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One-Pot Synthesis and Characterization of Magnesium Oxide Nanoparticles Prepared by *Calliandra calothyrsus* Leaf Extract

Indah Kurniawaty, Yoki Yulizar, Haryo Satrya Oktaviano, Adam Kusuma Rianto

***Abstract*—**Magnesium oxide nanoparticles (MgO NP) were successfully synthesized in this study using a one-pot green synthesis mediated by *Calliandra calothyrsus* leaf extract (CLE). CLE was prepared by maceration of the leaf using methanol with a ratio of 1:5 for 7 days. Secondary metabolites in CLE, such as alkaloids and flavonoids, served as a weak base provider and capping agent in the formation of MgO NP. CLE Fourier Transform Infra-Red (FTIR) spectra peak at 3255 cm^{-1}, 1600 cm^{-1}, 1384 cm^{-1}, 1205 cm^{-1}, 1041 cm^{-1}, and 667 cm^{-1} showing the presence of vibrations O-H stretching, N-H bending, C-C stretching, C-N stretching and N-H wagging. During the experiment, different CLE volumes and calcined temperatures were used, resulting in a variety of structures. Energy Dispersive X-ray Spectrometer (EDS) and FTIR were used to characterize metal oxide particles. MgO diffraction patterns at 2θ of 36.9°; 42.9°; 62.2°; 74.6°; and 78.5° can be assigned to crystal planes (111), (200), (220), (311), and (222), respectively. Scanning Electron Microscopy (SEM) was used to characterize the surface morphology. The morphology ranged from sphere to flower-like resulting in crystallite sizes of 28 nm, 23 nm, 12 nm, and 9 nm.

Keywords*—Calliandra calothyrsus*, green-synthesis, magnesium oxide, nanoparticle.

I. Introduction

DUE to various concerns about climate change, water pollution, limited equilibrium of natural resources, human health, and other issues, the development of environmentally friendly products and processes has gained traction in recent years. As a result, researchers have been working on a variety of methods to improve metal and metal oxide nanoparticle synthesis using greener technologies. The synthesis of nanostructured metals and metal oxides using biological substrates has been extensively investigated as a potential replacement for methods currently used in various industries [1]-[8].

Magnesium oxide (MgO) is an inorganic crystal with a NaCl-type structure that is widely used in applications such as sensors, antimicrobials, optical coatings, water treatment, catalysis, adsorbents, and fuel additives. This is primarily due to superior surface reactivity, a wide band gap, and chemical and thermal stability [9].

A significant amount of research has been conducted on the green synthesis of MgO nanoparticles (NP) in recent years. This paper attempts to discuss the use of the *Calliandra calothyrsus* leaf to produce MgO NP via green synthesis.

II. Experimental Section

A. Materials

Calliandra calothyrsus leaf was obtained from Biofarmaka IPB, Bogor, West Java Indonesia. Magnesium nitrate hexahydrate ($Mg(NO_3)_2.6H_2O$), methanol p.a. grade, n-hexane p.a. grade, and MgO p.a. were purchased from Merck, Germany. Distillate water used in this research was purified with Thermo Scientific Smart2Pure 6 UV/UF.

B. Instrumentation

FEI Quanta 450 SEM and Oxford instruments X-Max^N EDS were used to determine the morphology and elemental analysis. X-ray Diffraction (XRD) technique using Empyrean Malvern PANalytical 9430 X-ray analytical instrument with a filtered Cu K α radiation source (λ = 0.15406 nm) was used to analyze the structure phase. IR Prestige-21 Shimadzu FTIR spectroscopy was used to investigate the functional groups.

C. Procedure

Calliandra calothyrsus leaf powder was macerated in methanol with a ratio of 1:5 (m/v) for seven days. Then, the filtration was conducted to obtain crude methanol extract, which was further partitioned by using n-hexane in a ratio of 1:1 (v/v) to produce methanol and n-hexane fractions. Afterward, the methanol fraction was dried at 64 °C for 2 h. The residue of methanol was entirely dissolved in distilled water to acquire the water fraction of CLE [10]. MgO NP was prepared in one-pot synthesis by adopting the procedure as reported [5] with slight modifications. 50 ml of $Mg(NO_3)_2$ 0.03 M was gradually mixed with 5 ml, 10 ml, and 25 ml of CLE. The result was stirred and heated at 80 °C for 2 h. The formed colloid was dehydrated at 110 °C for 2 hours before being heated to 200 °C for 1 hour, then calcined at 450 and 700 °C for 3 h to generate a white powder of MgO NP.

III. Results and Discussion

It is expected that CLE contains alkaloids, flavonoids, and terpenoids/steroids. Alkaloids from the extract fraction can be used as a base source in the green synthesis of metal oxide NPs,

Indah Kurniawaty is a Ph.D. student from the University of Indonesia, Jakarta 10430 Indonesia (corresponding author, e-mail: Indah.kurniawaty01@ui.ac.id).

Yoki Yulizar is a Professor in Department of Chemistry, University of Indonesia, Jakarta 10430 Indonesia (e-mail: yokiy@sci.ui.ac.id).

Haryo Satriya Oktaviano and Adam Kusuma Rianto are researchers in Research & Technology Innovation Pertamina, Jakarta 13920 Indonesia (e-mail: haryo.oktaviano@pertamina.com, adam.rianto@pertamina.com).

whereas flavonoids and terpenoids/steroids act as capping agents to maintain metal oxide NPs stable [11]. Table I shows the result of preliminary test of phytochemical screening. The composition of the CLE obtained is consistent with research findings that the *Calliandra calothyrsus* leaf contains flavonoid and proanthocyanin compounds, as well as alkaloids, tannins, saponins, phytosterols, and flavonoids [12]-[17].

Functional groups in CLE were analyzed by FTIR to predict the content of secondary metabolites. Absorption at wave numbers 3255 cm^{-1}, 1600 cm^{-1}, 1384 cm^{-1}, 1205 cm^{-1}, 1041 cm^{-1}, and 667 cm^{-1} in the FTIR spectrum of CLE indicates the presence of bond vibrations of O-H stretching, N-H bending, C-C stretching, C-N stretching, and N-H wagging. One of the absorptions that indicate the presence of flavonoids in the CLE spectrum is the stretching vibration of the O-H bond. Furthermore, the vibrations of the N-H wagging and C-N stretching bonds on both spectra suggested the presence of alkaloids [4], [18]. Generally, the FTIR result is presented in Fig. 1 and Table II.

TABLE I
PRELIMINARY TEST OF PHYTOCHEMICAL SCREENING OF CRUDE LEAVES

Phytochemical components	Methanol extract	n-hexane extract	Aqueous extract (CLE)
Tannins	+	-	+
Saponins	+	-	-
Flavonoids	+	-	+
Terpenoids/Steroids	++	+	+
Alkoloids			
Bouchardat	+	+	+
Dragendorf	+	-	+
Meyer	-	-	-

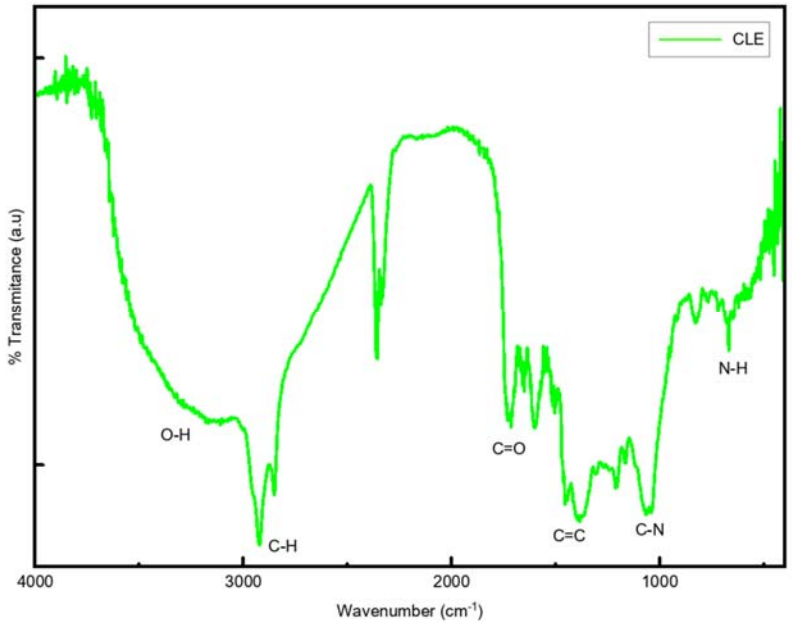

Fig. 1 FTIR spectra of CLE

TABLE II
FTIR RESULT OF CLE

Types of vibration	Wave-number (cm^{-1})
O-H stretching	3255
N-H bending	1600
C-C stretching	1384
C-O stretching	1205
C-N stretching	1041
N-H wagging	667

The sol-gel method was used to synthesize MgO by reacting a solution of $Mg(NO_3)_2$ with the CLE. The formation of colloidal sol $Mg(OH)_2$ with CLE was assisted by 2 hours of heating at 80 °C. The colloidal $Mg(OH)_2$ sol was then heated at 110 °C for 2 hours to reduce the solvent content and form an $Mg(OH)_2$ gel. The solid MgO was then obtained by calcining the $Mg(OH)_2$ gel at 450 °C and 700 °C. The proposed mechanism that occurs during the green synthesis of MgO using CLE are as follows:

$$Mg(NO_3)_2.6H_2O_{(aq)} \rightarrow Mg^{2+}{}_{(aq)} + 2NO_3{}^{-}{}_{(aq)} + 6H_2O_{(l)} \quad (1)$$

$$R_2 - N - CH_{3(aq)} + H_2O_{(l)} \leftrightarrow R_2 - N^{+}H - CH_{3(aq)} + OH^{-}{}_{(aq)} \quad (2)$$

$$Mg^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)} \rightarrow Mg(OH)_{2(s)} \quad (3)$$

$$Mg(OH)_{2(s)} \rightarrow MgO_{(s)} + H_2O_{(g)}. \quad (4)$$

Different volumes of CLE were used in this synthesis, 5 ml, 10 ml, and 25 ml of CLE. In an aqueous system, Mg^{2+} decomposed from $Mg(NO_3)_2$ will react with OH^- ions produced by the hydrolysis of water by nitrogen electrons on alkaloids in CLE. This reaction produces a colloidal sol of $Mg(OH)_2$, which is then heated to high temperatures to produce solid MgO NP.

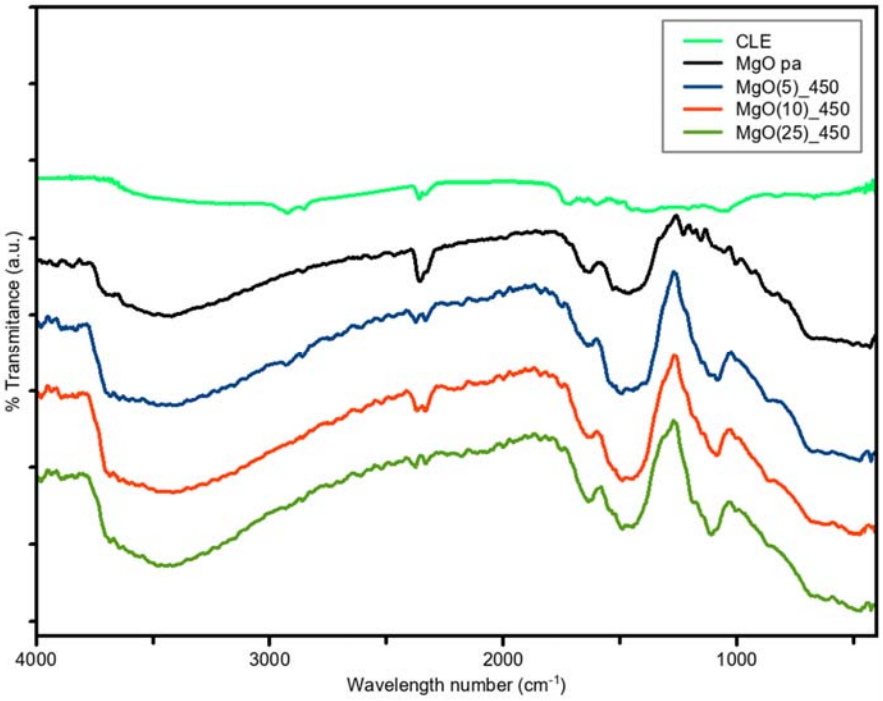

Fig. 2 FTIR spectra of MgO NP calcined in 450 °C

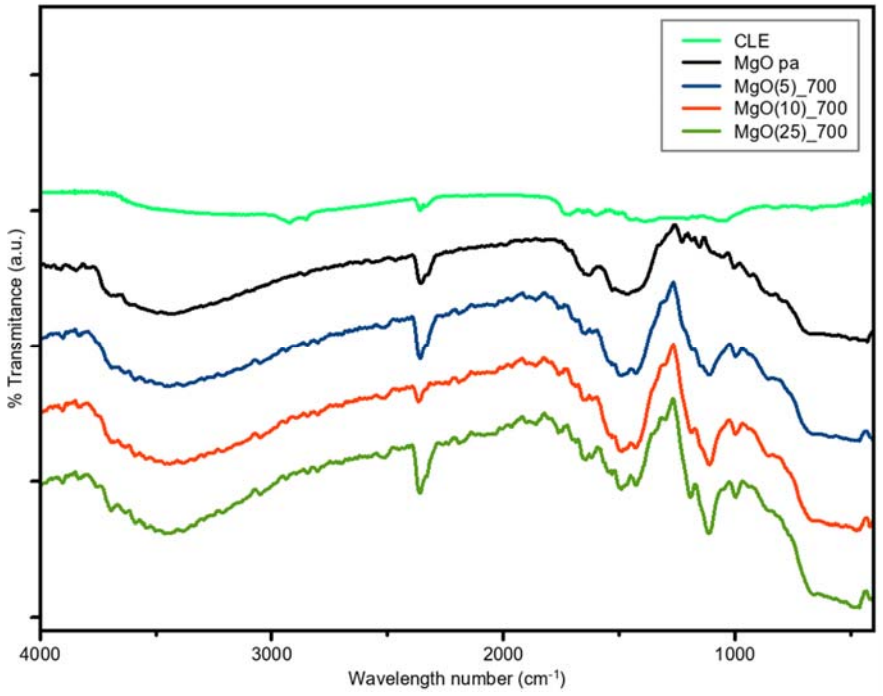

Fig. 3 FTIR spectra of MgO NP calcined in 700 ºC

MgO NPs synthesized with CLE are designated as MgO(5)_450, MgO(10)_450, MgO(25)_450, MgO(5)_700, MgO(10)_700, and MgO(25)_700, respectively. Fig. 2 depicts the results of the characterization of MgO NP samples obtained with varying amounts of CLE at 450 °C calcination and MgO p.a. The results of the characterization of MgO NP samples obtained at a calcination temperature of 700 °C are shown in Fig. 3. A commercial MgO sample was also analyzed using FTIR for comparison.

The stretching vibration at 600-850 cm^{-1} in Fig. 3 indicates the Mg-O-Mg bond. A different band was observed at 1434 cm^{-1}, indicating the presence of bending vibrations in the hydroxyl group. The presence of a broad band at 3300-3600 cm^{-1} indicates the formation of the MgO structure [18]. The FTIR spectra of MgO(5)_700 were most similar to commercial MgO.

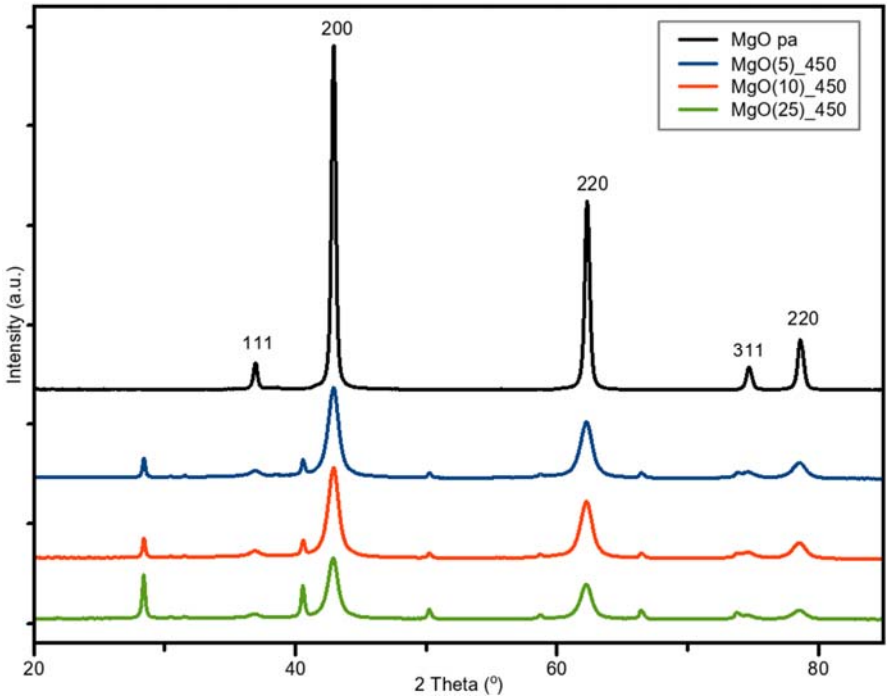

Fig. 4 XRD patterns of MgO NP calcined in 450 °C

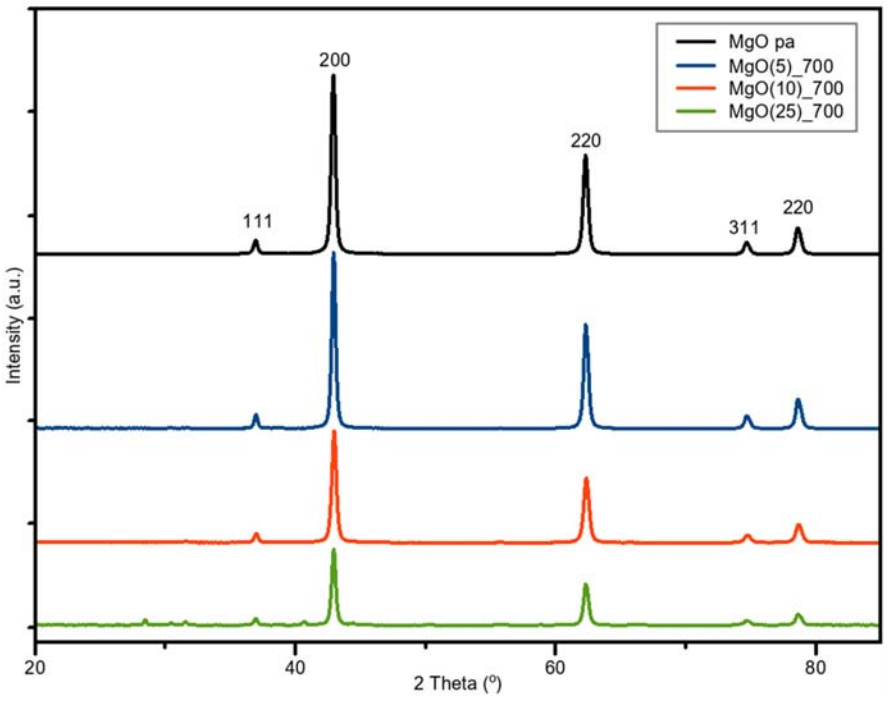

Fig. 5 XRD patterns of MgO NP calcined in 700 °C

The crystal structure, purity, and phase of MgO in MgO(5), MgO(10), and MgO(25) calcined at 450 °C and 700 °C were determined using XRD. Figs. 4 and 5 show the results of the XRD characterization. A commercial MgO was also subjected to XRD analysis for evaluation.

The formation of the MgO crystal phase was well demonstrated by the MgO(5) diffractogram at calcination temperatures of 450 °C and 700 °C. Other absorptions can be seen when the CLE volume is increased in addition to MgO. This implies that the purity of the MgO formed is insufficient. The lower the added CLE volume, the sharper the MgO diffractogram absorption and the lower the absorption of other impurities. MgO's crystalline phase was identified at $2\theta = 36.9°$; 42.9°; 62.2°; 74.6°; and 78.5°, which corresponds to the MgO fields (111), (200), (220), (311), and (222) (ICSD No. 98-003-0267).

The Debye-Scherer Equation (5) is used to calculate the crystallite size of MgO, where D is the crystallite size average, λ is the wavelength of the X-Ray (0.15406 nm), β is the FWHM, and θ is the diffraction angle. Table III displays the full width at half maximum (FWHM) value and crystallite size. This result indicates that the high calcination temperature can form a single-crystalline phase of MgO by the increase of crystalline size due to the thermally promoted crystallite growth. The crystallite size decreases with the addition of CLE where the effect of increasing the volume of a leaf extract from 5 ml to 25 ml causes the crystallite size to decrease [4].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{5}$$

SEM was used to characterize the surface morphology of MgO NPs. The results of the MgO SEM characterization are shown in Fig. 6. The amount of CLE added had a significant effect on the morphology of MgO. MgO(5)_450 has a spherical shape with a diameter of 30-60 nm, MgO(10)_450 has an agglomerated sphere shape with a diameter of 60-80 nm, and MgO(25)_450 has a flake shape [19]. The morphological differences are most likely caused by differences in the number of dissolved secondary metabolites. Secondary metabolites can act as ligands to form coordination complexes with metal ions due to the content and number of certain groups, such as the number of hydroxyl groups that are bonded to each other through hydrogen bonds in the solvent [20]. The MgO synthesis results at a calcination temperature of 700 °C all showed a sphere-like shape with sizes ranging from 20 nm to 80 nm. The shape of the MgO(25) sample changes between calcination temperatures of 450 °C and 700 °C, with 700 °C showing a sphere shape and 450 °C showing an irregular shape, similar to flower flakes.

TABLE III
THE CRYSTALLITE SIZE OF MGO NP FROM XRD PATTERN USING DEBYE-SCHERER'S EQUATION

Sample	FWHM (°)	Crystallite size (nm)
MgO(5)_450	0,3816	23
MgO(10)_450	0,7632	12
MgO(25)_450	0,9540	9
MgO(5)_700	0,3823	28
MgO(10)_700	0,7632	12
MgO(25)_700	0,9540	9

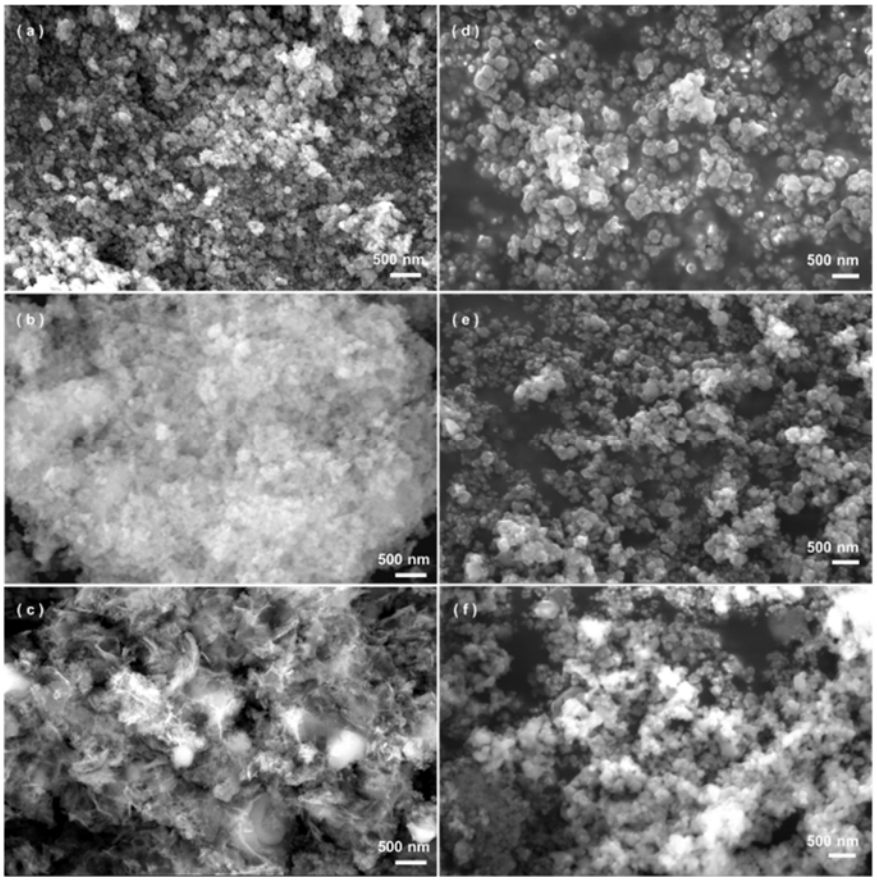

Fig. 6 SEM image of (a) MgO(5), (b) MgO (10), (c) MgO at calcination temperature of 450 °C (d) MgO(5), (e) MgO (10), (f) MgO at calcination temperature of 700 °C

EDS was used to determine the elemental composition of MgO NP as well as the presence of trace elements from CLE. The spectra of the EDS MgO NP characterization results for each sample are shown in Fig. 7. The elemental composition in Fig. 7 shows that MgO(5) has not yet formed pure MgO, as evidenced by the presence of trace elements such as S, Cl, and

K, which are most likely naturally derived from minerals in CLE. Similarly, FTIR and XRD characterization of MgO(10) and MgO(25) revealed no evidence of the formation of pure MgO. However, the Mg:O composition ratio in MgO(5)_700 is 2.48 : 2.38 (mol ratio), which is close to the stoichiometric ratio with fewer impurities. The results of MgO synthesis at a calcination temperature of 700 °C still showed trace elements such as P, S, Cl, and K, which were probably derived from leaf extracts, because the sample was not washed, which is consistent with the results of MgO synthesis using Artemisia abrotanum, where the results of EDS MgO show elements C, Al, Si, P, K, and Ca [3].

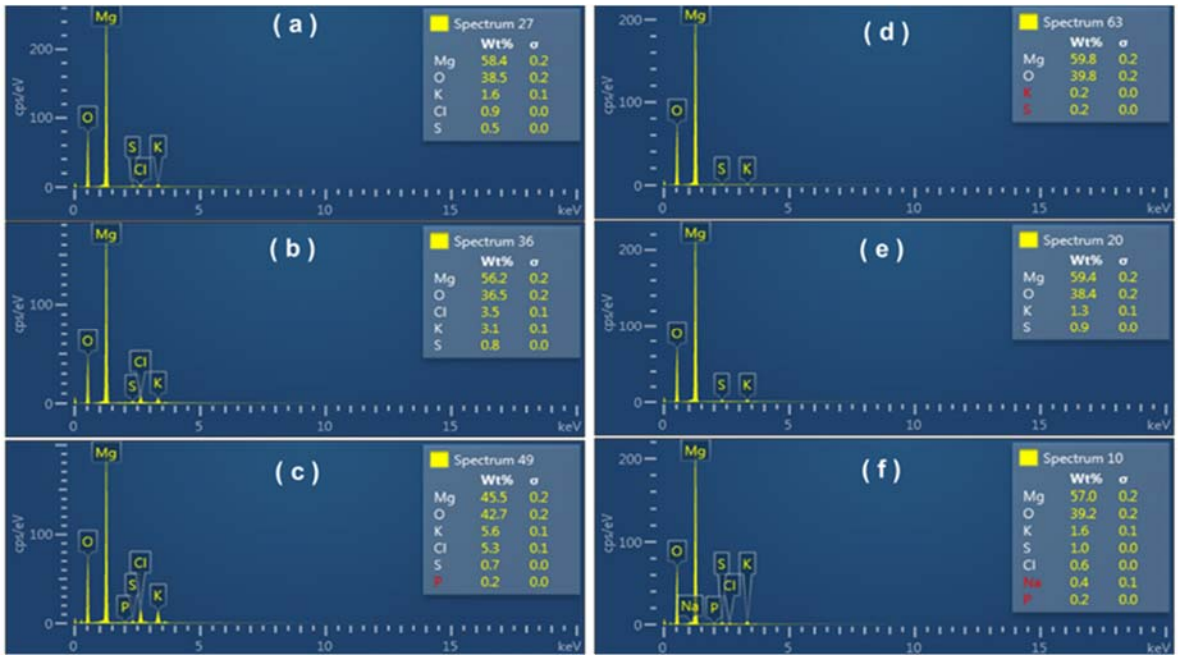

Fig. 7 EDS spectra of (a) MgO(5), (b) MgO (10), (c) MgO at calcination temperature of 450 ºC (d) MgO(5), (e) MgO (10), (f) MgO at calcination temperature of 700 ºC

IV. Conclusion

The addition of CLE contributed in the successful one-pot synthesis of MgO NP. The amount of CLE added, and the calcination temperature all influenced the morphology and type of crystals produced. The best formation of MgO NPs were obtained by adding 5 ml of CLE and calcining at 700 °C, giving a sphere shape and crystallite size of 28 nm.

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References

[1] J. Suresh, R. Yuvakkumar, M. Sundrarajan, S.I. Hong, *Green synthesis of magnesium oxide nanoparticles*, 952 (2014) 141–144.

[2] S.K. Moorthy, C.H. Ashok, K.V. Rao, C. Viswanathan, *MgO Nanoparticles by Neem Leaves Through Green Method, Mater*. Today Proc. 2 (2015) 4360–4368.

[3] R. Dobrucka, *Synthesis of MgO Nanoparticles Using Artemisia abrotanum Herba Extract and Their Antioxidant and Photocatalytic Properties*, Iran. J. Sci. Technol. Trans. A Sci. 42 (2018) 547–555.

[4] J. Jeevanandam, Y. San, *Aqueous Eucalyptus globulus leaf extract-mediated biosynthesis of MgO nanorods*, Appl. Biol. Chem. 61 (2018) 197–208.

[5] S. Joghee, P. Ganeshan, A. Vincent, S.I. Hong, *Ecofriendly Biosynthesis of Zinc Oxide and Magnesium Oxide Particles from Medicinal Plant Pisonia grandis* R. Br. *Leaf Extract and Their Antimicrobial Activity*, Bio Nano Sci. (2019) 141–154.

[6] P.P. Kumar, M.L.D. Bhatlu, K. Sukanya, S. Karthikeyan, N. Jayan, *Proceedings Synthesis of magnesium oxide nanoparticle by ecofriendly method (green synthesis) – A review*, Mater. Today Proc. 37 (2021) 3028–3030.

[7] A. Mohamed, E. Shafey, *Green synthesis of metal and metal oxide nanoparticles from plant leaf extracts and their applications: A review*, (2020) 304–339.

[8] N.A.I. Md Ishak, S.K. Kamarudin, S.N. Timmiati, Green synthesis of metal and metal oxide nanoparticles via plant extracts: an overview, Mater. Res. Express. 6 (2019).

[9] G. Balakrishnan, R. Velavan, K. Mujasam Batoo, E.H. Raslan, *Microstructure, optical and photocatalytic properties of MgO nanoparticles*, Results Phys. 16 (2020) 103013.

[10] R.M. Surya, Y. Yulizar, A.H. Cahyana, D.O.B. Apriandanu, *One-pot Cajanus cajan* (L.) Millsp. *leaf extract-mediated preparation of MgFe2O4 nanoparticles: Optical, structural, morphological and particle size analyses*, Solid State Commun. 326 (2021) 114170.

[11] H.A. Ariyanta, T.A. Ivandini, Y. Yulizar, *Novel NiO nanoparticles via phytosynthesis method: Structural, morphological and optical properties*, J. Mol. Struct. 1227 (2021) 129543.

[12] M.B. Salawu, T. Acamovic, C.S. Stewart, R.L. Roothaert, *Composition and degradability of different fractions of Calliandra leaves, pods and seeds*, Anim. Feed Sci. Technol. 77 (1999) 181–199.

[13] I. Setyawati, *Phytochemical content, extract standardization and antioxidant activity of Calliandra calothyrsus* Meissn *leaf, a potential phytoestrogen source*, Earth Environ. Sci. 347 (2019).

[14] N. Danu, A. Aminah, N. Yuniarti, D. Syamsuwida, D.D.N. Cahyono, N. Siregar, Y.M.M.A. Nugraheni, K.A. Hendarto, *Genetic Diversity of Calliandra (Calliandra calothyrsus* Meissn*.) Seedling from West Java*, J. Perbenihan Tanam. Hutan. 8 (2020) 121–132.

[15] S. Raja, V. Ramesh, V. Thivaharan, *Green biosynthesis of silver nanoparticles using Calliandra haematocephala leaf extract, their antibacterial activity and hydrogen peroxide sensing capability*, Arab. J. Chem. 10 (2017) 253–261.

[16] R. Vinayagam, R. Selvaraj, P. Arivalagan, T. Varadavenkatesan, *Synthesis, characterization and photocatalytic dye degradation capability of Calliandra haematocephala-mediated zinc oxide nanoflowers*, J. Photochem. Photobiol. B Biol. 203 (2020) 111760.

[17] K.D. Sirdeshpande, A. Sridhar, K.M. Cholkar, R. Selvaraj, *Structural characterization of mesoporous magnetite nanoparticles synthesized using the leaf extract of Calliandra haematocephala and their photocatalytic degradation of malachite green dye*, Appl. Nanosci. 8 (2018) 675–683.

[18] S. Narendhran, M. Manikandan, P. Baby Shakila, *Antibacterial, antioxidant properties of Solanum trilobatum and sodium hydroxide-mediated magnesium oxide nanoparticles: A green chemistry approach*, Bull. Mater. Sci. 42 (2019) 1–8.

[19] J. Pal, V. Singh, A. Sharma, G. Pandey, K. Hwa, *Approaches to synthesize MgO nanostructures for diverse applications, Heliyon*. 6 (2020) e04882.

[20] S. Abinaya, H.P. Kavitha, M. Prakash, A. Muthukrishnaraj, *Green synthesis of magnesium oxide nanoparticles and its applications: A review*, Sustain. Chem. Pharm. 19 (2021) 100368.