PHOTOCATALYTIC ACTIVITY OF BIOSYNTHESIZED ALUMINIUM OXIDE NANOPARTICLE FROM LEAVES OF *PROSOPIS AFRICANA* PLANT

Daniel Wasinda Malgwi*[1] , Charity Musa[1] , [1]Musa Master Micah, [2]Amina Aminu
[1]Modibbo Adama University, Yola
[2]Federal College of Education, Yola
*Corresponding author's e-mail: danielmalgwi@mau.edu.ng

Received: December 14, 2023 Accepted: March 28, 2024

Abstract: Nano chemistry, in its broadest sense, uses the tools of synthetic and material chemistry to generate nanomaterial with size, shape, and surface properties that can be designed to evoke a specific function with the aim to be utilized in a particular application/end use. Nanotechnology has garnered a great deal of attention in the last few years as miniaturization and nanomaterial are often seen as the key for a sustainable future. Concerning the causes of cancer, skin, respiratory, and digestive system disorders, organic synthetic non-degradable/decomposable compounds including phenol, methyl orange, and rhodamine B have been found to pollute water and the surrounding environment. Therefore, there is need to device a means of degrading or decomposing these substances into none harmful substances by the used of photo-catalyst which were safe for the environment. Aluminum oxide (Al_2O_3) nanoparticles have been produced by biosynthesis. Prosopis africana plant extract from its watery leaves was used to biosynthesize Al_2O_3. 10 ml of the extract was added to 50 ml of aluminum nitrate salt solution, and the mixture was continuously stirred until the color changed, in order to create the nanoparticles. The FT-IR and UV-visible spectrophotometers were used to characterize the nanoparticles. The FTIR shows some peaks at 3338.28 and 1634.05 cm3 in the nanoparticles and some peaks at 2862.70, 1974.80, 1396.10, and 1039.50 cm3 in the plant extract. The results of UV visible spectroscopy showed absorption maxima at 295 nm. Additionally, the FT-IR suggests that a protein functional group might be in charge of the bio reduction. Using methyl orange as a model molecule, the photocatalytic activity of the Al_2O_3 nanoparticles was investigated. The findings indicate that the proportion of methyl orange degradation decreases as time increases, with values of 61.34%, 51.59%, 42.01%, 31.17%, 23.15%, 15.50%, and 9.99 % for 0,20, 40, 60, 80, 100, and 120 minutes, respectively. The kinetics rate equal to k=0.0165 S^{-1} indicates that the rate of reaction is following pseudo first-order kinetics. With a high R-square value of 0.9107, the first order kinetics model is deemed adequate to describe the photo catalytic degradation process. This suggests that there is a robust association between the theoretical model and the experimental results. This suggests that methyl orange photo degradation can be accelerated by using the nanoparticles as a photo catalyst.

Keywords: Biosynthesis, FT-IR, Prosopis Africana, Photo catalyst.

Introduction

Manipulating matter at a molecular scale—much smaller than 100 nanometers—nanotechnology enables us to gather important data for the production of novel materials with highly reproducible and specialized features. In this context, a significant portion of the scientific community is currently concentrating on a very demanding and pertinent research avenue, which involves creating novel nanostructured materials that can absorb solar photonic energy and convert it to chemical or electrical energy (Colmenares *et al.*, 2009). In order to reach new classes of functional materials with hitherto unheard-of features and uses, nanostructured materials have been thoroughly investigated for basic scientific and technological reasons (Manigandan *et al.*, 2014).

According to Arora *et al*. (2016), metal oxides are crucial to several branches of Chemistry, physics, and materials science. Because of the co-ordination tendency of metal ions, oxide ions surround metal ions to create a co-ordination sphere, which results in the formation of tightly packed structures known as metal oxides. Chemists are very interested in the various physical, magnetic, optical, and chemical properties of metal oxides because of how sensitive these properties are to changes in composition and structure. A deeper knowledge of the chemical connection in crystal is obtained by extensive research on this interaction. Scientists are paying particular attention to metal oxides because of their simple formation process and versatile nature (Arora *et al*., 2016). Numerous metal oxide nanoparticles, including FeO_2 (Herrera *et al*., 2016) and Gd-doped $BiFeO_3$ (Zhang *et al*., 2016), have had their photo-catalytic activity assessed and reported. TiO_2, ZnO, (Hang, 2014), Ag_3PO_4/TiO_2 (Liua *et al.*, 2012), ZnO/CuO (Ang *et al.*, 2013), ZnO/SnO_2 (Firooz *et al.*, 2011), $BiVO_4$ (Sivakumar *et al.*, 2015), and SnO_2 (Kim *et al.*, 2016), and, because of their relatively high photo-catalytic activity, strong chemical stability, affordability, and nontoxicity, have been shown to be effective photo-catalysts for the photo-catalytic degradation of methylene blue, methyl orange, organic pollutants, inhibiting the growth of bacteria, decomposing NO_2, and photo-catalytic water splitting. They only absorb 1% to 5% of UV radiation, though, and it's thought that this can be increased by combining two or more nanomaterials or employing other nanomaterials. Due to its possible uses in photo-catalysis, gas sensors, solar cells, UV light emitters, electrical and optical devices, fuel cells, and smart materials, semiconductor nanoparticles have drawn more attention in the past 10 years. Their uses in environmental purification and the breakdown of organic and hazardous substances have focused a lot of interest on their photo-catalytic characteristics. To improve the photo-catalytic activity, it is

imperative to augment the crystallinity and specific surface area. Materials with crystalline nanostructures satisfy these criteria. Metal oxide nanoparticles have been prepared via a variety of techniques, including hydrothermal, sol-gel, chemical vapor deposition (CVD), and sputtering. Nanomaterials must be crystalline, meaning they must grow at very slow rates or at high temperatures, in order to have effective photo-catalytic activity (Arora *et al.,* 2016). Therefore, there is need to device a means of degrading or decomposing these substances into none harmful substances by the used of photo-catalyst which were safe for the environment. This research aim to is to synthesize, characterize and determine photo-catalytic activity of Al_2O_3 nanoparticle

Materials and Methods

Sample collection/Preparation of leaf extract

Leaves of *Prosopis Africana* (Kiriya) were gathered at the Vimtim Mubi North local government district. The leaves were photographed and the plant was recognized and classed by PlantNet software. Fresh leaves of *Prosopis Africana* (Kiriya) were washed and rinsed with distilled water. The leaf was sun-dried and then crushed using a pestle and mortar to a powder. Using a magnetic stirrer, 10 g of powdered dried leaves and 100 ml of water were combined to create the aqueous extract, which was then continuously stirred for 10 minutes. After three hours, the powdered dried leaves suspension in water was filtered using Whatman No. 1 filter paper, the filtrate was then used for Chemical analysis (Suriyavathana and Ramalingam, 2015).

Materials/Instruments

U-V visible spectrophotometer, measuring cylinder, heating mantle, weighing balance, FT-IR, magnetic stirrer, conical flask, $Al(NO_3)_2 \cdot 9H_2O$, distilled water, conical flask, *Prosopis Africana* (Kiriya) leaf, burette, retort stand, methyl orange.

Biosynthesis of Al_2O_3 nanoparticles

Al_2O_3 nanoparticles were bio synthesized in accordance with Suriyavathana and Ramalingam's (2015) method. Aluminum nitrate ($Al(NO_3)_2$) was synthesized in an aqueous solution of around 0.2 M, which was utilized in the manufacture of aluminum oxide nanoparticles. For reduction into aluminum oxide nanoparticles, 10 ml of *Prosopis Africana* leaf extract was added to 50 ml of an aqueous solution of 0.2 M aluminum nitrate and left to stand at room temperature. After the precipitate form was cleaned and rinsed three times with distilled water, FTIR and UV visible spectroscopy were used to characterize the nanoparticles.

Characterization of Synthesized Nanoparticles

The nanoparticles were evaluated by Fourier Transmission Infar Red (FT-IR) and a UV visible spectrophotometer, as reported by Ghosh *et al.*, (2015).

UV-Visible Spectroscopy

Twenty milliliters of distill water were used to dissolve 0.01 grams of aluminum oxide nanoparticles. After being transferred, the cuvette was put into the spectroscopic. The absorbance was measured in the 200–600 nm range. The data was then transferred to Microsoft Excel for analysis.

FT-IR Spectroscopy

The FT-IR sample cell was loaded with dried samples of the plant extract and aluminum oxide nanoparticles individually, and the samples were scanned between 4000 and 400 cm^{-1}.

Evaluation of the Photo-degradation of Methyl orange

Al_2O_3 nanoparticle photo catalysis was performed in accordance with Liua *et al.,* (2012) method. The photo-catalytic activity of aluminum oxide nanoparticles was investigated using the photo-catalysis of methyl orange (MO) as a model chemical. An aqueous solution containing 0.6 mg/L of MO was produced, and 100 ml was measured into a conical flask. A 100 ml conical flask was filled with 0.6 mg of photo-catalysts. After the photo-catalysts were ultrasonically distributed throughout the flask, the liquid was stirred for about five minutes. Following this procedure, the flask was simultaneously agitated and exposed to photo irradiation. The flask was then taken away from the light source at preset time intervals of 20 minutes and 10 ml of the mixtures was centrifuge to remove the catalysts. A JEN WAY UV-650 UV-Vis Spectrophotometer was used to measure the remaining MO concentration.

Results and Discussion

Characterization of Al_2O_2 nanoparticle using optical view

The color of the mixture containing the nanoparticle changed from brown (from the plant extract A) to brown-black in the reaction with colorless aluminum nitrate.

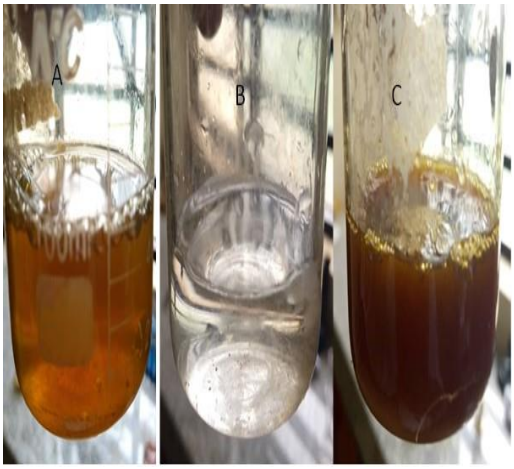

Figure 1.0 Color change of the reaction (A) plant extract (B) aluminum nitrate and (C) mixture containing nanoparticle

Characterization of Al_2O_3 nanoparticle using UV-Visible spectroscope

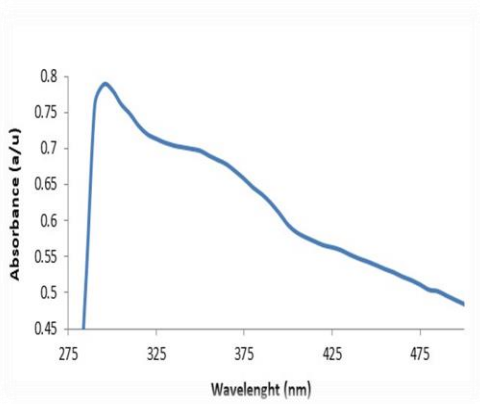

Figure 1.1: UV Visible characterization of Al_2O_3

The absorption spectra of deionized water containing suspended Al_2O_3 nanoparticles produced through biological synthesis are displayed in Figure 1.1 above. According to Veeradate *et al*. (2012), an absorption peak at 295 nm was observed, providing unequivocal evidence of Al_2O_3 nanoparticles in deionized water.

B

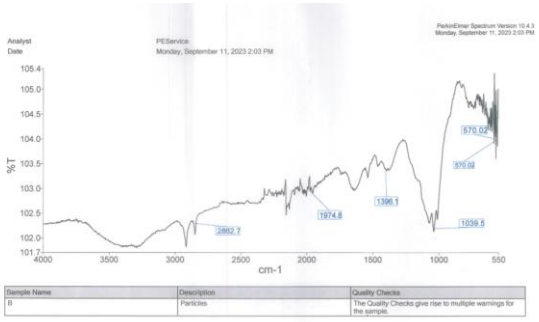

Figure 1.2, FTIR analysis of both plant extract (A) and nanoparticle (B).

***Description of FT-IR analysis of Al_2O_3 nanoparticles/* plant extracts**

The Al_2O_3 FT-IR analysis table displays the different frequencies together with their corresponding functional group. As can be observed in Table 1.0, the Al_2O_3 exhibits two peaks.

Table 1.0: FT-IR of Al_2O_3

S/No	Frequency (cm^{-1})	Functional group	Type of vibration	Characteristic absorption range (cm^{-1})	Intensity
1	3338.28	O-H	Stretched (H Bonded)	3200-3600	Strong, broad
2	1634.05	C=O	Bending	1630-1700	Strong

According to Table 1.1, the FT-IR analysis of Prosopis africana leaves reveals the presence of four distinct peaks, namely the C-H of alkane and the C=O bending of amide.

Table 1.1: FT-IR of *Prosopis africana* leaves

	Frequency (cm^{-1})	Functional group	Type of vibration	Characteristic absorption	Intensity
1	2862.70	C-H	Stretched	2850-2990	Medium
2	1974.80	C-H	Bending	2800 – 2700	Strong
3	1396.10	C-H	Stretch of aliphatic alkane	1390-1490	Strong
4	1039.50	C=O	Bending	1050-1600	Strong

The FT-IR spectra of aluminum oxide metal nanoparticles, which are produced by bio-reducing aluminum trioxonitratepentahydrate, are displayed in Figure 1.1.

FT-IR spectroscopy was used to determine which functional group aluminum oxide contains. The metal oxide exhibits an absorption peak at 3328.82 cm-1 and 1634.05 cm-1, which are indicative of the amide's C=O bending and the water-induced OH stretch vibration of the hydrogen bond. The absorption peaks at 2862.70 cm^{-1} observed in the *Prosopis africana* leaf correspond to C-H stretch of alkane. The *Prosopis africana* leaf extract's absorption bands at 1974.80 cm^{-1} and 1396.10 cm^{-1} are assigned to the C-H functional group. The plant's peak at 1039.50 cm-1 might be the result of amide C=O bending. Certain peaks are present in the plant and absent in the metal oxide because they are involved in the process of bioreduction; their absence indicates that they belong to the functional group of compounds that were not involved in the bio reduction; other peaks that are absent in the *Prosopis africana* leaf and found in the metal oxide may be caused by moisture from the water present in the nanoparticles. This outcome is consistent with what Kumar *et al*. (2013) reported.

Photo-catalytic activity of Aluminum Oxide Nanoparticles

The photocatalytic degradation result of aluminum oxide nanoparticles is plotted against time in minutes in figure

1.3, which also shows the variation of the degradation percentage as a function of time. As the time increases, the percentage of degradation decreases.

When evaluating a material's capacity to deteriorate, time is one of the most crucial factors to take into account.

As the amount of time grows, the measured percentage degradation numbers show a declining tendency. This suggests that the length of the photocatalytic process and the organophosphate's degradation have a favorable link Wang *et al.*, (2018). Degradation happens at a comparatively slow pace. Zhang et al. (2018) found that after 10 minutes, the maximum percentage of degradation was 61.34%, while after 120 minutes, the lowest percentage of degradation was recorded. this suggest that the photocatalytic process is not effective over an extended period. The first few time intervals of 10 to 40 minutes of shows a moderate % degradation Khan *et al.* (2019). This could point to the beginning of the photocatalytic process's lag phase. The rate of disintegration noticeably slows down after forty minutes. According to Nadia *et al.* (2015), the curve seems to be approaching a plateau, indicating that the efficiency of the photocatalytic process may have a limit in some circumstances. It is ineffective to advise and prolong this time frame. Moreover, the outcomes were not as good as those documented in the literature by Raut *et al.* (2014), who used AgNPs as a photo catalyst and reported a degradation rate of 67.89% at 15 minutes. This is in line with research on the photocatalytic destruction of pollutants employing different light sources and catalysis *Pealaez et al.*, (2012).

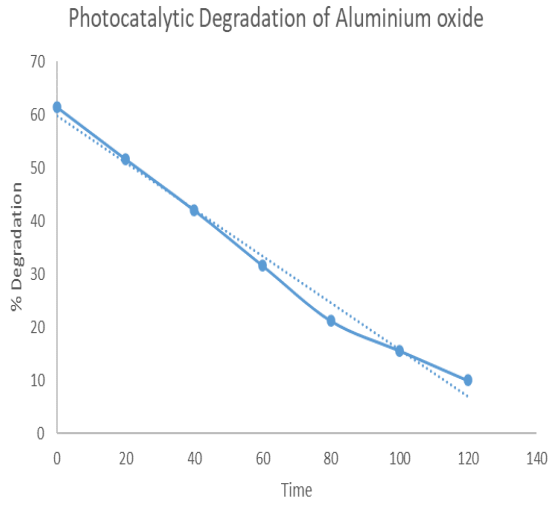

Figure 1.3: Photo-catalytic degradation of methyl orange by aluminum oxide

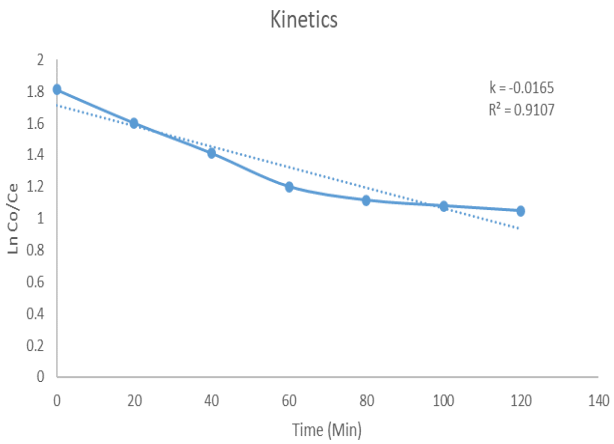

Figure 1.4: Photo-catalytic degradation of methyl orange by aluminum oxide

Additionally, the reaction's rate was examined, as shown in Fig. 1.4. The following formula was used to compute the photocatalytic results: Langmuir Hinshelwood

$Ln(Co/Ct) = kt$

According to Ngoepe et al. (2020), the rate of the reaction is represented by Ln, the initial concentration is Co, the end concentration is Ct, the rate of reaction constant is k, and the reaction time is t. The rate of reaction is following pseudo first-order kinetics, with the kinetics rate equal to $k=0.0165\ S^{-1}$, based on the plotted data in Fig. 1.4. With a high R-square value of 0.9107, the first order kinetics model is deemed adequate to describe the photocatalytic degradation process. This suggests that there is a robust association between the theoretical model and the experimental results. One important first order kinetics parameter is the rate constant k, which is $0.0165\ S^{-1}$. It shows the percentage of contaminated material that degrades over time. A quicker decline is indicated by a higher k value Raut *et al.* (2014). The Ln Co/Ce values' decreasing patterns over time (from 1.811 to 1.04) are consistent with first-order kinetics expectations. The natural logarithms of the ratio of starting to final concentration drop with increasing time. At each point, the degree of degradation is indicated by the Ln Co/Ct values. Significant degradation is indicated by smaller Ln Co/Ce values. The changing deterioration process is reflected in the Ln Co/Ct readings' advancement over time. The first-order kinetics model matches the experimental data, according to the R-square value of 0.9107. With a high goodness of fit, the model appears to be dependable in forecasting the deterioration behavior at untested time points in the investigated range. The resulting rate constant and R square value were compared to those for a comparable photocatalytic degradation process published in literature. Wang *et al.* (2018) found that the study's dependability is increased when there is consistency with known values.

Because of their high specific surface area, which provides more active surface sites for absorbing water molecules and forming active HO_2* and OH radicals by trapping photogenerated holes, the nanoparticles' photo degradation efficiency increased in the presence of UV light. The

decomposition of organic contaminants in the aqueous solution is facilitated by the photo degradation processes driven by these free active radicals (Manigandan *et al.*, 2014). Additionally, a high surface area helps color molecules absorb onto the surface of nanoparticles. Methyl blue (MB) molecules are absorbed by nanoparticle surfaces under UV light irradiation and create electrons. The electrons are absorbed by the O_2 molecules that have been adsorbed on the surface, producing HO_2• and O_2•− radicals. These radicals have a greater likelihood of coming into contact with dye molecules, which speeds up the reaction. Thus, the super oxide radical ions may eventually cause the methyl blue (MB) molecules to become mineralized. According to Manigandan *et al.* (2014), the reduced crystalline size of nanoparticles is thought to be advantageous for the oxidation of H_2O molecules and the reduction of O_2 because it traps electrons and holes, increasing the adsorbent's photocatalytic activity under UV light. This outcome is comparable to that which Maryam *et al.* (2014) and Mphilisi *et al*. (2015) reported.

Conclusion

This investigation has demonstrated that Al_2O_3 nanoparticle production has been completed. *Prosopis africana* plant extract was used to biosynthesize the Al_2O_3, and FT-IR and a UV visible spectrophotometer were used to characterize the product. It was discovered that the nanoparticles have strong photocatalytic activity. Using methyl orange as a model, the nanoparticle's photocatalytic activity was examined, and it was discovered to possess photocatalytic activity. This demonstrates that methyl orange photo degradation has a first order kinetic. To find out if these nanoparticles can increase the efficiency of solar cells, more research on them should be done.

Conflict of Interest

The authors declare no conflict of interest exist**.**

References

Ang, W., Li, X., Li, S., Yan-Jun, L., & Wei-Wei, L. (2013). CuO Nanoparticle Modified ZnO Nanorods with Improved Photocatalytic Activity. *CHIN. PHYS. LETT. Vol. 30, No. 4*, 046202-5.

Arora, A. K., Jaswal, V. S., Singh, K., & Singh, R. (2016). Applications of Metal/Mixed Metal Oxides as Photocatalyst: (A Review). *Orient J Chem; 32(4).*

Arora, A. K., Jaswal, V. S., Singh, K., & Singh, R. (2016). Applications of Metal/Mixed Metal Oxides as Photocatalyst: (A Review). *Orient J Chem; 32(4)*

Colmenares, J. C., Luque, R., Campelo, J. M., Colmenares, F., Karpiński, Z., & Romero, A. A. (2009). Nanostructured Photocatalysts and Their Applications in the Photocatalytic Transformation of Lignocellulosic Biomass: An Overview. *Materials, 2; doi:10.3390/ma2042228*, 2228-2258.

Firooz, A. A., Mahjoub, A. R., & Khodadadi, A. A. (2011). Hydrothermal Synthesis of ZnO/SnO2 Nanoparticles with High Photocatalytic Activity. *International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering Vol:5, No:4*, 254-256.

Hang, N. Y. (2014). PHOTOCATALYTIC APPLICATION OF METAL OXIDE NANOSTRUCTURES. *A dissertation submitted in partial fulfillment of the requirements for the degree of Master of Philosophy at The University of Hong Kong*, 1-67.

Herrera, A., Reyes, A., & Colina-Márquez, J. (2016). Evaluation of the photocatalytic activity of iron oxide nanoparticles functionalized with titanium dioxide. *Journal of Physics: Conference Series 687*, 1-4.

Kim, S., Choi, M., & Choi, H. (2016). Photocatalytic activity of SnO2 nanoparticles in methylene blue degradation. *Material Research and Bulleting Volume 74*, 85-89.

Kumar, H., Manisha, & Sangwan, P. (2013). Synthesis and Characterization MnO Nanoparticles Using Co-Precipitation Techniques. *International Journal of Chemistry and Chemical Engineering Volume 3, Number 3*, 155-160.

Liua, R., Hub, P., & Chenb, S. (2012). Photocatalytic activity of Ag3PO4 nanoparticle/TiO2 nanobelt heterostructures. *Applied Surface Science 258*, 9805– 9809.

Manigandan, R., Giribabu, K., Suresh, R., Munusamy, S., Praveen, k. S., Muthamizh, S., . Narayanan, V. (2014). Characterization and Photocatalytic activity of Nickel oxide nanoparticles. *International Journal of ChemTech Research Vol.6, No.6,*, 3395-3398.

Maryam, L., Gholamali, F., & Nasrin, E. (2014). Synthesis and surface modification of aluminum oxide nanoparticles. *Journal of Ceramic Processing Research. Vol. 15, No. 5,*, 316~319 .

Mphilisi, M., Ngila, C., & Mamba, B. B. (2015). Recent Developments in Environmental Photocatalytic Degradation of Organic Pollutants: The Case of Titanium Dioxide Nanoparticles—A Review. *Journal of Nanomaterials Volume 2015*, pp 28-34

Sivakumar, V., Suresh, R., Giribabu, K., & Narayanan, V. (2015). BiVO4 nanoparticles: Preparation, characterization and photocatalytic activity. *Cogent Chemistry Volume 1, Issue 1*.

Suriyavathana, M., & Ramalingam, K. (2015). Nanoparticles Synthesis and Antibacterial Study on Anisomeles Malabarica using Manganese Oxide (MnO). *International Journal of ChemTech Research Vol.8, No.11*, 466-473.

Veeradate Piriyawong, Voranuch thongpool,Piyapong Asanithi and Pichet Limsuwan (2012). Preparation and Characterization of Alumina Nanoparticles in Deionized Water Using Laser Ablation Technique. Journal of Nanomaterials https://doi.org/10.1155/2012/819403

Zhang, N., Chen, D., Niu, F., Wang, S., Qin, L., & Huang, Y. (2016). Enhanced visible light photocatalytic activity of Gd-doped BiFeO3 nanoparticles and mechanism insight. *Scientific Reports 6, Article number: 26467l*