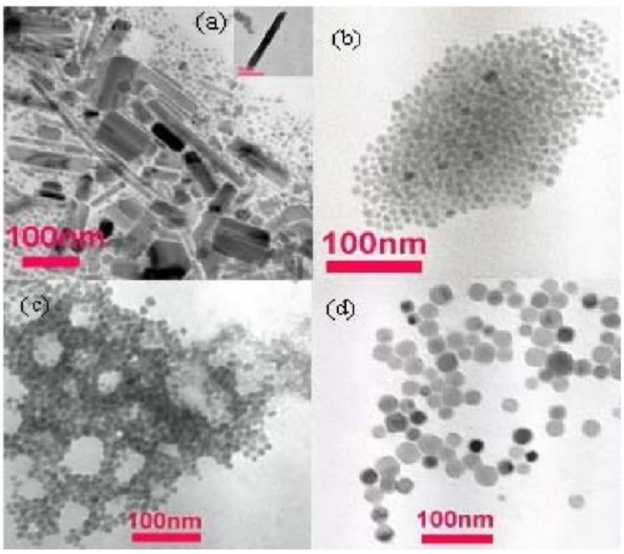


**Figure 2**: (TEM) showing prepared nanoparticles of nickel sulfide using molecule precursor (a) mixture of long, selender and short, stout microcods, (b) mixture of cubes and polyhedrons, (c) nanocubes (d) regular size cubes (Tian, 2009).

Cite the Article: Usman Mureed, Zohaib Saddique, Fakhra Asad, Kiran Asad (2023). Nanosized Nickel Sulfide Photocatalyst for Removal of Organic Dyes from Textile Wastewater. *Acta Chemica Malaysia, 7(2): 83-88*.

NiS Nanoparticles can also be fabricated by using molecular precursor technique. In this, precursor molecule is [(TMEDA) Ni (SC {O} $C_6H_5)_2$] and this is dissolved immediately after formation in DT to form green solution. This solution is degassed for about 15 minutes and then heated at 180°C for 1 hour under nitrogen atmosphere. At the end black precipitates are formed and this is added with small amount of toluene and large amount of ethanol (EtOH) and then placed in centrifugal machine to separate out nickel sulfide Nanoparticles (Tian, 2009).

Nickel sulfide Nanoparticles are being tested for use in lithium ion batteries due to their reversibility and high capability as an electrode and so far this experiments is standing successful. Nickel sulfide Nanoparticles are also being investigated for enhancement of battery capacity and increase conduction in lithium batteries. Due to its low cost, easy and diverse method of preparation and abundance of raw material for preparation Nickel Sulfide Nanoparticles are used in hydrogen evolution reactions (HER) as catalysts. Researches demonstrated its success by both economically and costly as catalyst in hydrogen evolution reaction (HER) and it is more viable than platinum used as catalyst in same reaction. Lithium sulfur battery is modern generation secondary battery that is in process of prefect development and in this battery sulfur is used as cathode and this battery promise theoretically high energy density. In this battery nickel sulfide nanoparticle act as host material and can be used as stabilizer in same battery. Water molecule is split for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) and this splitting face problem due to instability of catalyst used for this and high cost of some catalysts. Nickel sulfide Nanoparticles are excellent and effective electrocatalysis for production of oxygen by splitting of water. Nickel sulfide Nanosheets arrays are excellent catalysts for water splitting for OER and HER within economical cost. Nickel sulfide Nanoparticles have rich redox chemistry and high electrical conductivity and due to these properties these are ideal for super capacitor materials and these are being tested for commercial use. In hydrogenation of chlorobenzene and nitrobenzene, Nickel Sulfide Nanoparticles are used, for selective hydrogenation of chlorobenzene flower like Nanoparticles of nickel sulfide with petal and spikes are excellent catalyst and produce desired product in fine quality. Flower like Nanoparticles of nickel sulfide exhibit excellent conductivity toward hydrogen peroxide and glucose and therefore they can have used in sensor for detection and measurement of peroxides and glucose in any solution (Pan, et al, 2015; Liu, et al., 2016; Idris et al., 2011; Wang et al., 2015; Zhang et al., 2015; Ji et al., 2-16; Cao, et al., 2010; Li et al., 2016; Wu et al., 2016; Feng et al., 2015)

Photocatalysts absorb light photons and participate in the chemical reactions of reactants repeatedly engaging with them in temporary interactions and regenerate their chemical composition after each cycle of interactions. These are typically made up of metal sulfides, metal oxide, oxysulfides, oxynitride and their composites. A photocatalyst is defined as a substance which is activated by adsorbing a photon and is capable of accelerating a reaction without being consumed. These substances are invariably semiconductors (Umar, 2013).

There are several known factors that can affect Photocatalysis process, a few are briefly explained here. Pace of Photocatalysis increase with amount of photocatalyst in process. This is due to exposure of more active site of photocatalyst to light and more formation of radicles and positive holes and these radicles and positive hole participate in the photocatalytic process and resulting in increase of Photocatalysis. (Gusain et al., 2020; Sohrabnezhad et al., 2009). pH of reaction medium effect significantly the speed of reaction. pH of medium affects surface charge, agglomeration, amount of absorption of substrate and formation of radicals and positive holes in the process. By influencing all these steps PH can affect the whole speed of Photocatalysis. Increase in PH of medium increase the isoelectronic point of Photocatalyst and inducing negative charge on the surface of photocatalyst and attracting positive substance present in the medium ultimately hindering the process of Photocatalysis (Venkatachalam, N.

2007). Photocatalysis speed can be enhanced by delaying recombination period of electrons and positive holes in the reaction under illumination of solar light. Oxidants are foreign agents that are added as irreversible electron acceptor to induce wide gap in ratio of electrons and holes and induce production of radicals to increase the photocatalytic reaction speed. Oxidants can enhance speed of Photocatalysis by delaying recombination time of electrons and positive holes, creating more radicals and producing oxidizing species to increase oxidation of substrate (Wang, 1999; Gusain, et al., 2020).

Evolution of hydrogen from splitting of water using photocatalyst is promising way for ending global energy environmental problem. Nickel sulfide is not only cheap but good photocatalyst in Photocatalysis of water for production of hydrogen. Photocatalysis Capacity of titanium oxide and cadmium sulfide Nanoparticles can be enhanced loading them with nickel sulfide. Biodegradation using Photocatalysis of organic substance in water can be catalyzed by nickel sulfide Nanoparticles and there are promising results. (Zhang, et al., 2012).

## 2. Experimental Work

### 2.1 Synthesis of NiS Nanoparticles

1.1 mg of allyl thiourea (Sigma Aldrich, 99.9%) was taken to prepare 1M solution in 100 ml beaker. 1.06 mg of nickel sulfate (Sigma Aldrich, 98%) was used to prepare 1 M solution in 100 ml beaker. Added both prepared solution to 50 ml deionized water (Spelco, 99,98%) and stirred vigorously using magnetic stirrer for about 10 minutes. Solution was shifted in Teflon-line stainless steel autoclave of 65 ml capacity and it was sealed tightly. This autoclave was put into a heating oven and temperature was set to 170°C for 10 hours. After 10 hours autoclave was taken out of heating oven and temperature was reduced naturally and removed out the precipitate from autoclave. Precipitates were washed with deionized water (Spelco, 99,98%) and absolute ethanol (Sigma Aldrich, 99.9%) multiple times and then dried using filter paper. After drying, these particles were placed in 60°C for 3 hours. Final product was obtained for further studies.

### 2.2 Photocatalytic Activity

Distilled water (Sigma Aldrich, 99.9%) was taken in 200 ml beaker and about 10 mg methylene blue was added in it. The ratio used for methylene blue (MB) aqueous solution was 50mg/L. This aqueous solution of methylene blue was added to photocatalytic reactor. In this solution 40 mg of self-prepare Nickel Sulfide Nanoparticles were dispersed. UV lamp of 250 W was used as source of light in this experiment. After every 20 minutes sampling was done during illumination and UV-Vis spectra of solution was obtained. Similar procedure was followed while investigating degradation of MO. Two different reaction conditions were employed for degradation i.e. under sunlight and under photocatalytic chamber.

## 3. Results and Discussion

Synthesized photocatalyst is analyzed to determine morphology and size of NPs, Figure 3 presents TEM analysis of NiS at resolution of 100 nm. Deduced size from TEM image is estimated to be within the range of 25-30 nm, which is highly desirable for excellent photocatalytic activity owing to increase surface area and active sites with this small size. 3D image shows presence of uniformed size NPs with similar all three dimensions and black parts indicate presence of space among NPs and it proof absence of aggregation of NPs. Event profile is measure of ups and downs on uniformly dispersed NPs and in this case it provides excellent event profile for a photocatalytic process. Figure 3 (d) shows topographic profile of photocatalyst which is reconstructed from 2D image it clearly shows that topography of NPs surface is highly recommended for degradation of dyes in textile wastewater. In photocatalytic process, size and surface area are main factor that determines the properties of nanosized photocatalyst. In this case, TEM analysis obviate the presence of highly desirable physical and morphological features in NiS NPs that are instrumental in degrading organic dyes from textile wastewater.

Optical properties of photocatalyst are also important along with physical features for photocatalytic activity. Figure 4 presents UV-Vis and DRS spectra of synthesized NiS NPs recorded after suspending NPs in deionized water after through sonication. UV-Vis spectra informs us about formation of materials and it also indicates size distribution and uniformity of particles. In this case, observation of UV absorbance peak around 220 nm indicates formation of nanosized photocatalyst while width of absorption peak is proof of formation of narrow sized particles with highly uniform distribution. Optical band gap energy of semi-conductor based photocatalyst is important factor that drive photocatalytic property of nanosized photocatalyst. Band gap energy is determined by UV DRS, Figure 4 (b) presents DRS of self-prepared NiS NPs and estimated band gap for photocatalyst is around 3.63 eV. Optical band gap energy is minimum energy required to initiate a photocatalytic reaction through excitation of electron from valence band to conduction band and it is calculated through Tauc plot equation as provided

$$a\,h\,v = A\,(hv - Eg)^{1/2}$$

Where a is absorption coefficient, h is Planck's constant, v is frequency of light, Eg is band gap energy and A is proportional constant. In this case band gap energy of 3.63 eV means absorption edged is around 340 nm in wavelength.

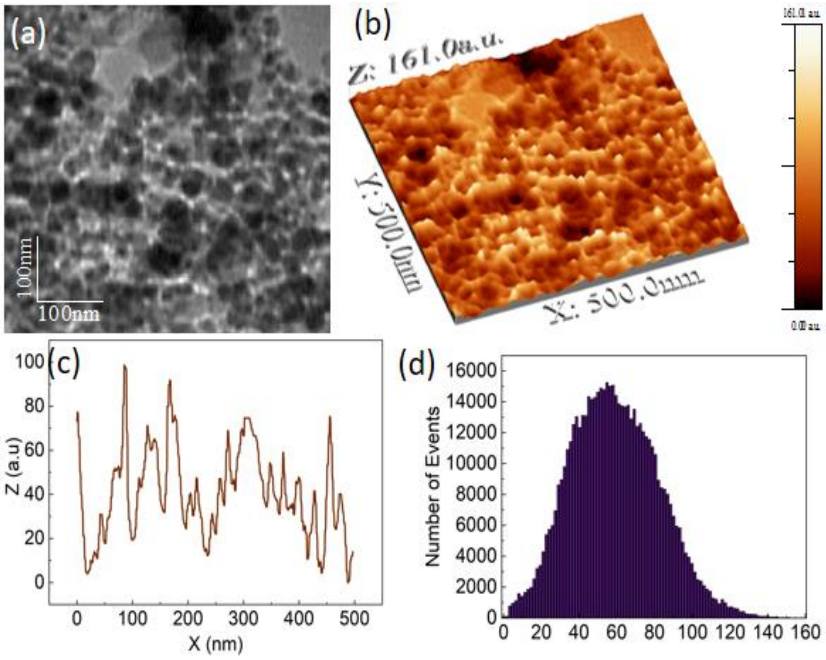


**Figure 3:** TEM analysis of self-prepared NiS NPs; (a) 2D image of NPS showing morphology, (b) 3D image with scale bare showing 3D size of NPs, (c) Event profile of photocatalyst material demonstrating uniformity and absence of aggregation, and (d) Topographic analysis of photocatalyst surface.

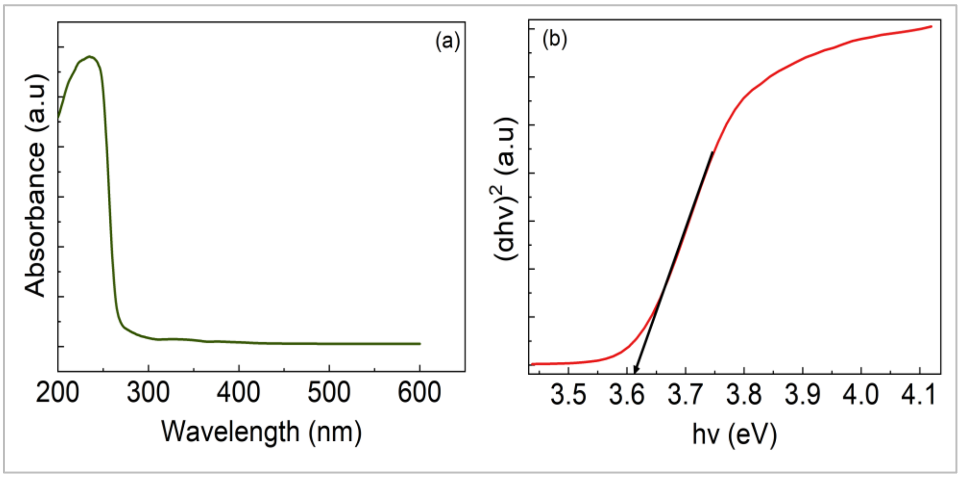


**Figure 4:** Optical analysis of synthesized NiS NPs; (a) UV spectra of photocatalyst proving formation and (b) diffuse reflectance spectra (DRS of photocatalyst for calculation of band gap energy.

For investigation of photocatalytic activity of self-prepared nanosized photocatalyst, two model pollutants were degraded in two different environments. Owing to abundance of methylene blue (MB) and methyl orange (MO) in textile wastewater, these two are degraded in the presence of sunlight and photocatalytic chamber. Figure 5 presents photocatalytic degradation of MB in two different conditions, i.e, in sunlight and photocatalytic chamber. Degradation is observed by UV spectra as MB gave absorbance around 664 nm and with decreasing concentration intensity of the absorbance peaks decrease due to degradation. Under sunlight, photocatalyst is able to remove MB gradually for 60 mins and then there is abrupt change in absorbance spectra that indicate higher rate of degradation which is attributed to highest adsorption level leading to higher rate of degradation. After 60 mins, there is again gradual degradation till 140 mins with overall degradation of 84 % of initial concentration of organic dye. Figure 5 (b&d) present MB photocatalytic degradation under photocatalytic chamber. In photocatalytic chamber UV-simulated light is provided for initiation of reaction and results indicate there is gradual degradation of organic pollutant MB with linearity in degradation slope. This behavior under photocatalytic chamber is attributed to higher and uniform response of photocatalyst toward UV light owing to its band gap energy of 3.63 eV, which lies in UV region. Under photocatalytic chamber, NiS photocatalyst showed 4% degradation of MB as compared to that under sunlight.

Methyl orange is the second most utilized organic dye in textile industry, we selected it to investigate photocatalytic properties of nanosized photocatalyst based in NiS NPs. Degradation of MO is observed through UV absorbance spectra after every interval of 20 min and decrease in intensity of absorbance peaks around 464 nm is decreased. This experiment is performed under two conditions, i.e. under sunlight and under sunlight simulated photocatalytic chamber. Figure 6 present photocatalytic degradation of MO under sunlight (a &c) and in photocatalytic chamber (b & d). under sunlight photocatalyst degraded MO gradually for and response is recorded after every interval of 20 min. After 140 min photocatalyst showed degradation of around 60 % and this sort of degradation behavior is attributed to band gap of semi-conductor based photocatalyst. Similarly, when degradation is performed in photocatalytic chamber, degradation efficiency increased up to 84 %. In photocatalytic chamber major portion of light is provided in UV region which is highly recommended for this sort of photocatalyst having band gap of 3.63 eV. Nevertheless, recorded degradation efficiency is comparable and further optimization can lead to its applications at industrial scale with cost effectiveness.

To conclude and optimize best condition for application of nanosized NiS photocatalyst for degradation of organic dyes in textile waste water and comparative graph is presented in Figure 7 where graph (a) present comparison of different condition for degradation of MB and resultantly, NiS showed better photocatalysis performance under photocatalytic chamber as compared to under sunlight. Similar behavior is observed in degradation of MO where NiS photocatalyst showed higher degradation efficiency in photocatalytic chamber. This feature is attributed to band gap energy of NiS which lies in UV region and chamber provided maximum portion of UV light. Nevertheless, synthesized Photocatalyst is cost effective and cheap and it has potential application in wastewater treatment technologies and self-cleaning textiles.

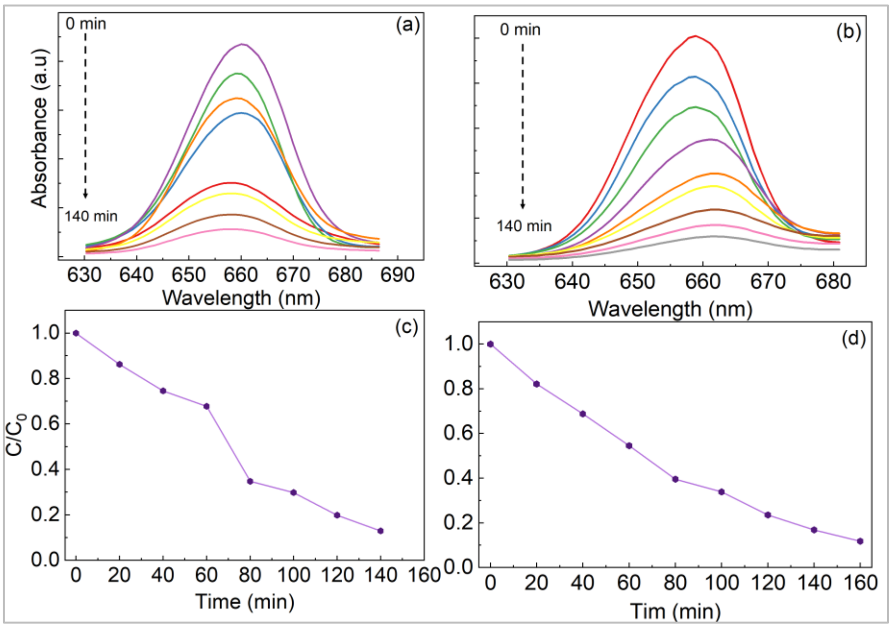


Figure 5: Investigation of photocatalytic degradation activity of self-prepared nanosized photocatalyst against MB in two different environmental conditions; (a) UV absorbance spectra of MB during degradation process for 140 minute with interval of 20 mins under sunlight, (c) degradation activity after different interval and (b) under photocatalytic chamber degradation efficiency MB after interval of 20 mins and (d) degradation activity graph after interval of 20 mins.

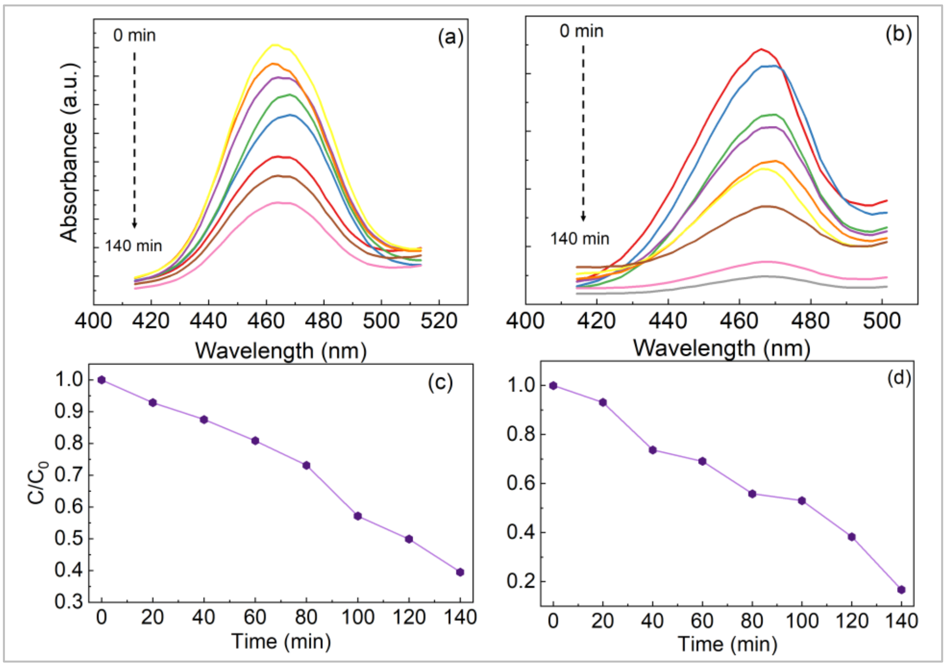


**Figure 6:** Photocatalytic removal of MO by NiS photocatalyst under (a) sunlight with degradation activity in (c) and (b & d) removal under photocatalytic chamber.

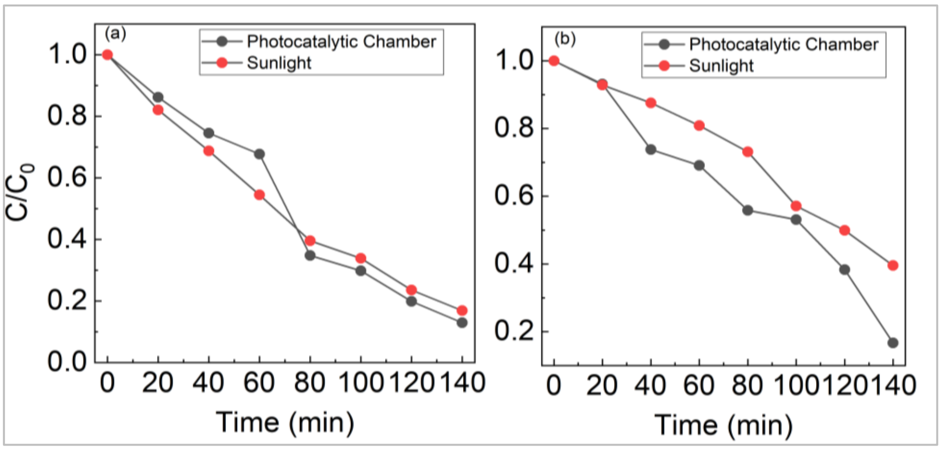


Figure 7: Comparison of photocatalytic performance of nanosized NiS photocatalyst under two different conditions for two different organic dyes. (a) Degradation of MB under photocatalytic chamber and sunlight, (b) degradation of MO under sunlight and photocatalytic chamber.

## 4. Conclusion

Nanotechnology has been playing important role in providing solution to challenges faced by world. Environmental pollution in the form of abundance of organic dyes in textile wastewater is one of them. To provide solution to this problem we adopted a cheap and cost effective method for synthesis of NiS NPs and employed for photocatalytic degradation of two most abundant dyes i.e., MB and MO. Photocatalyst degraded both dyes efficiently in photocatalytic chamber. Synthesized NPs has potential application in wastewater treatment plants and self-cleaning textiles.

## References


An, C., Zhang, Z., Chen, X. and Liu, Y., 2006. Selective synthesis of Ni3S4 nanocrystallites with hollow structures through a solution-phase approach. Materials Letters, 60 Pp. 29-30. Pp.3631-3634.

Batista, S., Larson, G., Kotov, A., 2015. Nonadditivity of nanoparticle interactions. Science 350 (6257)

Biswas, P., Chang-Yu, W., 2005 Nanoparticles and the Environment, Journal of the Air and Electrochimica Acta, 58, Pp. 456–462.

Cao, F., Liu, R., Zhou, L., Song, S., Lei, Y., Shi, W., Zhang, H., 2010. One-pot synthesis of flowerlike Ni7S6and its application in selective hydrogenation of chloronitrobenzene. *J.* Mater. Chem., 20(6), Pp. 1078–1085

Fazli, Y., Pourmortazavi, S. M., Kohsari, I., Karimi, M. S., and Tajdari, M., 2016. Synthesis, characterization and photocatalytic property of nickel sulfide nanoparticles. Journal of Materials Science: Materials in Electronics, 27(7), Pp. 7192–7199

Feng, L.-L., Yu, G., Wu, Y., Li, G.-D., Li, H., Sun, Y., Zou, X., 2015. High-Index Faceted Ni3S2 Nanosheet Arrays as Highly Active and Ultrastable Electrocatalysts for Water Splitting. Journal of the American Chemical Society, 137(44), Pp. 14023–14026

Gusain, R., Kumar, N., and Ray, S. S., 2020. Factors Influencing the Photocatalytic Activity of Photocatalysts in Wastewater Treatment. Photocatalysts in Advanced Oxidation Processes for Wastewater Treatment, Pp. 229–270.

Han, S.C., Kim, H.S., Song, M.S., Kim, J.H., Ahn, H.J. and Lee, J.Y., 2003. Nickel sulfide synthesized by ball milling as an attractive cathode material for rechargeable lithium batteries. Journal of alloys and compounds, 351(1-2), Pp.273-278.

Idris, N. H., Rahman, M. M., Chou, S.-L., Wang, J.-Z., Wexler, D., Liu, H.-K., 2011. Rapid synthesis of binary α-NiS–β-NiS by microwave autoclave for rechargeable lithium batteries.

Ji, S., Zhang, L., Yu, L., Xu, X., and Liu, J., 2016. In situ carbon-coating and Ostwald ripeningbased route for hollow Ni3S4@C spheres with superior Li-ion storage performances. RSC Advances*,* 6(104), Pp. 101752–101759.

Li, H., Shao, Y., Su, Y., Gao, Y., Wang, X., 2016. Vapor-Phase Atomic Layer Deposition of Nickel Sulfide and Its Application for Efficient Oxygen-Evolution Electrocatalysis. Chemistry of Materials, 28(4), Pp. 1155–1164

Liu, Z., Zheng, X., Luo, S., Xu, S., Yuan, N., and Ding, J., 2016. High performance Li–S battery based on amorphous NiS2 as the host material for the S cathode. Journal of Materials Chemistry A, 4(35), Pp. 13395–13399

Mary Ealia,S., and Saravanakumar, M P., 2017.IOP Conf. Ser.: Mater. Sci. Eng.263 032019

Moore, D., and Wang, Z. L., Mater, J., Chem., 2006. 16, 3898 NiS single-crystalline nanorods. Journal of Alloys and Compounds, 481(1-2), Pp. 450–454

Pan, Y., Chen, Y., Li, X., Liu, Y., Liu, C., 2015. Nanostructured nickel sulfides: phase evolution, characterization and electrocatalytic properties for the hydrogen evolution reaction. RSC Advances, 5(127), Pp. 104740–104749.

Salavati-Niasari, M., Banaiean-Monfared, G., Emadi, H., Enhessari, M., 2013. Synthesis and characterization of nickel sulfide nanoparticles via cyclic microwave radiation. Comptes Rendus Chimie, 16(10), Pp. 929–936

Sohrabnezhad, S., Pourahmad, A., Radaee, E., 2009. Photocatalytic degradation of basic blue

Sohrabnezhad, S.H., Pourahmad, A., Radaee, E., 2009. a9 by CoS nanoparticles supported on AlMCM-41 material as a catalyst. J. Hazard. Mater., 170, Pp. 184–190,

Tang, C., Zang, C., Su, J., Zhang, D., Li, G., Zhang, Y., Yu, K., 2011. Structure and magnetic properties of flower-like α-NiS nanostructures. Applied Surface Science, 257(8),

Thakkar, K. N., Mhatre, S. S., Parikh, R. Y., 2010. Biological synthesis of metallic nanoparticles. Nanomedicine: Nanotechnology, Biology and Medicine, 6(2), Pp. 257–262

Tian, L., Yep, L. Y., Ong, T. T., Yi, J., Ding, J., Vittal, J. J., 2009. Synthesis of NiS and MnS nanocrystals from the molecular precursors (TMEDA) M (SC {O} C6H5) 2 (M= Ni, Mn). Crystal Growth and Design, 9(1), Pp. 352-357.

Umar, M., Abdul, H., 2013. Photocatalytic Degradation of Organic Pollutants in Water. Organic Pollutants - Monitoring, Risk and Treatment Waste Management Association, 55:6, 708-746

Venkatachalam, N., Palanichamy, M., Arabindoo, B., Murugesan, V., 2007. Enhanced photocatalytic degradation of 4-chlorophenol by Zr4+ doped nano TiO2. J. Mol. Catal. A Chem., 266, Pp. 158–165,

Wang, X., Batter, B., Xie, Y., Pan, K., Liao, Y., Lv, C., Fu, H., 2015. Highly crystalline, small sized, monodisperse α-NiS nanocrystal ink as an efficient counter electrode for dyesensitized solar cells. Journal of Materials Chemistry A, 3(31), Pp. 15905–15912

Wang, Y. and Hong, C., 1999. Effect of hydrogen peroxide, periodate and persulfate on photocatalysis of 2-chlorobiphenyl in aqueous TiO2 suspensions. Water Res., 33, 2031–2036,

Whitesides, George M., 2005 .Nanoscience, Nanotechnology, and Chemistry. Small 2005, 1, No. 2, Pp. 172 –179

Wu, W., Li, Y., Jin, J., Wu, H., Wang, S., Xia, Q., 2016. A novel nonenzymatic electrochemical sensor based on 3D flower-like Ni 7 S 6 for hydrogen peroxide and glucose. Sensors and Actuators B*:* Chemical, 232, Pp. 633–641

Yang, P., Song, B., Wu, R., Zheng, Y., Sun, Y., Jian, J. K., 2009. Solvothermal growth of

Zhang, L., Tian, B., Chen, F., and Zhang, J., 2012. Nickel sulfide as co-catalyst on nanostructured TiO2 for photocatalytic hydrogen evolution. International Journal of Hydrogen Energy, 37(22), Pp. 17060–17067

Zhang, W., Wang, Y., Wang, Z., Zhong, Z. Y., and Xu, R., 2010. Chem. Commun., 46, Pp. 7631.

Zhang, Y., Sun, W., Rui, X., Li, B., Tan, H. T., Guo, G., Yan, Q., 2015. One-Pot Synthesis of Tunable Crystalline Ni3 S4 @Amorphous MoS2 Core/Shell Nanospheres for HighPerformance Supercapacitors. Small, 11(30), Pp. 3694–3702

Zhang, Y.H. and Wang, Q., 2012. The new progress of nickel sulfide synthesis. In Advanced Materials Research, Vol. 366, Pp. 318-321. Trans Tech Publications Ltd*.*