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Functionalized MgO Nanoparticles as Sensor for Ni(II) ions in Simulated Effluents

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ABSTRACT

Sequestration of toxic heavy metals in solution using plant extract anchored on nanomaterials is on the increase as cost-effective and efficient method. In this study, magnesium oxide nanoparticles (MgO-NPs) were synthesized with *Thaumatococcus danielli* leaf extract. Characterization of the synthesized magnesium oxide nanoparticles was carried out using ultraviolet-visible spectrophotometer (UV-visible), Fourier transform infrared spectrophotometer (FTIR), scanning electron microscope (SEM) and X-ray diffractometer (XRD). Ultraviolet-visible analysis of the magnesium oxide nanoparticles showed surface plasmon absorption with maximum absorption at 420 nm. FTIR analysis indicated that C-H of alkane at 2919.12 cm^{-1}, 2850 cm^{-1} and 1431.84 cm^{-1}; C=C of aromatic compound at 1619.75 cm^{-1} and C-O of alcohol at 1320.64 cm^{-1}, 1107.71 cm^{-1} and 1061.72 cm^{-1} are functional groups that are responsible for the bio-reduction of magnesium oxide ions to magnesium oxide nanoparticles while SEM analysis revealed that the surface morphology of the magnesium oxide nanoparticles had a coarse granulite irregular shape of various sizes and pores that are agglomerated. It also revealed smooth surface of the particles upon magnification. The XRD result showed the formation of the magnesium oxide nanoparticles that are crystalline in nature with crystallite size of 26.3. The colorimetric detection of Ni(II) ions in aqueous solutions using colloidal magnesium oxide nanoparticles showed highest detection point at wavelength of 400 nm when the concentration of aqueous solution of Ni(II) ions was at 10 µM. This indicated that magnesium oxide nanoparticles has the ability to detect Ni(II) ions in solutions even at low concentrations. Therefore the obtained results encourage the use of economical synthesis of magnesium oxide nanoparticles in the development of nanosensor to detect pollutants present in industrial wastewater and other metal bearing effluents.

Keywords: *Thaumatococcus danielli*, Magnesium oxide nanoparticles, Ni(II) ions, UV- visible spectroscopy, FTIR, SEM, XRD, Colorimeter.

INTRODUCTION

Environmental pollution by toxic heavy metals due to excess anthropogenic activities has been a cause for concern. Heavy metals are trace metals with an atomic density greater than 5 g/cm^3 [1] and they have been described as the most common pollutants in wastewater [2]. Some heavy metals of concern include; Hg, Cd, Ni, Pb, Cu, Zn, Cr, Co, As etc.

. According to Goyer [3], asthmatic condition has been documented for inhalation exposure to nickel while acute inhalation exposure to nickel may produce headache, nausea, respiratory disorders and death [3, 4]. Due to the toxicity of nickel there is need for detection and detoxification in any medium especially in effluents before discharge.

Nanoparticles are particles of the size of nanometer or 10^{-9} in diameter with distinctive chemical, physical and biological properties [5]. Synthesis of nanoparticles by chemical method has some drawbacks as it is expensive, requires high pressure and temperature, requires complex reactions and the process is hazardous through liberations of toxic chemicals which are harmful to the environment unlike the use of green synthesis as unconventional method [6]. Green synthesis is easily scaled up for large scale synthesis and its unique ability for the production of precise shape and controlled structures [7]. The use of green synthesis for nanoparticles has become unabated.

According to Ahmed *et al* [8] and Saranya *et al* [9], phytochemicals in plant extracts such as proteins, polysaccharides, organic acids, vitamins, as well as secondary metabolites, such such as flavonoids, alkaloids, polyphenol, terpenoids and heterocyclic compounds have significant roles in metal salt reduction and furthermore, act as capping and stabilizing agents for synthesized nanoparticle.

Several phytochemical components of the plant extracts of *Thaumatococcus danielli* exist including, alkaloids, tannins, terpenoids, saponins, flavonoids, polyphenols, anthraquinones, cardiac glycosides, anthracene, glycosides [10-12] hence its interest in the synthesis of magnesium oxide nanoparticles.

MgO is increasingly utilized in the production of magnesium batteries, biosensors, toxic metal ion sensors, catalysts, superconducting goods, refractory additives, and toxic wastewater treatment [13]. The multifunctional properties of MgO, such as its nontoxicity, environmental friendliness, high-specific surface area, exceptional biocompatibility, and global availability of its source, have been reported [14] and these have sparked the interest of this work in using its nanoparticles as a sensor in detecting toxic metal in effluents. Hence, the aim and objective of this study is to explore the efficacy of metabolites secreted by *Thaumatococcus danielli*, as a biocatalyst to biologically synthesize MgO-NPs.

The formed MgO-NPs was characterized by UV-vis spectroscopy, FT-IR spectroscopy, SEM and XRD. Moreover, biosynthesized MgO-NPs are utilized to detect Ni(II) ions in simulated effluents colorimetrically.

MATERIALS AND METHOD

Collection of plant materials

Fresh leaves of *Thamatococcus danielli* were collected from the environ of Michael Okpara University of Agriculture, Umudike, Abia State, Nigeria, identified and equally authenticated at the Taxonomy Unit, Forestry Department in Michael Okpara University of Agriculture Umudike, Nigeria.

Preparation of aqueous plant extract

This was done according to the method proposed by Okwunodulu *et al* [15] with slight modification. Thorough washing of the sliced leaves of *Thamatococcus danielli* with deionized water was done, air dried at room temperature for three weeks and milled to a fine powder using a blender. Exactly 50 grams of the milled sample was dispersed in a 500 mL of deionized water in 1000 mL glass beaker and boiled at100 °C for 15 min in a hot plate and was allowed to cool. Then, the solution was filtered using a Whatman No. 1 filter paper (Springfield Mill. Maidstone. Kent, England) and the immediate use of the filtrate was done for the synthesis of magnesium oxide nanoparticles.

Synthesis of magnesium nanoparticles

The procedure used by Mahdavi *et al* [16] was employed for the synthesis of *Thamatococcus danielli*/MgO-NPs, with slight modification. Magnesium oxide nanoparticles was synthesized by adding 100 mL of the aqueous leaves extract to 900 mL of 1×10^{-3} M aqueous (MgO. $7H_20$) solution in a 1000 mL round bottom flask and stirred for about 40 min. Colour change from brown to dark brown was observed within 48 hr indicating the formation of magnesium oxide nanoparticles. Repeated centrifugation of magnesium oxide nanoparticles solution was carried out at 4000 rpm for 15 minutes for purification followed by re-dispersion of the pellet in deionized water. Finally, the magnesium oxide nanoparticles were dried in an oven at 80 °C and allowed to cool and stored in an airtight container for further analysis.

UV-visible spectroscopy analysis

Exactly 1 mL of aqueous magnesium oxide nanoparticles was measured by sampling 1 mL aliquot and compared with 1 mL of distilled water used as blank. UV-visible spectrum was monitored on Cary Series UV-visible spectrophotometer Agilent Technology that was operated within the wavelength range of 200 to 800 nm.

FT-IR spectroscopy measurement

FTIR analysis of *Thaumatococcus danielli* leaves extract and magnesium oxide nanoparticles were carried out and their measurements were performed using FTIR-Cary 630 which operated at a resolution of 14 cm^{-1} in potassium bromide (KBr) pellets within the wave number range of 4000-5000 cm^{-1}.

Scanning electron microscopy analysis

SEM analysis of the magnesium oxide nanoparticles was studied in order to ascertain its morphology using electron magnification of 80 - 150,000x (MODEL-PHENOM ProX Scanning Element Microscope manufactured by Phenom World Eindhoven, Netherlands).

X-ray diffraction analysis

XRD analysis was carried out using a diffractometer (Empyrean Model, Netherlands) that operated at a voltage of 45 KV and a current of 40 mA using Cu-K(alpha) radiation in a -2 configuration with a wavelength (λ) of 0.1541. Smoother portion of magnesium oxide nanoparticles was fed on a slide which was then charged into the machine after adjusting the machine parameters and was operated via a monitor.

Colorimetric detection of Ni(II) ions from simulated effluents using magnesium oxide nanoparticles (MgO-NPs).

For the sensing and identification of Ni(II) ions in simulated effluents, Taufiq *et al* [17] method was used with slight modification. Exactly 2 mL of colloidal magnesium oxide nanoparticles solution was added to various concentrations (5- 25) μM of nickel chloride salt solution that was prepared by serial dilution from 1 mM of stock solution of nickel salt. The mixtures were allowed to stand for 15 min before subjected to UV-vis spectrometer. Absorbance was in the range of 200–800 nm.

RESULTS AND DISCUSSION

Uv-visible Analysis

Ultraviolet visible spectroscopy (UV-Vis) refers to the absorption spectroscopy or reference spectroscopy in the ultraviolet-visible spectral region. It is the measurement of light passing through a sample (/) and compares it to the intensity of light before it passes through the sample (%). The ratio I/I0 is called the transmittance and usually expressed as percentage (% T). The absorbance A is based on the transmittance: A= -log (%T). The Uv-visible analysis of zero-valent magnesium oxide nanoparticles was determined using ultraviolent visible spectrophotometer. The absorption spectrum of the zero-valent magnesium oxide nanoparticlesis is shown in Fig. 1 with maximum absorption at 420 nm indicating surface plasmon absorption.

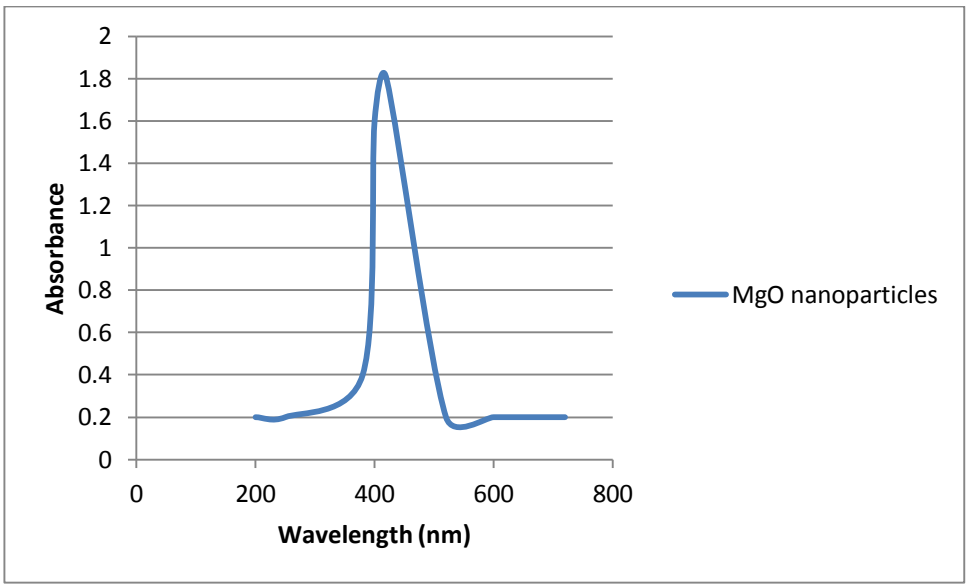

Fig. 1: Uv- visible spectrum of magnesium oxide nanoparticles

Fourier Transform Infrared Spectroscopy

FTIR analysis of *Thaumotococcus danielli* leaf extract before and after synthesis of the magnesium oxide nanoparticles were determined to ascertain the possible functional group/s responsible for the reduction of magnesium oxide ions to magnesium oxide nanoparticles. Fig. 2 depicts the FTIR spectrum of *Thaumotococcus danielli* leaf extract before synthesis while its functional groups are presented in Table 1. Equally Fig. 3 shows the FTIR spectrum of magnesium oxide nanoparticles after synthesis and its functional groups are also shown in Table 2. According to the results, it was revealed that C-H of alkane at 2919.12 cm^{-1},

2850 cm^{-1} and 1431.84 cm^{-1}; C=C of aromatic compound at 1619.75 cm^{-1} and C-O of alcohol at 1320.64 cm^{-1}, 1107.71 cm^{-1} and 1061.72 cm^{-1} functional groups were involved in the bio-reduction process. Therefore, these functional groups were responsible for the capping, stabilization and reduction of magnesium oxide ions to magnesium oxide nanoparticles.

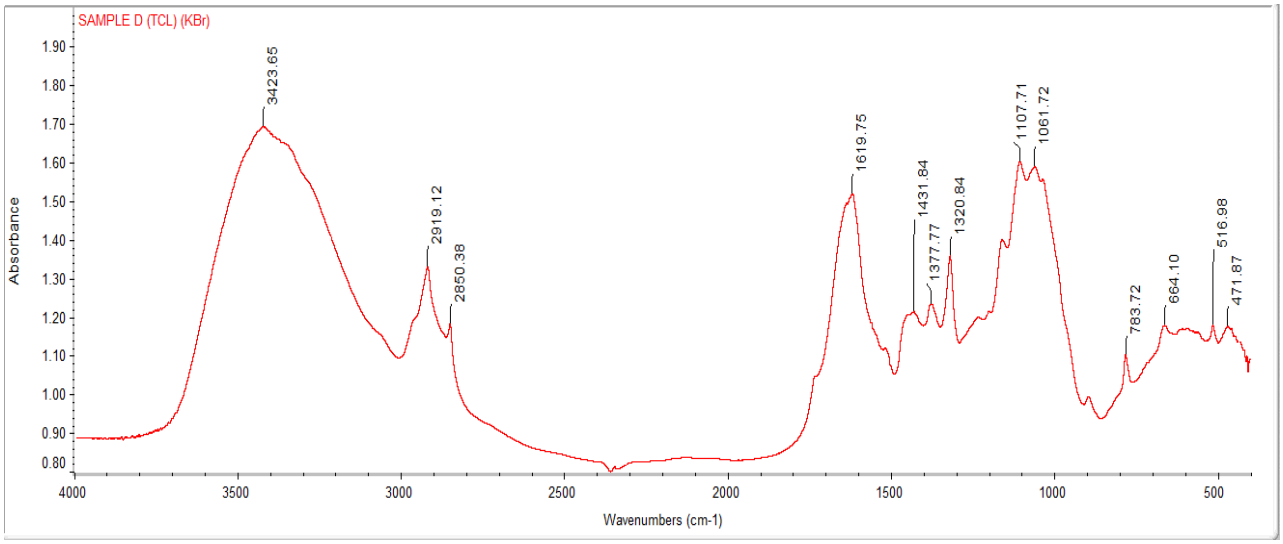

Fig. 2: FTIR spectrum of Thaumotococcus *danielli* leaf extract

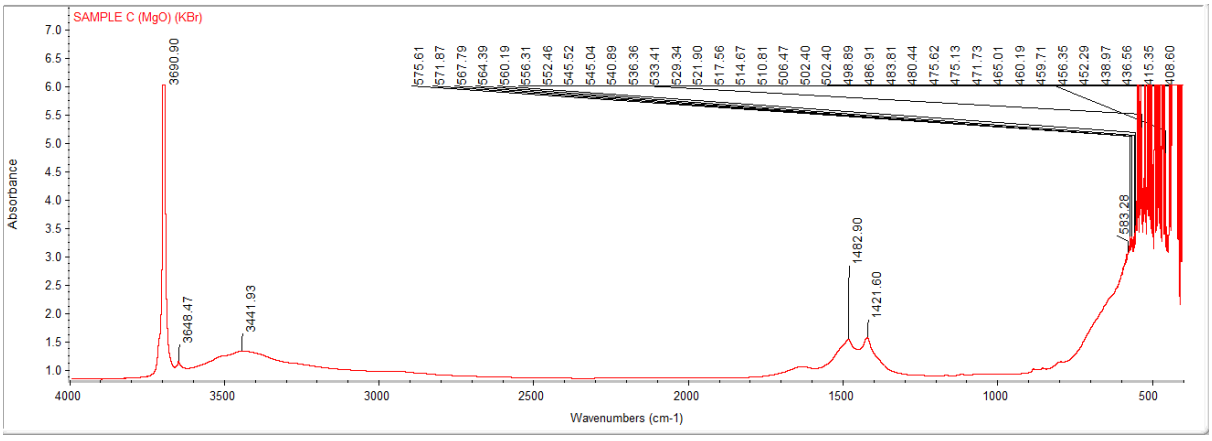

Fig. 3: FTIR spectrum of magnesium oxide nanoparticles

Table 1: Functional groups present in *Thaumotococcus danielli* leaf extract.

Wave number (cm^{-1})	Functional groups
3423.65	O-H of alcohol
2919.12	C-H of alkane
2850.38	C-H of alkane
1619.75	C=C of aromatic compound
1431.84	C-C of alkane
1320.64	C-O of alcohol
1107.71	C-O of alcohol
1061.72	C-O of alcohol

Table 2: Functional groups present in magnesium oxide nanoparticles

Wavenumber (cm^{-1})	Functional groups
3648.47	O-H of alcohol
3441.93	O-H of alcohol
1421.60	C-C of alkane

Scanning Electron Microscopy Analysis

Magnesium oxide nanoparticles SEM images are depicted in Fig. 4 and Fig. 5. The morphology of these nanoparticles showed coarse granulites irregular shape of various sizes that are porous and agglomerated. Upon magnification, the image possesses smooth surface.

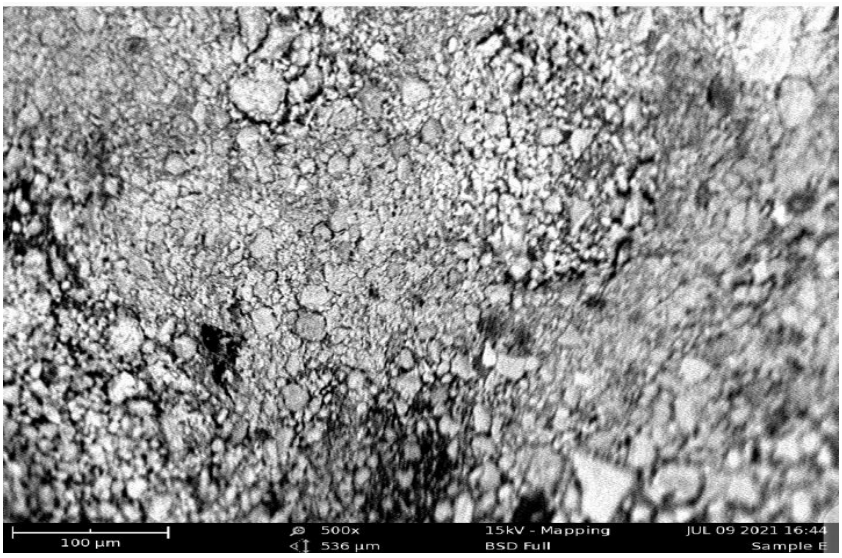

Fig. 4: SEM image of magnesium oxide nanoparticles

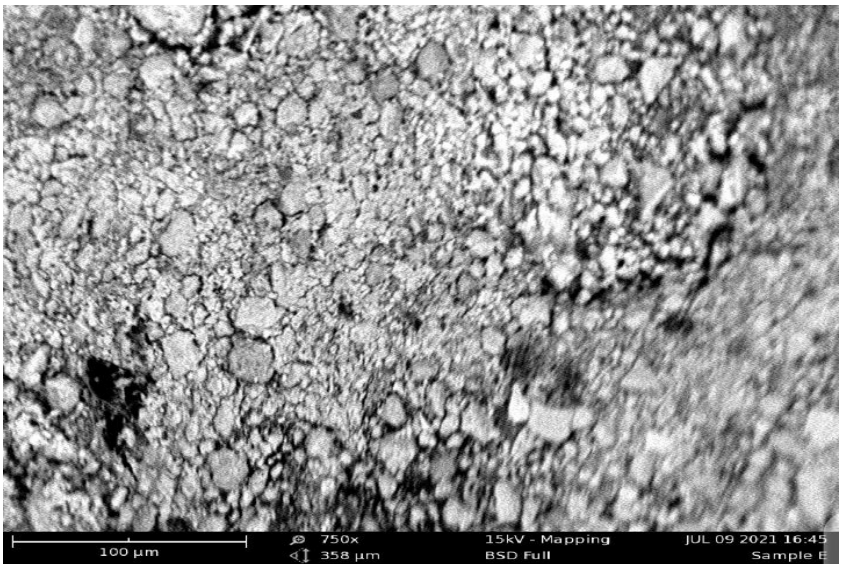

Fig. 5: Zoom SEM image of magnesium oxide nanoparticles

X-ray Diffraction Analysis

The XRD pattern of magnesium oxide nanoparticles is shown in Fig. 6. Characteristics reflections are shown to appear at 2θ values of 10.90, 30.80, 40.30, 50.10, 50.90, 60.20, 60.80, 70.20 and 80.25 within the angle range of 10 to 90. Based on the XRD analysis, magnesium oxide nanoparticles formed are crystalline in nature with irregular shapes and sizes. Its crystallite size is 26.3 based on Debye- Scherrer equation. The peaks displayed very sharp and had strong intensities.

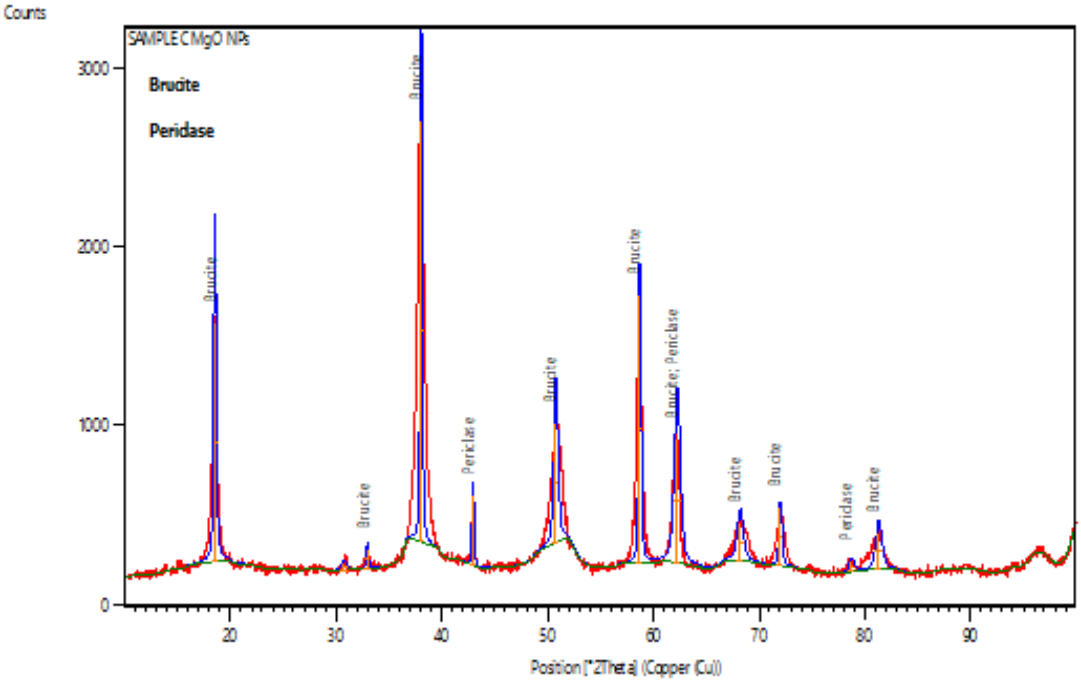

Fig. 6: X-ray diffraction spectrum of magnesium oxide nanoparticles.

Colorimetric Analysis

Firstly, the detection was carried out against various concentrations (5-25) µM of Ni(II). The MgO-NPs response is observed visually through the colour change of the solution. Among the five solutions tested, solution with concentration of 10 µM showed the most significant colour change, from dark brown to clear solution. Other solutions of different concentrations showed a change in colour but not as significant as solution of 10 µM. This indicated that the MgO-NPs were more sensitive to Ni(II) ions at concentration of 10 µM than other concentrations tested. This colour shift occurred due to MgO-NPs aggregation that induced by the presence of Ni(II) ions at 10 µM and interference of the Ni(II) ions on the interaction of MgO-NPs with any radical present [18] which then reduced the stability of MgO-NPs and resulted in the aggregation. When these solutions were subjected to UV-visible spectrometer, different absorbance peaks were shown with significant decrease of absorbance at various concentrations as shown in Figure 7. At various concentrations (5-25) µM, MgO-NPs showed high detections of Ni(II) as 0.44 µM, 0.48 µM, 0.45 µM, 0.35 µM and 0.39 µM at wavelength of 400 with highest detection at 10 µM (Table 3). At 10 µM, there was an instant colour change from dark brown to clear solution unlike in other solutions that required a longer response time. Therefore at lower concentrations of Ni(II) ions, MgO-NPs bands were

detected but the intensity was highest at 10 µM but reduced when compared to band of MgO-NPs (Fig. 1) and shifted to lower wavelength (Figure 3). Based on these results, MgO-NPs has the ability to detect Ni(II) ions in solutions even at low concentrations.

Table 3: Amount of Ni(II) ions detected by magnesium oxide nanoparticles

Concentration	200	300	400	500	600	700	800
(µM)	Wavelength (nm)						
5	0.13	0.39	0.44	0.39	0.20	0.20	0.20
10	0.15	0.23	0.48	0.31	0.36	0.27	0.25
15	0.25	0.27	0.45	0.33	0.35	0.21	0.20
20	0.21	0.26	0.35	0.25	0.22	0.21	0.20
25	0.15	0.19	0.39	0.32	0.26	0.22	0.21

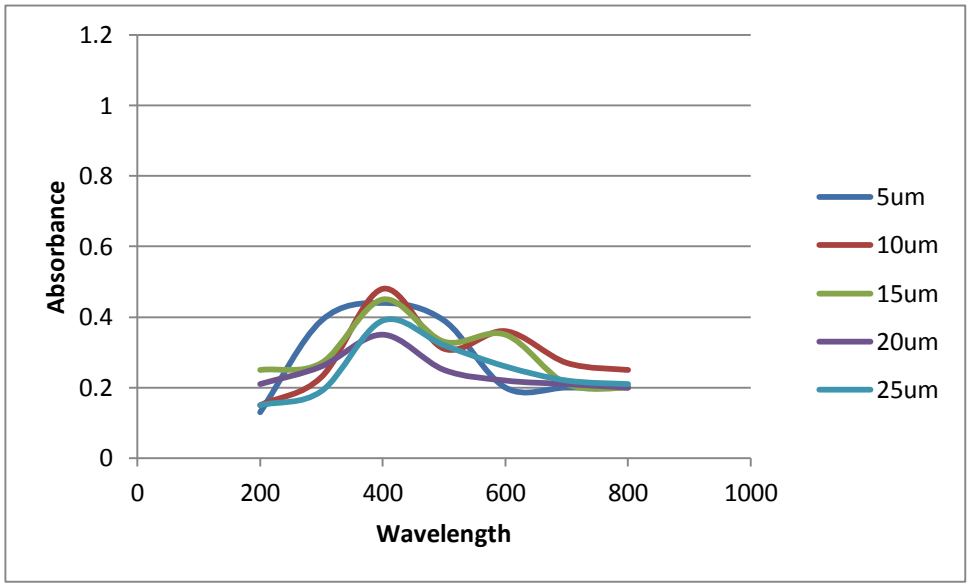

Fig. 7: UV-Vis spectra on Ni(II) detection by MgO-NPs with various concentration.

CONCLUSION

Biological synthesis of stable magnesium oxide nanoparticles was achieved. Characterization of the magnesium oxide nanoparticles using UV–vis spectroscopy, FTIR spectroscopy, SEM and XRD was equally achieved. Surface plasmon absorption, various functional groups responsible for the reduction of magnesium oxide ions to magnesium oxide nanoparticles, morphology and crystallite of the magnesium oxide nanoparticles were all revealed via these techniques. The use of the colloidal magnesium oxide nanoparticles in detecting Ni(II) ions in

aqueous solutions was successful because detections were made even at low concentrations. Therefore this colorimetric method should be adopted for easy detection. Moreso, the obtained results encourage the use of economical synthesis of magnesium oxide nanoparticles in the development of nanosensor to detect the pollutants present in industrial effluents.

REFERENCES

1. Csuros, M. & Csuros, C. (2002). 1st ed. Environmental sampling and analysis for metals (Lewis, Florida, 2002), p. 5.
2. Akpor, O. B., Ohiobor, G. O. & Olaolu, T. D. (2014). Heavy metal pollutants in wastewater effluents: Sources, effects and remediation. *Adv. Biosci. Bioeng*., 2, 37-43.
3. Goyer, R. (1991). Toxic effects of metals, In: Casarett and Doull's Toxicology, 4th ed. Amidur, M. O., Doull, J. D and Klaassen, C. D. eds. Pergamon Press, New York. pp. 623-680.
4. Rendall, R. E. G., Philips, J. I. & Renton, K. A. (1994). Death following exposure to fine particulate nickel from a mental arc. *Process, Ann. Occup. Hyg*., 38, 921-930.
5. Gul, H. T., Saseed, S., Khan F. Z. A. & Manzoor, S. A. (2014). Potential of nanotechnology in agriculture and crop protection: A Review. *App. Sci and Bus. Eco.*, 1, 23-28.
6. Ali, A., Zafar, A., Zia, M., Hag, I. U., Phull, F. R., Ali, J. S. & Hussain, A. (2016). Synthesized, characterization, application and challenges of iron oxide nanoparticles *Mat. Sci. Nanotech*., 9, 49-67.
7. Prakash, P., Gnanaprakasam, P., Emmauel, R., Arokiyaraj, S. & Saravanan, M. (2013). Green synthesis of silver nanoparticles from leaf extract of *Mimusopselenyi* L. for enhanced antibatieral activity against multi drug resistant clinical isolated. *Colloid, surf. B: Biointer.,* 108, 255-259. http://dx.doi.org/10.1016/j.colsurfb.2013.03.017
8. Ahmed, S., Ahmed, M., Swami, B. L. & Ikram, S. (2016). A review on plant extract mediated synthesis of silver nanoparticles for antimicrobial applications: A green expertize. *J. Adv. Res*., 7, 17-28.
9. Saranya**, S.,** Vijayarani, K. & Pavithra**, S. (**2017). Green synthesis of iron nanoparticles using aqueous extract of *Musa ornata* flower sheath against pathogenic bacteria. *Indian J. Pharm. Sci*., 79, 688-694.

10. Ojekale, A. B., Makinde, S. C. O. & Osileye, O. (2007). Phytochemistry and antimicrobial evaluation of *Thaumatococcus daniellii(Benth*) leaves. *Nig. Food J.*, 25, 176- 183.
11. Hamid, A. A., Aliyu, M. A. , Abubakar, L. Z. , Mukadam, A. A., Shehu, A., Egharevba, G., Adisa, M. J., Ajibade, S. O., Zubair, A. O. & Fagbohun, E. O. (2017). *Thaumatococcus daniellii* leaves: Its chemical compositions, antioxidant and antimicrobial activities. *Ife Sci. J.*, 19, 409-416.
12. Ukwubile, C., Oise, I. & Nyiayem, J. (2017). Preliminary screening and antibacterial activity of *Thaumatococcus daniellii (Benn) Benth (Marantacae)* leaf extract. *J. Bacteriol Myclo Open Access*, 4, 00086.
13. Dahri, M. K., B. L., Lim, L., Kooh, M. R. R. & Chan, C. M. (2017). Adsorption of brilliant green from aqueous solution by unmodified and chemically modified *Tarap* (*Artocarpus odoratissimus*) peel. *International Journal of Environmental Science and Technology*, 14, 2683–2694.
14. Ding, H. L., Zhang, Y. X., Wang, S., Xu, J. M., Xu, S. C. & Li, G. H. (2012). Fe_3O_4@ SiO2 core/shell nanoparticles: the silica coating regulations with a single core for different core sizes and shell thicknesses. *Chemistry of Materials*, 24, 4572–4580.
15. Okwunodulu, F. U., Ufearoh, S. M., Amaku F. J. & Ani, A. N. (2020). Colorimetric detection of Hg(II) ions present in industrial wastewater using zinc nanoparticle synthesized biologically with Rauwolfia vomitoria leaf extract. *Communication in Physical Sciences*, 5, 509-517.
16. Mahdavi, M., Ahmad, M., Haron, M. J., Namvar, F., Nadi, B., Rahman, M. & Amin, J. (2013). Synthesis, surface modification and characterization of biocompatible magnetic iron oxide nanoparticles for biomedical applications. *Molecules*, 18, 7533-7548.
17. Taufiq, M., Eden, W. T., Sumarni, W. & Alauhdin, M. (2021). Colorimetric detection of metal ions using green-synthesized silver nanoparticles. *J. Phys.: Conf. Ser.*, 1918, 032002.
18. Shrivas, K., Sahu, B., Deb, M. K., Thakur, S. S., Sahu, S., Kurrey, R., Kant, T., Patle, T. K. & Jangde, R. (2019). Colorimetric and paper-based detection of lead using PVA capped silver nanoparticles: Experimental and theoretical approach. *Microchem. J.*, 150, 104156.