Jurnal Akademika Kimia, 11(3): 146-152, August 2022
ISSN (online) 2477-5185 | ISSN (print) 2302-6030
http://jurnal.fkip.untad.ac.id/index.php/jak/

OPEN ACCESS

Plant-mediated Green Synthesis of Nanoparticles $NiCoFe_2O_4$ Photocatalyst Using Africa Leaves Infusion

Siti Rodiah* & Catur O. Ditiyaningrum

Kimia, Fakultas Sains dan Teknologi, Universitas Islam Negeri Raden Fatah Palembang, Palembang - Indonesia

Received 15 June 2022, Revised 14 July 2022, Accepted 11 August 2022
doi: 10.22487/j24775185.2022.v11.i3.pp146-152

Abstract

Nanoparticles (NPs) can be synthesized using a simple and environmentally friendly method by utilizing infuse of the plant. The secondary metabolites contained in infused Africa leaves were used as reducing and stabilizing agents in the synthesis of $NiCoFe_2O_4$ NPs. The characteristics and photocatalytic activity of $NiCoFe_2O_4$ against the photodegradation of diazinon have been investigated using UV-Vis, FTIR, XRD, and SEM. The UV-Vis spectra showed that $NiCoFe_2O_4$ had been formed, as established with a maximum absorbance peak at 277 nm. The FTIR results also confirmed the presence of a ferrite spinel group at a wave number of 565cm-1. The XRD diffractogram showed a cubic crystal of $NiCoFe_2O_4$ with a size of 8.79 nm, which was also confirmed from the SEM images that the NPs were slightly agglomerated with an average size of 94.37 nm. The photocatalytic performance of $NiCoFe_2O_4$ against diazinon which was carried out for 300 minutes under UV light obtained a degradation percentage of 72.40% producing diazoxide, 2-isopropyl-6-methyl-4-pyramidal (IMP) and diethyl phosphonate. It was concluded that infused African leaves had an active role in the synthesis of $NiCoFe_2O_4$.

Keywords: $NiCoFe_2O_4$ nanoparticles, photodegradation, diazinon

Introduction

Ferrite-based nanoparticles are starting to develop due to their wide use in technology and industry (Gibin & Sivagurunathan, 2017). Among the spinel ferrite group, nickel cobalt ferrite ($NiCoFe_2O_4$) attracts special attention, because it had good chemical properties such as thermal stability, high electrical resistivity, and high cursivity (Velhal et al., 2015). Previous studies synthesized $NiCoFe_2O_4$ which was applied as catalysts in the degradation of pollutant compounds, including reduction of nitroaromatic compounds and photo-oxidative degradation of rhodamine B (Singh et al., 2014), methylene blue (Naik et al., 2019), alizarin reds (Srinivas, 2019) and congo red (Abbas et al., 2021).

Synthesis of nanoparticles can be carried out using the sol-gel method (Ridha & Khader, 2021), co-precipitation (Nurmadina et al., 2021), and hydrothermal (Balideh et al., 2021). Synthesis of nanoparticles also can be carried out using a simpler and environmentally friendly method by utilizing secondary metabolites, such as flavonoids, alkaloids, tannins, and saponins that can be used as reducing and stabilizing agents (Sulaiman et al, 2018). Several studies reported that plant extracts such as Physalis angulate, (Sulaiman et al., 2018) stem Foeniculum vulgare, and Mentha arvensis (Ahmad et al., 2020) could synthesize each of these compounds lanthanum oxide (La_2O_3), vanadium pentoxide (V_2O_5), and titanium dioxide (TiO_2). The flavonoids, saponins, tannins, terpenoids, and steroid glycosides contained in African leaf (*Vernonia amygdalina* Del) extract also have the potential as reducing and stabilizing agents (Mwanauta et al., 2014).

In previous studies, most of the secondary metabolites used in the synthesis of NPs were extracted by maceration method using organic solvents. This research led to an extract preparation method that was more environmentally friendly with the use of an abundantly available solvent. Infused Africa leaves were elaborated on their performance as reducing and stabilizing agents in the synthesis of $NiCoFe_2O_4$. The characterization of $NiCoFe_2O_4$ was carried out using UV-Vis, FTIR, XRD, and SEM. The NPs performance on degraded diazinon pollutants has been investigated.

Methods

Materials

The equipment used in this research were glassware, spray bottle, oven, analytical balance, hot plate, and magnetic stirrer, centrifuge, spatula, sonicator, furnace, degradation equipment.

*Correspondence:
Author Siti Rodiah
e-mail: siti.rodiah_uin@radenfatah.ac.id

The instrument used to analyze such is UV-Vis Spectrophotometry (Shimadzu UV-1900), Fourier Transform Infrared (Bruker Alpha 2), X-ray Diffraction (Rigaku MiniFlex 600), and Scanning Electron Microscopy (Tescan Vega3).

The chemicals included NaOH, diazinon, $Ni(NO_3)_3.6H_2O$, $FeCl_3.6H_2O$, $Co(NO_3)_2.6H_2O$ were purchased from Merck, and African leaves (*Vernonia amygdalina* Del) were collected from Palembang, South Sumatra.

Preparation of infused African leaves

The 5 grams of clean African leaf was boiled in 100 ml of distilled water for 30 minutes. Then cooled and filtered to obtain an infused African leaf (Gingasu et al., 2016).

Synthesis of $NiCoFe_2O_4$

The10 ml of infused African leaves were added to the precursor's solution of $Ni(NO_3)_3.6H_2O$, $Co(NO_3)_2.6H_2O$, $FeCl_3.6H_2O$ in a ratio of 1: 1:2. The solution was sonicated for 30 minutes while adding 0.2 M NaOH. Then it was calcined using a muffle furnace at 800 °C for 1 hour and characterized using UV-Vis, FT-IR, XRD, and SEM.

Photocatalytic degradation of diazinon

A 20 ml solution of 18 ppm diazinon was added $NiCoFe_2O_4$ with variations of 3 mg, 6 mg, 9 mg, 12 mg, 15 mg, 18 mg, 21 mg, and 24 mg, then irradiated with a UV lamp for 300 minutes. The degraded solution was centrifuged for 2 minutes at a speed of 9500 rpm, to separate the nano-catalyst from the solution. The solution obtained was measured by UV-Vis spectrophotometry at a wavelength of 247.5 nm (Khoiriah et al., 2020). Then the GC-Ms analysis was performed.

Results and Discussion

Synthesis of $NiCoFe_2O_4$

Figure 1 presents the results of the synthesis of $NiCoFe_2O_4$ using infused African leaves. Synthesized $NiCoFe_2O_4$ nanoparticles were black crystals and could be attracted by a magnet. This explains that the infuse used has an active role in the synthesis process.

The content of secondary metabolites in African leaves (*Vernonia amygdalina* Del) such as phenolic acids, saponins, flavonoids, coumarins, terpenes, luteolin, and lignans (Ijeh & Ejike, 2011) played an important role in synthesizing $NiCoFe_2O_4$ nanoparticles as reducing and stabilizing agents. Phenolic compounds in *Vernonia amygdalina* Del act as organic ligands and reduce metal ions. In addition, polyphenols can undergo enol-keto tautomeric transformation to release reactive hydrogen atom species that play a role in reducing metal ions (Desalegn et al., 2020).

Figure 1. $NiCoFe_2O_4$ Synthesized

UV-Vis analysis

As **Figure 2**, the UV-Vis spectra of $NiCoFe_2O_4$ showed absorption at a wavelength of 277 nm. Previous research found that $CoFe_2O_4$ nanoparticles had an absorption at a wavelength of 273.6 nm (Kulshrestha & Anand, 2019) and NiO nanoparticles have absorption at a wavelength of 290 nm (Racik et al., 2018). This indicates that $NiCoFe_2O_4$ NPs had been formed and were experiencing electron excitation which was indicated by a shift in wavelength at 277 nm.

FTIR analysis

The FTIR spectrum of $NiCoFe_2O_4$ (**Figure 3**) showed the presence of a ferrite spinel group at a wave number of 565 cm^{-1}. The spinel ferrite phase characteristics were in the range of 500-600 in the higher frequency band, the absorption area is due to the distribution of cations at the tetrahedral sites of MFe_2O_4 (Naik et al., 2019; Vinosha et al., 2018).

XRD analysis

Figure 4 shows an X-ray diffractogram of $NiCoFe_2O_4$ nanoparticles confirming the formation of ferrite appearing at peaks of 2θ 18.5°, 35.9°, 37.4°, 43.2°, 53.7°, 57.4° that the Miller index of

NPs identified at (111), (311), (222), (400), (422), and (511) in accordance to JCPDS database No1-1121 (Naik et al., 2019). The synthesized $NiCoFe_2O_4$ had a cubic structure. Miller index is 311 which shows that there is a plane intersection on the x, y, and z axes at points 3, 1, and 1 with the z-axis being perpendicular (Reddy et al., 2016). The crystal size of the nanoparticles calculated using the Debye-Scherrer equation (Eq. 1) was 8.79 nm, where D is the crystal size, k is the diffraction constant (0.9), λ is wavelength and β is Full-Width Half-Maximum.

$$D = \frac{k\lambda}{\beta \cos \theta}$$

Vernonia amygdalina leaf extract was used to synthesize MnO_2 NPs that obtained an average size in the range between 20 nm and 22 nm (Dessie et al., 2020).

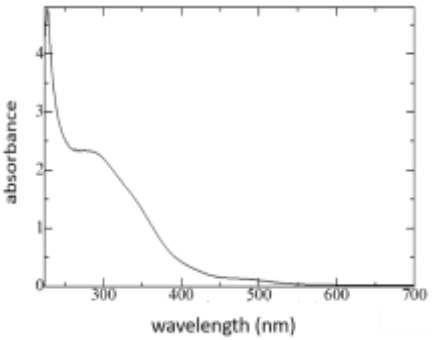

Figure 2. $NiCoFe_2O_4$ UV-Vis absorption spectrum

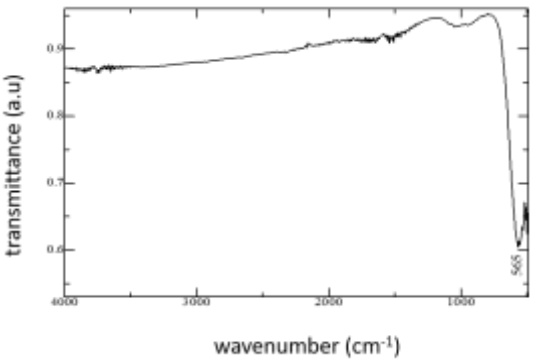

Figure 3. FTIR spectrum of $NiCoFe_2O_4$

SEM analysis

The morphology of $NiCoFe_2O_4$ shown in **Figure 5** is that the $NiCoFe_2O_4$ NPs were cubic in an average size of 94.37 nm and looked slightly agglomerated. The agglomeration occurred because of chemical compounds in the nanoparticles by adding the infused Africa leave (Sari et al., 2017).

Degradation of diazinon

Synthesis of $NiCoFe_2O_4$ was used to degrade diazinon into harmless compounds through photodegradation. $NiCoFe_2O_4$ was exposed to UV light, then absorbed the photons that caused electrons in the valence band to move to the conduction band. The displacement produced a hole in the valence band. The hole generated by the displacement interacts with H_2O on the surface of the photocatalyst to form •OH as a reducing agent. O_2 with electrons in the conduction band forms superoxide radicals as oxidizing agents. These reducing and oxidizing agents attacked the diazinon.

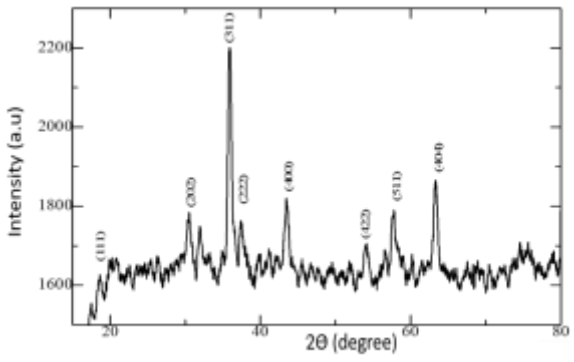

Figure 4. XRD diffractogram of $NiCoFe_2O_4$

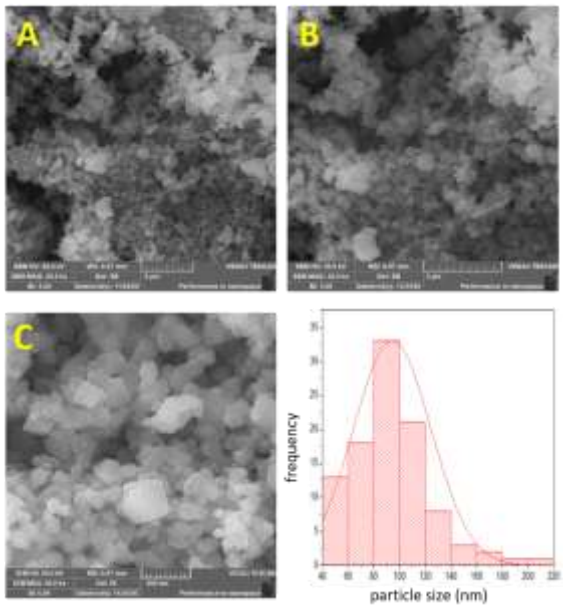

Figure 5. SEM of NiCoFe2O4 nanoparticles magnification (a) 20,000 times, (b) 30,000 times, (c) 50,000 times, (d) Particle size histogram of $NiCoFe_2O_4$

The maximum wavelength of diazinon produced in the current study was 247.5 nm. The effect of adding catalyst mass is shown in **Figure 6**. The more mass of catalyst used, the more increase percentage of degradation, due to the increased surface area of the catalyst and the increasing number of photon absorption on the surface of the catalyst, so that the production of active species increases (Khoiriah et al., 2020). Percent degradation increased with increasing catalyst amount from 3-12 mg, however, the degradation percentage decreased when the catalyst mass was above 12 mg. On the other hand, percent degradation decreased sharply when the catalyst mass was 15 mg, it was caused by the electron-hole undergoing recombination of electrons that occurs very quickly and releases color which was not useful in photocatalysts (Bey, 2009).

The addition of excess catalyst mass (18 – 24 mg) also reduced the percentage of degradation due to agglomeration of the catalyst which inhibited the degradation (Hossaini et al., 2014), as well as the decreased penetration of photons from light to the diazinon solution (Khoiriah et al., 2020).

A previous study utilizing *Vernonia amygdalina* Del leaf extract to synthesize Ag_2O NPs reported that NPs had a band gap of 1.56 eV, and were able to degrade 71.59% of methylene blue (Widyaningtyas et al., 2019). In addition, *Vernonia amygdalina* Del leaf extract was also used to synthesize green silver nanostructures showing a significant synergistic antibacterial effect against *S. aureus, E. coli, P. aeruginosa, and E. aerogenes* (Desalegn et al., 2020).

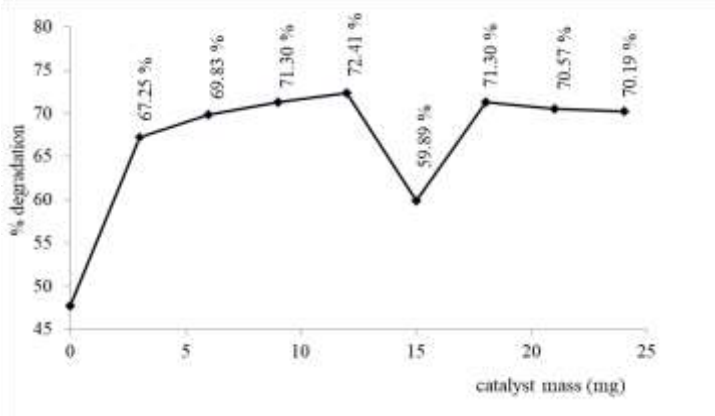

Figure 6. The curve of the effect of adding mass to the catalyst

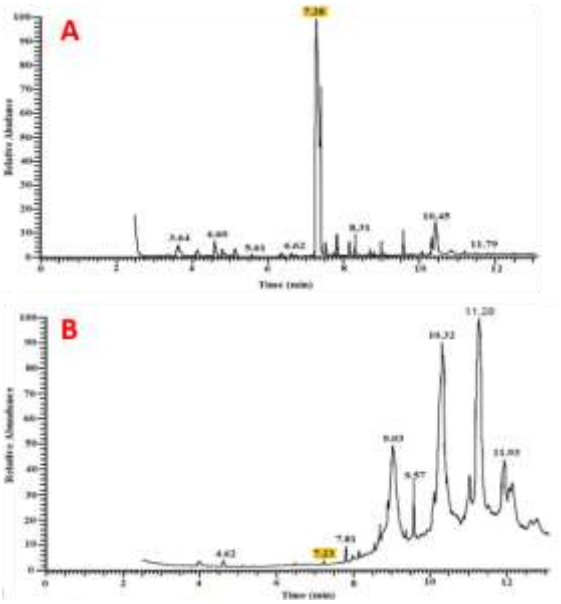

Figure 7. GC spectra of diazinon (a) before (b) after degradation

Fragmentation of diazinon was confirmed using *Gas Chromatography and Mass Spectroscopy* (GC-MS). A chromatogram of diazinon **(Figure 7)** showed a retention time of diazinon before degradation was 7.28 minutes and a shift to 7.23 minutes after degradation. Peak intensity decreased after degradation, indicating that diazinon had been degraded. Diazinon (m/z 304) was fragmented into several compounds as shown in **Figure 8**. Main product of fragmentation diazinon were diazoxide (m/z 289), 2-isopropyl-6-methyl-4-pyrimdiol (IMP) (m/z 152) and diethyl phosphonate (m/z 137) (Sakkas et al., 2005; Wang & Shih, 2016). Diazoxide was formed by the substitution of sulfur with oxygen at the P=S bond through oxidation, then IMP is formed due to the hydrolysis of diazoxide which results in breaking the PO bond in the pyrimidine group (Wang & Shih, 2016). When diazinon was degraded, the OH attack on the –O- functional group forms diazinon into two by-products, namely diethyl phosphonate and IMP (Basfar et al., 2007). Diazinon fragmentation was shown in **Figure 9.**

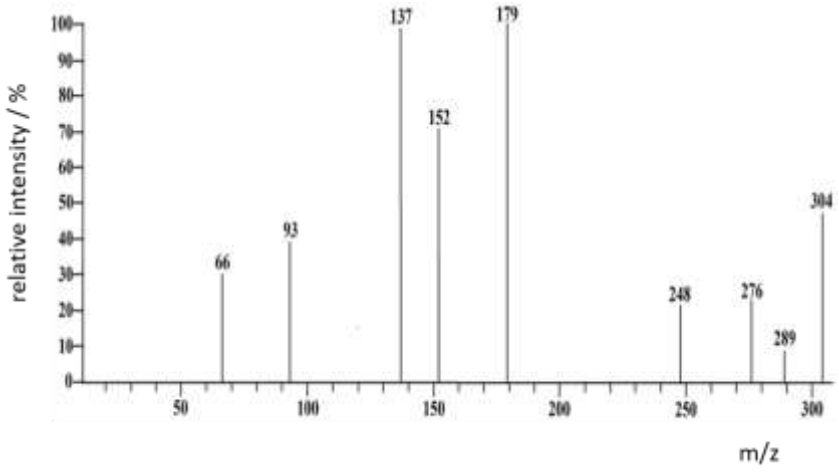

Figure 8. MS spectrum of diazinon

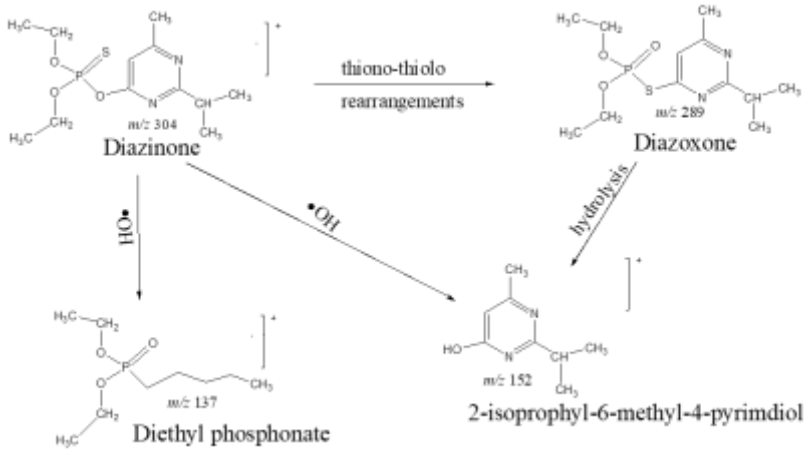

Figure 9. Diazinon fragmentation

Conclusions

Infused African leaves played an active role in the synthesis of $NiCoFe_2O_4$ NPs. Synthesized $NiCoFe_2O_4$ NPs were black crystals, cubic in the average size of 94.37 nm, and slightly agglomerated. The percent degradation of $NiCoFe_2O_4$ NPs to diazinon pesticide through photodegradation was 72.41% with the optimum catalyst mass being 12 mg.

Acknowledgment

The authors would like to thank the integrated laboratory of Universitas Islam Negeri Raden Fatah Palembang for providing laboratory facilities.

References

Abbas, N., Rubab, N., Kim, K., Chaudhry, R., Manzoor, S., Raza, N., Manzoor, S., Raza, N., Tariq, M., Lee, J., & Manzoor, S. (2021). The photocatalytic performance and structural characteristics of nickel cobalt ferrite nanocomposites after doping with bismuth. *Journal of Colloid and Interface Science*, *594*(July), 902–913.

Ahmad, W., Jaiswal, K. K., & Soni, S. (2020). Green synthesis of titanium dioxide (TiO_2) nanoparticles by using mentha arvensis leaves extract and its antimicrobial properties. *Inorganic and Nano-Metal Chemistry*, *50*(10), 1032–1038.

Balideh, S., Avazpour, A., Rezaei, G., & Nikzad, A. (2021). Structural and magnetic properties of spinel nickel-cobalt ferrite nanoparticles substituted by dysprosium cation synthesized by hydrothermal method. *Acta Physica Polonica A*, *140*(1), 14–19.

Basfar, A. A., Mohamed, K. A., Al-Abduly, A. J., Al-Kuraiji, T. S., & Al-Shahrani, A. A. (2007). Degradation of diazinon contaminated waters by ionizing radiation. *Radiation Physics and Chemistry*, *76*(8–9), 1474–1479.

Bey, S. (2009). *Pengujian kinerja fotokatalis berbasis TiO_2 untuk produksi hidrogen dari air*. Unpublished undergraduate's thesis. Jakarta: Fakultas Teknik Universitas Indonesia.

Desalegn, T., Ravikumar, C. R., & Murthy, H. C. A. (2020). Eco-friendly synthesis of silver nanostructures using medicinal plant vernonia amygdalina del. leaf extract for multifunctional applications. *Applied Nanoscience*, *11*(February), 535-551.

Dessie, Y., Tadesse, S., & Eswaramoorthy, R. (2020). Physicochemical parameter influences and their optimization on the biosynthesis of MnO_2 nanoparticles using vernonia amygdalina leaf extract. *Arabian Journal of Chemistry*, *13*(8), 6472–6492.

Gibin, S. R., & Sivagurunathan, P. (2017). Synthesis and characterization of nickel cobalt ferrite ($Ni_{1-x}Co_xFe_2O_4$) nano particles by co-precipitation method with citrate as chelating agent. *Journal of Materials Science: Materials in Electronics*, *28*(January), 1985–1996.

Gingasu, D., Mindru, I., Patron, L., Calderon-Moreno, J. M., Mocioiu, O. C., Preda, S., Stanica, N., Nita, S., Dobre, N., Popa, M., Gradisteanu, G., & Chifiriuc, M. C. (2016). Green synthesis methods of $CoFe_2O_4$ and Ag-$CoFe_2O_4$ nanoparticles using hibiscus extracts and their antimicrobial potential. *Journal of Nanomaterials*, *2016*(2106756) 1-12.

Hossaini, H., Moussavi, G., & Farrokhi, M. (2014). The investigation of the LED-activated FeFNS-TiO_2 nanocatalyst for photocatalytic degradation and mineralization of organophosphate pesticides in water. *Water Research*, *59*(August), 130–144.

Ijeh, I. I., & Ejike, C. E. C. C. (2011). Current perspectives on the medicinal potentials of vernonia amygdalina del. *Journal of Medicinal Plants Research, 5*(7), 1051-1061.

Khoiriah, K., Wellia, D. V., Gunlazuardi, J., & Safni, S. (2020). Photocatalytic degradation of commercial diazinon pesticide using C,N-codoped TiO_2 as photocatalyst. *Indonesian Journal of Chemistry, 20*(3), 587–596.

Kulshrestha, R., & Anand, V. (2019). Synthesis and characterization of pure cobalt ferrite for DC electrical. *International Journal of Innovative Technology and Exploring Engineering (IJITEE)*, *8*(12S), 203–207.

Mwanauta, R. W., Mtei, K. A., & Ndakidemi, P. A. (2014). Prospective bioactive compounds from vernonia amygdalina, lippia javanica, dysphania ambrosioides and tithonia diversifolia in controlling legume insect pests. *Agricultural Sciences*, *5*(12), 1129–1139.

Naik, M. M., Naik, H. S. B., Kottam, N., Vinuth, M., Nagaraju, G., & Prabhakara, M. C. (2019). Multifunctional properties of microwave-assisted bioengineered nickel doped cobalt ferrite nanoparticles. *Journal of Sol-Gel Science and Technology*, *91*(September), 578–595.

Nurmadina., Gareso, P. L., Asri, N. S., Tetuko, A. P., & Setiadi, E. A. (2021). The effect of Ni^{2+} substitution on $CoFe_2O_4$ based on natural iron sand using co-presipitation method. *International Journal of Engineering and Science Applications*, *8*(1), 8-15.

Reddy, M. P., Shakoor, R. A., Mohamed, A. M. A., Gupta, M., & Huang, Q. (2016). Effect of sintering temperature on structural and magnetic properties of $MgFe_2O_4$ ceramics prepared by spark plasma sintering. *Ceramics International*, *42*(3), 4221-4227.

Racik, K. M., Madhavan, J., & Raj, M. V. A. (2018). Synthesis, characterization and optical properties of spherical NiO nanoparticles. *National Laser Symposium (NLS-27), RRCAT* (pp. 1-6). Mumbai: Department of Atomic Energy.

Ridha, S. M. A., & Khader, H. A. (2021). XRD and SEM characteristics of Co-Ni ferrite nanoparticles synthesized using sol-gel method. *Turkish Journal of Computer and Mathematics Education*, *12*(14), 675–687.

Sakkas, V. A., Dimou, A., Pitarakis, K., Mantis, G., & Albanis, T. (2005). TiO2 photocatalyzed degradation of diazinon in an aqueous medium. *Environmental Chemistry Letters*, *3*(November), 57–61.

Sari, R. N., Nurhasni, N., & Yaqin, M. A. (2017). Sintesis nanopartikel ZnO ekstrak sargassum sp. dan karakteristik produknya. *Jurnal Pengolahan Hasil Perikanan Indonesia*, *20*(2), 238-254.

Singh, C., Goyal, A., & Singhal, S. (2014). Nickel-doped cobalt ferrite nanoparticles: Efficient catalysts for the reduction of nitroaromatic compounds and photo-oxidative degradation of toxic dyes. *Nanoscale*, *6*(14), 7959-7970.

Srinivas, M. (2019). Preparation, characterization and photocatalytic activity of nickel-substituted $CoFe_2O_4$: Exploration of changes in the micro structural parameters and distribution of cations in the lattice. *Materials Research Express*, *6*(11), 12-18.

Sulaiman, N., Yulizar, Y., & Apriandanu, D. O. B. (2018). Eco-friendly method for synthesis of La_2O_3 nanoparticles using physalis angulata leaf extract. *Proceedings of the 3rd International Symposium on Current Progress in Mathematics and Sciences 2017* (pp. 1-5). American: AIP Conference Proceedings.

Velhal, N. B., Patil, N. D., Shelke, A. R., Deshpande, N. G., & Puri, V. R. (2015). Structural, dielectric and magnetic properties of nickel substituted cobalt ferrite nanoparticles: Effect of nickel concentration. *AIP Advances*, *5*(097166), 1-11.

Vinosha, P. A., Xavier, B., Anceila, D., & Das, S. J. (2018). Nanocrystalline ferrite (MFe_2O_4, M=Ni, Cu, Mn and Sr) photocatalysts synthesized by homogeneous co-precipitation technique. *Optik*, *157*(March), 441–448.

Wang, C., & Shih, Y. (2016). Facilitated ultrasonic irradiation in the degradation of diazinon insecticide. *Sustainable Environment Research*, *26*(3), 110–116.

Widyaningtyas, A. L., Yulizar, Y., & Apriandanu, D. O. B. (2019). Ag_2O nanoparticles fabrication by vernonia amygdalina del. leaf extract: Synthesis, characterization, and its photocatalytic activities. *IOP Conference Series: Materials Science and Engineering*, *509*(012022), 1-6.