Article:

Nejo, A.O., Adetona, A.J. and Lawal, A. (2024) Green synthesis of nickel oxide nanoparticles and its application in the degradation of methyl red. Lafia Journal of Scientific and Industrial Research, 2 (2). pp. 54-60. ISSN 3026-9288

https://doi.org/10.62050/ljsir2024.v2n2.328

Lafia Journal of Scientific & Industrial Research (LJSIR), Vol. 2(2), 2024
p-ISSN: 3026 - 9288 e-ISSN: 3027 - 1800 pages: 54 - 60
https://lafiascijournals.org.ng/index.php/ljsir/index ⇒ Published by the Faculty of Science,
Federal University of Lafia, Nasarawa State, Nigeria

Green Synthesis of Nickel Oxide Nanoparticles and its Application in the Degradation of Methyl Red

Ayorinde O. Nejo[1]*, Ademola J. Adetona[2] & Adetoun Lawal[1]
[1]Department of Chemistry, University of Lagos, Nigeria
[2]Department of Materials Science and Engineering, the University of Sheffield, UK. S1 3JD

Abstract

Environmental pollution is a threat to human health, with methyl red dye used in printing and textile dyeing being a notable pollutant that can cause eye, skin, and digestive system irritation. This study investigates the degradation of methyl red dye using nanoparticles of Nickel Oxide (NiO NPs) as photocatalysts. NiO NPs were synthesised at room temperature through thermal decomposition using antioxidant-rich extracts from strawberries (Fragaria ananassa), grapes (Vitis vinifera), and grapefruits (Citrus paradisi). Characterisation of the NiO NPs was performed using FTIR, UV-Vis spectroscopy and SEM. FTIR spectra confirmed the formation of NiO NPs with peaks between 577 – 585 cm^{-1}. UV-Vis spectroscopy showed absorption wavelengths between 322-326 nm for the synthesised NiO NPs and a blue shift to 422-470 nm during methyl red degradation. This study presents a sustainable method for synthesising NiO nanoparticles and demonstrates their effectiveness in environmental remediation, specifically for the removal of pollutant dyes.

Keywords: Green synthesis, NiO nanoparticles, Azo dye, FTIR, SEM

Article History
Submitted
February 22, 2024
Revised
June 4, 2024
First Published Online
June 11, 2024

Corresponding author
A. O. Nejo ✉
funaina2014@gmail.com

doi.org/10.62050/ljsir2024.v2n2.328

Introduction

Nickel oxide (NiO) nanoparticles have garnered significant attention over the years due to their exceptional properties and diverse applications across various fields [1-3]. These nanoparticles demonstrate remarkable thermal and chemical stability [4], a wide bandgap [5] and good electrical properties, rendering them well-suited for a diverse array of technological applications [6]. The benefits of NiO nanoparticles encompass their efficacy in catalysis, good performance in energy storage systems [6, 7] and effectiveness in environmental remediation processes [8]. In addition, their magnetic and capacity to form nanocomposites further enhance their advantages in biomedical fields [9], including targeted drug delivery and MRI [9]. The syntheses of NiO nanoparticles are continuously advancing, presenting promising developments in both industrial and scientific domains. However, the potential environmental and health concerns of NiO-NPs are valid. The World Health Organization (WHO) has classified NiO-NPs as carcinogens, underscoring the need for caution [10]. However, green chemistry synthesis of NiO NPs offers a sustainable and environmentally friendly approach to NiO NPs synthesis, mitigating these risks and ensuring their safe use.

Green synthesis involves the use of optimal solvent systems and natural resources such as plant and fruit extracts, which enables large-scale production of nanoparticles. By using plant and fruit extracts, green synthesis provides a simple method compared to other biological approaches, and produces biogenic nanoparticles. This technique takes advantage of plant biodiversity and phytochemicals present in the leaves, fruits and roots, which can influence parameters such as solvent, temperature, pressure, and pH.Several studies have prepared NiO NPs by green syntheses using different plants as capping agents. Various plants/roots/fruit extracts have been reported in the green preparation of NiO NPs are Moringa oleifera [11], Agarose [12], Agathosma betulina [13], Callistemon viminalis [14], Tamarix serotine [15], G. wallichianum leaves extract [16], Peels of fresh Punica granatum [17] and Nephelium lappaceum [18]. However, no report on the use of fresh fruits such as grapes, strawberries and grapefruit.

Here, nickel oxide nanoparticles weresynthesised using various fruits, Fragaria × ananassa (strawberries), *Vitis vinifera* (grapes), and Citrus × paradisi (grapefruit), as capping agents. The morphology, electronic transition, and vibrational band of the NiO NPs were investigated. The photocatalytic properties of the nanoparticles were investigated for the degradation of methyl red (Azo) dye.

Materials and Methods

Experimental methods

Preparation of capping agents: 100 g of each capping agent (Vitis vinifera – grapes, Fragaria × ananassa – strawberries, and Citrus × paradisi – grapefruit) were washed and boiled separately at 100°C for 45 min before blending. Eachfruit was blended andtriple-filtered before beingstored in the refrigerator at 5°C. The pH of the fruit extracts (capping agent)was recorded at room temperature (RT).

Green synthesis of NiO nanoparticles: 28 mg of $NiSO_4 \cdot 6H_2O$ was dissolved in 70 mL distilled water, and the solution was constantly stirred at 70°C for 20 min. 10 mL of grape extract was added to the solution as a capping agent with a pH of 1.8. Thereafter, 20 mL of 1M NaOH solution was added and stirred constantly at 70°C for 30 min until a dark-brown coloration was observed. The pH of the solution was measured to be 11. The dark-brown colourationsolution was settled and cooled to RT, and the suspension was carefully decanted and filtered, resulting in potential NiOH nanoparticles. After calcination of the NiOH NPs at 600°C for 40 min, a black powder was assumed to be NiO NPs and characterised.The procedure was repeated for Citrus × paradisi – grapefruitextracts pH ≈1.6 and Fragaria × ananassa – strawberriese extracts ≈1.9.

Characterisation of the NiO NPs: The chemical, physical, and optical properties of the NiO NPs were studied using different spectroscopic techniques. The NiO NP powder microstructures were examined in an FEI Inspect F Scanning Electron Microscope (SEM). The vibrational mode of the NiO nanoparticles was studied by Bruker FTIR spectrometer, and the electronic transition was investigated by the UV Shimadzu series.

Degradation of methyl red (Azo) dye: 100 ml of methyl red (Azo dye) solution, 80 mg of NiO NP, and 60 ml of $NaBH_4$ (catalyst) were combined in a beaker and stirred on a magnetic stirrer at room temperature for 30 min. The degradation of the methyl red solution was monitored using UV-visible spectroscopy in the range of 200 – 700 nm for 100 min.

Results and Discussion

UV visible spectra

The UV-visible absorbance spectrum of the green synthesised NiO nanoparticles (NiO-NPs) using extracts from Vitis vinifera (grapes), Fragaria × ananassa (strawberries), and Citrus × paradisi (grapefruit) is shown in Fig. 1. The spectrareveal distinct absorption peaks corresponding to each type of fruit extract used in the synthesis process. For the NiO-NPs synthesised with Fragaria × ananassa (strawberries) extract, an absorption peak was observed at 335 nm, Fig. 1a. This peak indicates the presence of NiO nanoparticles with the wavelength suggesting interactions between the nanoparticle surface and the Fragaria × ananassa (strawberry) extract. The NiO-NPs synthesised with Vitis vinifera (grapes) extract exhibited an absorption peak at 312 nm, Fig. 1b. This peak is blue-shifted compared to the peak observed for the Fragaria × ananassa (strawberry) extract. The shift towards a shorter wavelength indicates differences in the size, shape, or surface chemistry of the nanoparticles, possibly due to the phytochemical composition of the Vitis vinifera extracts. For the NiO-NPs synthesised with Citrus × paradisi (grapefruit) extract, an absorption peak was observed at 326 nm, Fig. 1c. This peak lies between the peaks observed for the Fragaria × ananassa (strawberry) and Vitis vinifera (grapes) extracts. The intermediate position of this peak suggests that the grapefruit extract produces NiO nanoparticles with a distinct characteristic compared to the other two extracts but shares some similarities with both. The shifts in the absorption peaks among the different fruit extracts highlight the influence of the phytochemical properties of the extracts on the optical properties of NiO nanoparticles, and the results are comparable to the literature [16-18]. These variations are a result of the size and morphology differences of the NiO nanoparticles, as well as the type of fruit extracts capping the nanoparticle surfaces. The observed shifts indicate that the fruit extract plays a major role in tuning the optical composition of the green synthesised NiO-NPs.

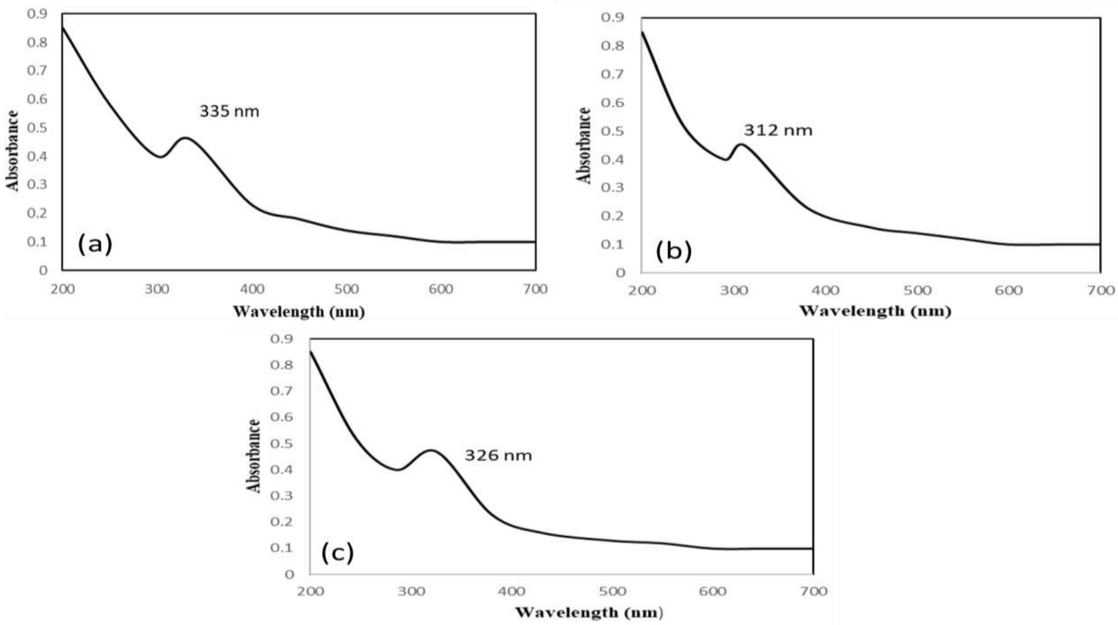


Figure 1: UV-Vis spectra of NiO NPs green synthesised by (a) Fragaria × ananassa (strawberries) extract, (b) Vitis vinifera (grapes) extract, and (c) Citrus × paradisi (grapefruit) extract

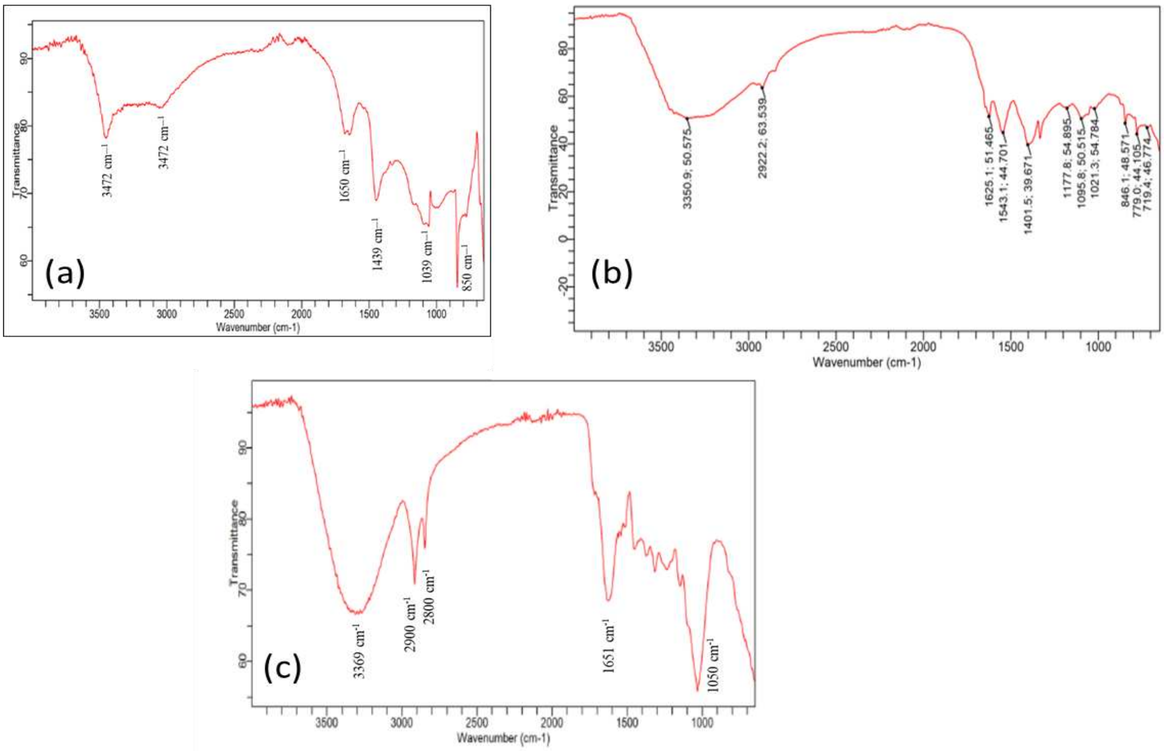


Figure 2: FT-IR spectra of NiO NPs green synthesised by (a) Fragaria × ananassa (strawberries) extract, (b) Vitis vinifera (grapes) extract, and (c) Citrus × paradisi (grapefruit) extract

Infra spectra

Figure 2 (a-c) shows the spectra of NiO NPs synthesisedutilising extracts from Fragaria × ananassa (strawberry), Fig. 2a, Vitis vinifera (grape), Fig. 2b, and Citrus × paradisi (grapefruit), Fig. 2c. Characteristic peaks were observed below 1000 cm^{-1}, indicative of metal-oxygen bonds, affirming the preparation of NiO NPs in all samples, with prominent peaks between 520 – 600 cm^{-1} attributed to the Ni–O bond, validating the successful synthesis of nickel oxide nanoparticles from fruit extracts. However, additional bands were present in the spectra. Broad peaks in the range of 3350 – 3472 cm^{-1} are characteristic of O-H groups, while bands between 2850 – 3040 cm^{-1} correspond to C-H stretching bonds. These extra bonds were also reported in the literature [16, 17] for the green syntheses of NiO NPs. Additional FTIR spectra for the syntheses of NiO NPs are presented in supplementary section (see Appen. S1 – S3).

Band gap energy

The band gap energy determines the colour of light that a material can absorb. Compounds with bigger band gaps absorb light at shorter wavelengths, which corresponds to higher energy, while compounds with smaller band gaps absorb light at longer wavelengths, indicating lower energy absorption. NiO NPs band gaps prepared from the extracts of Fragaria × ananassa (strawberry), Vitis vinifera (grape), and Citrus × paradisi (grapefruit) were calculated according to equation 1, and it is shown in Table 1. The values obtained were similar to the literature [14, 16, 17].

The wavelength was obtained from the FTIR spectral.

$$E = \frac{hc}{\lambda} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where λ = wavelength, C = speed of light and h = Planck's constant = 6.626 x 10^{-34}Js.

Table: Band gap energy of NiO NPs from different fruit extracts

Fruit extracts	Wavelength (λ)	Planck's Constant (Js)	Speed of Light (m/s)	NiO NPs Band gap energy (J)	NiO NPs band gap energy (eV)
Fragaria × ananassa	335×10^{-9}	6.626 x 10^{-34}	3 x 10^{8}	5.93 x 10^{-19}	3.7
Vitis vinifera	312×10^{-9}	6.626 x 10^{-34}	3 x 10^{8}	6.37 x 10^{-19}	3.98
Citrus × paradisi	326×10^{-9}	6.626 x 10^{-34}	3 x 10^{8}	6.09 x 10^{-19}	3.8

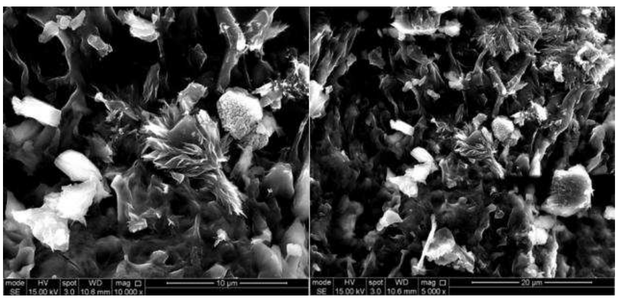


Figure 3: SEM micrographs of NiO NPs green synthesised by Citrus × paradisi (grapefruit) extract

Scanning electron microscopy
Figure 3 shows the SEM micrographs of NiO NPs synthesised using Citrus × paradisi (grapefruit) extract. The micrographs reveal compacted grains with varied morphologies and sizes, showing significant agglomeration into crumb-like clusters. Suggesting that the nanoparticles are prone to forming aggregates, likely influenced by the organic compounds in the grapefruit extract. Due to equipment constraints, we were unable to obtain SEM micrographs for NiO NPs synthesised using Fragaria × ananassa (strawberry) and Vitis vinifera (grape) extracts. This limitation prevents a comparative analysis of the morphological differences between the nanoparticles synthesised with different fruit extracts. Albeit, the results show that the synthesis method, particularly the fruit-type extract used, significantly affects the morphology and agglomeration of NiO NPs. Further studies are needed to explore these effects comprehensively.

Energy dispersive x-ray spectroscopy (EDAX)
Figure 4 shows the elemental analysis of the NiO NPs, obtained from Energy Dispersive X-ray Analysis (EDAX) integrated with the SEM micrographs. The EDS spectra of NiO NPs green synthesised using Citrus × paradisi (grapefruit) extract confirmed nickel and oxygen peaks, with someimpurities peaks. The EDX result supports the results obtained from FTIR.

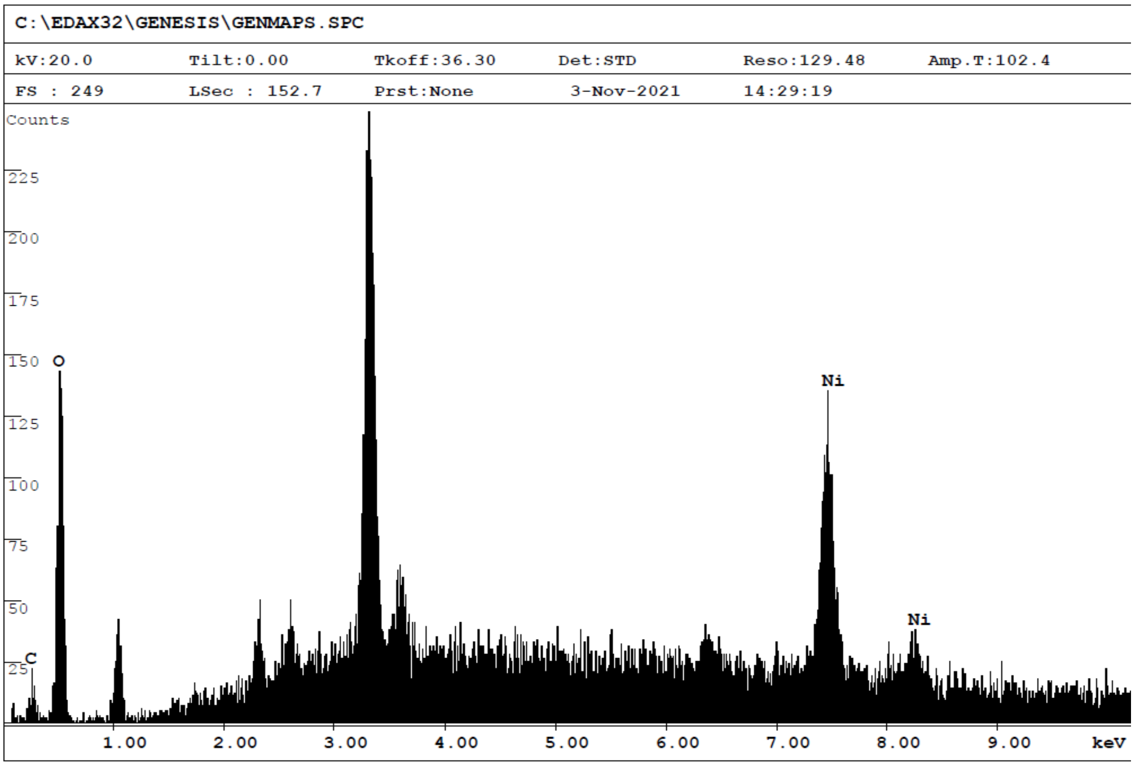


Figure 4: EDX image of NiO NPs green synthesised by Citrus × paradisi (grapefruit) extract

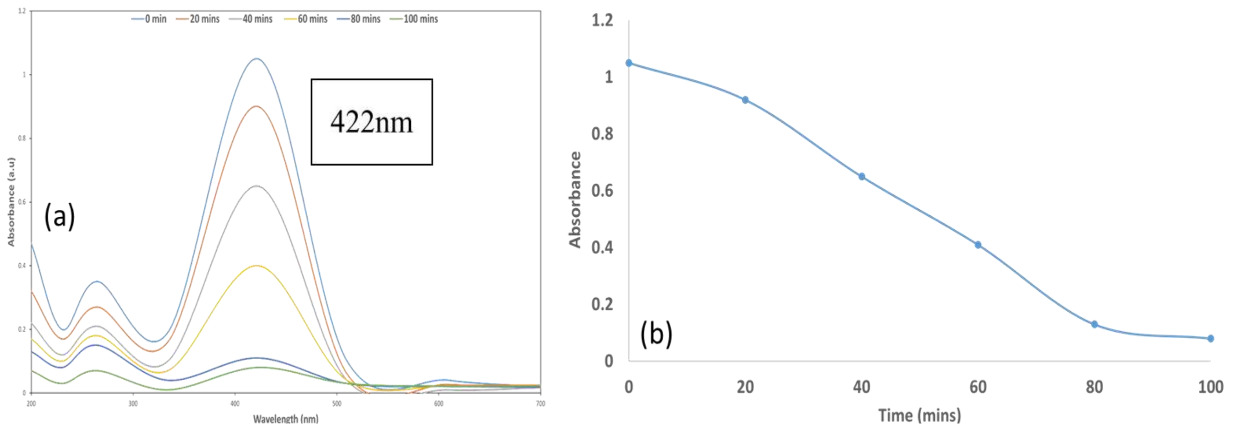


Figure 5: (a) UV-Vis spectra of methyl red degradation by using $NaBH_4$ and NiO NPs synthesised from Fragaria × ananassa (strawberry) and (b) Absorbance monitoring the decrease in methyl red intensity

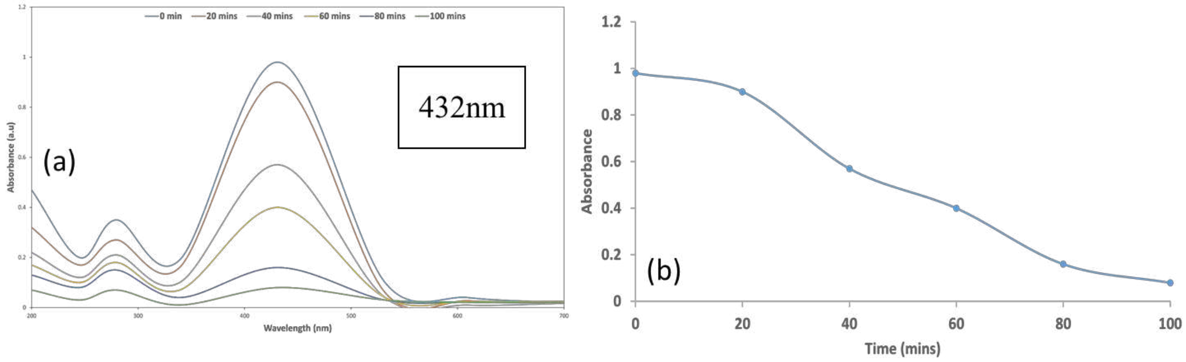


Figure 6: (a) UV-Vis spectra of methyl red degradation by using $NaBH_4$ and NiO NPs synthesised from Vitis vinifera (grape) and (b) Absorbance monitoring the decrease in methyl red intensity

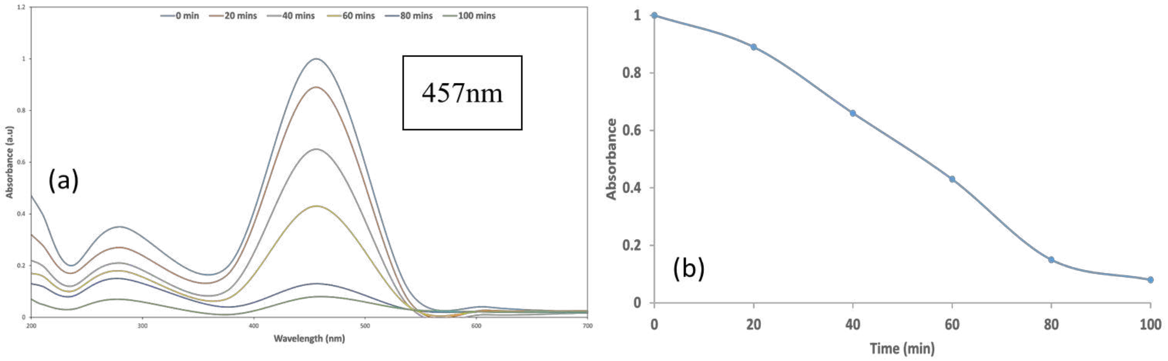


Figure 7: (a) UV-Vis spectra of methyl red degradation by using $NaBH_4$ and NiO NPs synthesised from Citrus × paradisi (grapefruit) and (b) Absorbance monitoring the decrease in methyl red intensity

Azo dye degradation

The methyl red solution (azo dye) degradation was monitored by a UV-vis spectrophotometer, revealing a timeline of colour transformation and absorbance reduction. Within the first 20 min, significant methyl red degradation was evident for the NiO NPs, as indicated by a noticeable decrease in absorbance, Figs 5 – 7. The complete transition from pale yellow to colourless was achieved in approximately 100 min. This process was tracked by observing the decline in absorbance at the maximum wavelengths specific to each NiO NPs synthesised from fruit extracts: 422 nm for Fragaria × ananassa (strawberries), 432 nm for Vitis vinifera (grapes), and 457 nm for Citrus × paradisi (grapefruit). The shift in wavelengths indicates the NiO NPs characteristic, and these findings prove the effectiveness of the dye degradation by NiO NPs.

Conclusions

We successfully synthesised nickel oxide nanoparticles using a green synthesis approach, employing fruit extracts from Vitis vinifera (grapes), Fragaria × ananassa (strawberries), and Citrus × paradisi (grapefruit) as capping agents. The NiO NPs were characterised using various spectroscopic techniques, including UV-Vis, FTIR, and SEM. The FTIR spectra exhibited distinct peaks at 577, 585, and 579 cm^{-1}, confirming the formation of NiO nanoparticles. The synthesised NiO NPs demonstrated significant catalytic efficiency in the degradation of methyl red dye. Employing $NaBH_4$ as a reducing agent and monitoring the reaction through UV-Vis spectrophotometry at different time intervals, this study provides a sustainable and eco-friendly method for synthesising NiO nanoparticles and highlights their potential application in environmental remediation, specifically in the removal of pollutant dyes.

Declaration and conflict of interest: The authors declare that they have no known competing financial interests that could have influenced the work reported in this paper.

Acknowledgements: The authors acknowledge the support of the Department of Chemistry, University of Lagos.

References

[1] Sagadevan, S., Fatimah, I., Lett, J. A., Rahman, M. Z., Leonard, E. Oh, W. C. (2023). Eco-friendly green approach of nickel oxide nanoparticles for biomedical applications. *Open Chemistry,* 21. https://doi.org/10.1515/chem-2023-0141.

[2] Kate, R. S., Khalate, S. A. & Deokate, R. J. (2018). Overview of nanostructured metal oxides and pure nickel oxide (NiO) electrodes for supercapacitors: A review. *Journal of Alloys and Compounds,* 734, 89–111. https://doi.org/10.1016/j.jallcom.2017.10.262

[3] Singh, A., Goyal, V., Singh, J., Kaur, H., Kumar, S., Batoo, K. M., Gaur, J., Pal, M., Rawat, M. & Hussain, S. (2022). Structurally and morphologically engineered single-pot biogenic synthesis of NiO nanoparticles with enhanced photocatalytic and antimicrobial activities. *J. of Cleaner Produc.,* 343, 131026. doi.org/10.1016/j.jclepro.2022.131026.

[4] Kathiravan, P., Thillaivelavan, K., Viruthagiri, G., Shanmugam, N. (2024). Investigations of thermal, structural, optical, morphological and magnetic properties of chemical precipitation synthesized NiO nanoparticles for optoelectronic applications. *Journal of the Indian Chemical Society,* 101171. https://doi.org/10.1016/j.jics.2024.101171

[5] Gandhi, A. & Wu, S. (2017). Strong deep-level-emission photoluminescence in NiO nanoparticles. *nanomaterials*, 7, 231–231. https://doi.org/10.3390/nano7080231

[6] Kumar Rai, A. Tuan Anh, L. Park, C.-J. & Kim, J. (2013). Electrochemical study of NiO nanoparticles electrode for application in rechargeable lithium-ion batteries. *Ceramics Int.*, 39, 6611–6618. https://doi.org/10.1016/j.ceramint.2013.01.097

[7] Biju, V., Abdul Khadar, M. (2001). DC conductivity of consolidated nanoparticles of NiO. *Materials Research Bulletin* 36, 21–33. https://doi.org/10.1016/s0025-5408(01)00488-3.

[8] Ali, T., Warsi, M. F., Zulfiqar, S., Sami, A., Ullah, S., Rasheed, A., Alsafari, I. A., Agboola, P. O., Shakir, I. & Baig, M. M. (2022). Green nickel/nickel oxide nanoparticles for prospective antibacterial and environmental remediation applications. *Ceramics Int.,* 48, 8331–8340. https://doi.org/10.1016/j.ceramint.2021.12.039

[9] Venkatalakshmi, N., Jyothi Kini, H. & Bhojya Naik, H. S. (2023). Green-synthesized nickel oxide nanoparticles: Magnetic and biomedical applications. *Inorganic Chemistry Communications*, 110490. https://doi.org/10.1016/j.inoche.2023.110490.

[10] Karlsson, H. L., Toprak, M. S. & Bengt Fadeel (2022). Toxicity of metal and metal oxide nanoparticles. *Elsevier EBooks*, 87–126. doi.org/10.1016/b978-0-12-823292-7.00002-4.

[11] Ezhilarasi, A. A., Vijaya, J. J., Kaviyarasu, K., Maaza, M., Ayeshamariam, A. & Kennedy, L. J. (2016). Green synthesis of NiO nanoparticles using *Moringa oleifera* extract and their biomedical applications: Cytotoxicity effect of nanoparticles against HT-29 cancer cells. *Journal of Photochemistry and Photobiology B: Biology*, 164, 352–360. https://doi.org/10.1016/j.jphotobiol.2016.10.003.

[12] Alagiri, M., Ponnusamy, S. & Muthamizhchelvan, C. (2011). Synthesis and characterization of NiO nanoparticles by sol-gel method. *J. of Mater. Sci.: Mater. in Electro.*, 23, 728–732. https://doi.org/10.1007/s10854-011-0479-6.

[13] Ahmed, A. A. A., Issa, S. A., Al-Marbie, S. A., Al-Geraei, M. A., Al-Mtouakell, H. A., Al-Mangathi, S.A., Abduljaleel, J. M. & Qaid, A. A. (2020). Structural, optical and antibacterial characteristics of CdO nanostructure prepared via simple method. *Albaydha University Journal*, 2, 16–24. https://doi.org/10.56807/buj.v2i2.51.

[14] Sone, B. T. (2016). Physical & electrochemical properties of green synthesized bunsenite NiO nanoparticles via callistemon viminalis' extracts. *Int. J. of Electrochem. Sci.*, 8204–8220. https://doi.org/10.20964/2016.10.17.

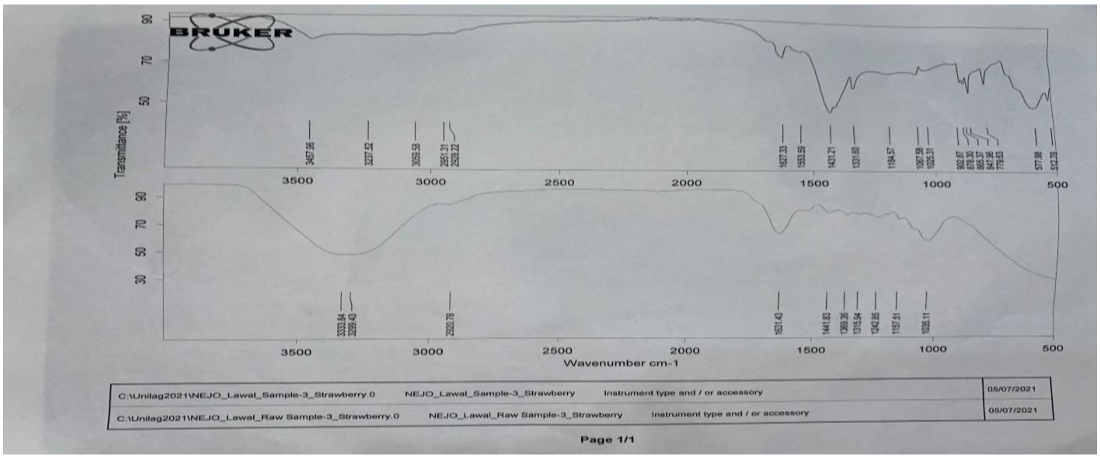
[15] Nasseri, M. A., Ahrari, F. & Zakerinasab, B. (2016). A green biosynthesis of NiO nanoparticles using aqueous extract of *Tamarixserotina* and their characterization and application. *Appl. Organometallic Chem.,* 30, 978–984. https://doi.org/10.1002/aoc.3530.

[16] Abbasi, B. A., Iqbal, J., Mahmood, T., Ahmad, R. Kanwal, S. & Afridi, S. (2019). Plant-mediated synthesis of nickel oxide nanoparticles (NiO) via Geranium wallichianum: characterization and different biological applications. *Materials Research Express,* 6, 0850a7. https://doi.org/10.1088/2053-1591/ab23e1.

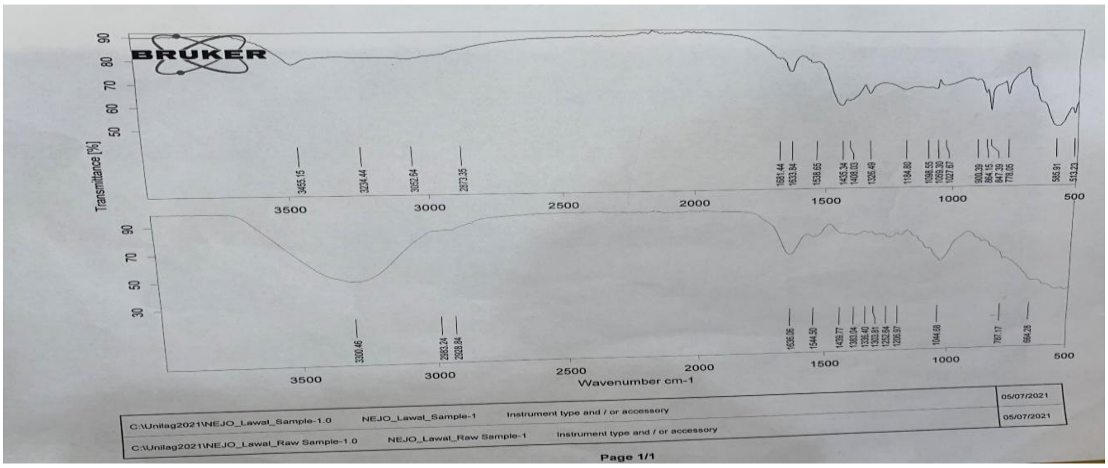
[17] Biplab Kumar Mandal, Mandal, R., Suranjan Sikdar, Sarma, S., Srinivasan, A., Subhajit Roy Chowdhury, Das, B. & Das, R. (2023). Green synthesis of NiO nanoparticle using Punica granatum peel extract and its characterization for methyl orange degradation. *Materials Today Communications,* 34, 105302–105302. doi.org/10.1016/j.mtcomm.2022.105302.

[18] R. Yuvakkumar, J., Suresh, A. J., Nathanael, M., Sundrarajan, S. I., Hong, Rambutan (2014). (*Nephelium lappaceum* L.) peel extract assisted biomimetic synthesis of nickel oxide nanocrystals. *Materials Letters,* 128, 170–174. https://doi.org/10.1016/j.matlet.2014.04.112

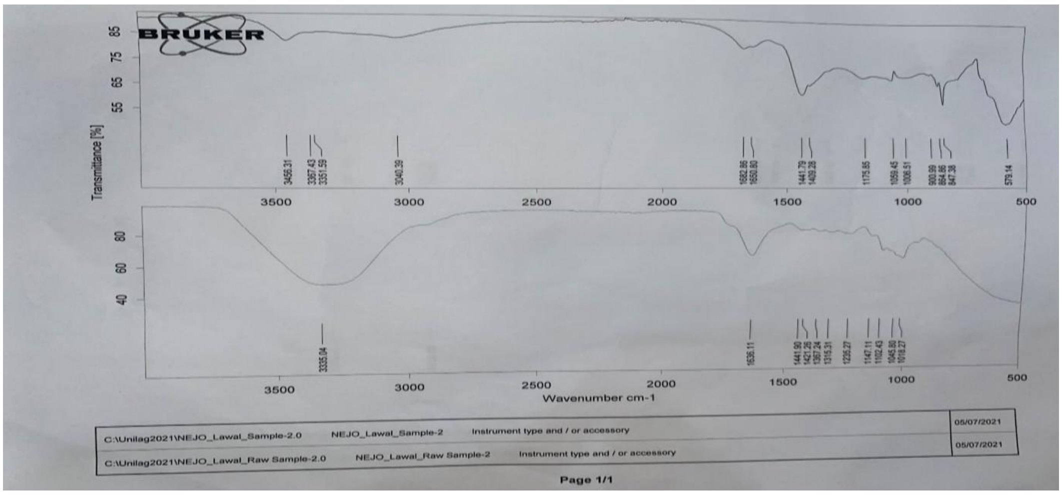
APPENDICES



Appendix S1: FT-IR spectra of NiO NPs green synthesised by Fragaria × ananassa (strawberries) extract



Appendix S2: FT-IR spectra of NiO NPs green synthesised by Vitis vinifera (grapes) extract



Appendix S3: FT-IR spectra of NiO NPs green synthesised by Citrus × paradisi (grapefruit) extract

Citing this Article

Nejo, A. O., Adetona, A. J. & Lawal, A. (2024). Green synthesis of nickel oxide nanoparticles and its application in the degradation of methyl red. *Lafia Journal of Scientific and Industrial Research,* 2(2), 54 – 60. https://doi.org/10.62050/ljsir2024.v2n2.328