GREEN SYNTHESIS OF NiFe_2O_4 SPINEL FERRITES MAGNETIC IN THE PRESENCE OF *Hibiscus rosa-sinensis* LEAVES EXTRACT: MORPHOLOGY, STRUCTURE AND ACTIVITY

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ABSTRACT

Spinel ferrite magnetic of NiFe_2O_4 particles were prepared using a green synthesis approach with *Hibiscus rosa-sinensis* extract. The characterization of obtained samples was conducted using X-ray diffraction, transmission electron microscopy, diffuse reflectance spectroscopy UV-Vis, vibrating sample magnetometer, Fourier transformed infra-red, and X-ray photoelectron spectroscopy. The activity of the samples was evaluated by measuring the degradation of Direct Yellow 27 and batik waste dyes under sunlight irradiation. Structural analysis by comparison of the X-ray diffraction pattern against standard data confirmed the formation of spinel ferrite. The morphology observation revealed that NiFe_2O_4 nanoparticles had a rod-like and spherical shape. All samples show magnetic behavior. The calcination process affected the magnetic properties and band gap of prepared particles. Furthermore, Fourier transforms infra-red spectra showed vibration of Fe-O and Ni-O at $300\text{-}600\text{ cm}^{-1}$ for tetragonal and octahedral sites in spinel ferrite structures. The samples showed good photocatalytic activity under sunlight; degradation was 95% and 84% for Direct Yellow 27 and batik waste dyes respectively.

Keywords: NiFe_2O_4 , Hydrothermal, *Hibiscus rosa-sinensis*, Magnetic, Photocatalytic.

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INTRODUCTION

Spinel ferrites have the general formula MFe_2O_4 where M represents a divalent metal ion. They are cubic in structure and have extensive technological applications. Over the last decade, ferrite nanoparticles have attracted attention due to their high permeability, electrical resistivity and electromagnetic properties make them suitable for many purposes such as magnetic storage, microwave devices, biosensors, drug delivery, disease diagnosis, gas sensors, energy conversion, photocatalysts and magnetic separation.^{1,2}

Nickel ferrite (NiFe_2O_4), is an industrially important soft ferrite with properties that make it ideal not only for soft magnetic core materials in power transformers but also as a photocatalyst. It has low coercivity and high electrochemical stability. NiFe_2O_4 has an inverse spinel cubic structure where Fe^{3+} ions occupy both tetrahedral (A) and octahedral sites (B), and Ni^{2+} ions occupy octahedral sites (B). A cubic unit cell of nickel ferrite contains 8 Ni^{2+} , 16 Fe^{3+} , and 32 O^{2-} ions. Small nickel ferrite particles are spinel while larger masses have inverse spinel properties.²⁻⁴

Synthesis of NiFe_2O_4 spinel ferrite nanoparticles has been developed intensively using several preparation techniques such as sol-gel combustion and co-precipitation^{3,4}, combustion⁵, solvothermal⁶, thermal decomposition and seed growth⁷, hydrothermal synthesis⁸, solid-state reactions⁹, and honey-mediated sol-gel combustion.¹⁰ Due to growing ecological concerns, there is a growing interest in green synthesis of inorganic materials in which simple environmentally friendly methods are used. Material is prepared using natural extracts as capping agents and water as a solvent. Spinel ferrites produced by this method have a smaller particle size, are smooth, stable, and have a homogenous structure. Many plants such as *Malachra capitata*, rambutan, lemon eucalyptus, *Mirabilis jalapa*, black nightshade, neem, and *Hibiscus rosa-sinensis* have been used in green synthesis of metal oxides including spinel ferrites.¹¹⁻¹⁸ However, as

far as we know there is no published account of green synthesis of NiFe_2O_4 spinel using *hibiscus* leaf extract or its application as a catalyst to degrade of dyes under sunlight. Which is the topic of this present report.

Hibiscus leaf extract was used as a capping agent and metal nitrates as precursors. Extracts of *Hibiscus* leaves contain taraxol acetate, oxalic acid, fructose, flavonoids, and flavonoid glycosides which can act as a capping, chelating and stabilizing agents replacing hazardous chemicals. In addition, *Hibiscus* leaf extract is environmentally friendly, economical and easy to obtain and prepare.^{19, 20} The synthesized magnetic materials were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transformed infra-Red (FTIR), diffuse reflectance spectroscopy UV-Vis (DRS UV-Vis), vibrating sampler magnetometer (VSM), and X-ray photoelectron spectroscopy (XPS) and their photocatalytic degradative activity measured on Direct Yellow 27 and batik waste dyes under sunlight irradiation.

EXPERIMENTAL

Materials

All of the reagents were used without further purification. $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and NaOH were purchased from Merck. Distilled water was used as a solvent for all samples. *Hibiscus rosa-sinensis* leaves were obtained from Pariaman, Indonesia. Direct Yellow 27 and batik waste dyes were used to test the resulting spinel ferrite effectiveness as a photocatalytic agent.

Preparation of Extract and Synthesis of Spinel Ferrites

The extract of *Hibiscus rosa-sinensis* leaves was prepared using a modification of a previously used procedure.¹⁸ 25 g of fresh *Hibiscus* leaves were washed and pounded finely and the resulting gel separated from the fibrous material. This gel was dissolved in 100 ml distilled water and continuously stirred for 45 minutes until homogeneous then temporarily stored in the refrigerator.

NiFe_2O_4 particles were synthesized hydrothermally using metal nitrates as precursors and *Hibiscus* leaf extract as the capping agent.²¹ A molar ratio of 1:2 of $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was combined with 75 ml of the extract solution (extract + distilled water). The mixture was poured into an autoclave tube and heated at 180°C for 3 h. After that, the resulting precipitate was filtered and rinsed with distilled water to $\text{pH} = 7$, then dried at 100°C for 4 h. The powder obtained was labeled NiE. A NiEN labeled sample was synthesized the same way in the presence of NaOH (2 M) as a mineralizer. For NiENK labeled sample was synthesized like NiEN sample then calcined at 700°C . As a comparison, and NiN labeled sample was also synthesized hydrothermally in the presence of NaOH without the leaf extract.

The obtained NiFe_2O_4 spinel ferrites were characterized by XRD (XPRT-PRO diffractometer system), TEM (JEOL JEM 1400), FTIR (Perkin Elmer 1600 series), DRS UV-Vis (SPECORD 210 PLUS-223F1936C), VSM (OXFORD VSM 1.2H), and XPS (ULVAC-PHI Quantera SXM) in order to analyze the structure, morphology and crystallinity, interactions within the spinel, optical and magnetic properties, and bending energy.

The photodegradation activity of the samples was evaluated on Direct Yellow 27 and batik waste dyes under sunlight irradiation using a procedure adapted from previous work.²¹ For each experiment, 0.02 g of spinel ferrite was dispersed in 20 mL of Direct Yellow (30 mg/L) or batik waste dyes in aqueous solution. The mixture was kept under sunlight irradiation for 0.5-2 h (from 11:00 am to 14:00 pm) and then 5 mL of solution was analyzed by measuring absorbance in a UV-vis spectrophotometer.

RESULTS AND DISCUSSION

Characterizations

The XRD diffraction patterns of NiE, NiEN, NiENK, NiN nickel ferrites are shown in Fig.-1. It can be observed that there are no sharp diffraction peaks for the NiE sample which indicates that the sample is still in the amorphous phase. NiEN, NiENK and NiN spinel ferrites all had dominant peaks at $2\theta = 30.3^\circ$, 35.7° , 43.4° , 57.4° , and 62.9° . These diffraction peaks were sharp and narrow indicating crystallinity and were indexed as (220), (311), (400), (511), and (440) of the hkl crystal plane is similar to the published ICDD standard data (Card no. 01-071-3850) for a cubic spinel ferrite. An impurity peak indicating hematite ($\alpha\text{-Fe}_2\text{O}_3$) was observed for the sample NiENK and was probably due to the high calcination

temperatures used causing degradation of the ferrite structures. Previous researchers have also found Fe_2O_3 as an impurity in NiFe_2O_4 with samples calcined at 700°C .¹¹

The crystallite size of samples was measured using the Scherrer equation as in previous research²² and can be seen in Table 1. The intensity of the peaks increased as crystallite size increased. The calcination process caused the size of the crystals to be larger. However, the crystal size of NiENK sample was smaller than the NiN sample that was prepared in the same way without the extract.

Fig.-1: Powder XRD Pattern of NiE, NiEN, NiENK and NiN Samples

The morphology and structure of samples were analyzed using transmission electron microscopy. Figure-2 shows the morphologies of NiEN (a-c) and NiENK (d-f) ferrites at different magnifications. It is clearly seen that the NiEN sample is a rod-like particle, whereas the NiENK sample is a spherical-like nanoparticle. There was some agglomeration observed for NiEN caused by the presence of organic material from the extract left in the sample. The TEM image of NiE ferrite was not analyzed because it was still in an amorphous phase as seen in XRD patterns.²³ This result suggests that the treatment used influenced morphology and crystal formation. The *Hibiscus* extract can slow up the nucleation and affected the growth of the ferrite crystals so that NiENK samples can be smaller even though calcined at high temperatures.²⁴

Fig.-2: TEM Images of NiEN (a-c), NiENK (d-e) at Different Magnifications

Fig.-3: Hysteresis Curves of (a) NiE, (b) NiEN, (c) NiENK, and d) NiN Samples

The magnetic properties of NiE, NiEN, NiENK, and NiN spinel ferrites were measured by VSM at room temperature as shown in Fig.-3. The magnetization behavior of the NiE and NiEN samples were of a typical paramagnetic compound. This paramagnetic behavior emerged since the formation of spinel ferrite crystals was incomplete impacting magnetic dipole orientation. The NiENK sample was soft ferromagnetic and NiN ferrimagnetic. The remanent magnetization (M_r), saturation magnetization (M_s), and coercivity field (H_c) are summarized in Table-1. The lower magnetization value of ferrite samples is caused by phase, crystallite size, use of the *Hibiscus* extract and the calcination process. The magnetic saturation value of NiENK is higher than that found by a previous researcher for NiFe_2O_4 ($M_s=12.7$ emu/g) made using aloe vera extract as a capping agent then calcined at the same temperature.¹¹ The enhanced magnetic properties of NiENK would allow it to be easily separated from liquid for reuse when used as a photocatalyst.

The optical behavior of the spinel ferrites was studied using UV-Vis diffuse reflectance spectroscopy at room temperature. In order to estimate the bandgap energy, the absorption value of each sample obtained was substituted into the Planck's equation: $E_g = hc / \lambda = 1240/\lambda$, where E_g is the bandgap energy (eV), h is Planck's constant, c is the speed of light (m/s), and λ is the maximum wavelength (nm) absorbed.²⁵ Fig. 5 shows the absorption curves of all the samples. Maximum absorbance values indicate that the spinel ferrites were active in the visible light area. Each treatment step in the production of the extract catalyzed spinel ferrites reduced the bandgap energy (Table-1) perhaps due to the crystallite size decreasing at each treatment step leading to a quantum confinement effect.²⁰ The bandgap energy for NiENK and NiEN sample was close to that of samples obtained in previous studies (1.64 eV)^{26, 27} and (~ 2.1 eV).²⁸

The chemical state of the elements in the NiENK spinel ferrite was investigated using an XPS instrument. The visible peaks are shown in Fig. 6(a) correspond to Ni, Fe, O and C elements. The XPS survey O1s, Fe2p and Ni2p XPS spectra are shown in Fig. 6(b–d). Spin-orbit interaction for Ni and Fe led to splitting of the 2p states into $2p_{1/2}$ and $2p_{3/2}$ levels. The peaks located at 532.2 eV can be assigned to (O1s), at 712

and 736 eV can be indexed to the bending energy of Fe 2p_{3/2} and Fe 2p_{1/2}, and bending energies of 857 and 875 eV correspond to Ni 2p_{3/2} and Ni 2p_{1/2}, confirming the formation of nickel ferrite.¹⁰ The presence of C 1s peak can be ascribed to carbon from the XPS instrument.

FT-IR spectral analysis confirmed the presence of spinel structures in the ferrite samples. Fig.-6 shows the FT-IR spectrum of the synthesized ferrite samples in the range 300-1300 cm⁻¹. The FT-IR spectra of the ferrite samples show two main absorption bands in the range 300-900 cm⁻¹. Maximum absorption was in the range 500-560 cm⁻¹ (v1) matching the fundamental stretching vibration of the metal at a tetrahedral site (M_{tetra}-O), while the other absorption bands in the range 300-400 cm⁻¹ (v2) correspond to stretching vibrations of the metal at an octahedral site (M_{octa}-O). These v1 and v2 bands confirm the presence of the ferrite spinel NiFe₂O₄ in the prepared samples. For the NiE sample, the absorption bands were the range 993-1191 cm⁻¹ and likely to be due to residual organic matter from the *Hibiscus rosa-sinensis* extract.^{3,10}

Table 1. Crystallite size, bandgap, magnetic saturation, magnetic remanent and coercivity field of Ni-ferrites

Catalyst	Crystallite size (nm)	Band gap (eV)	Magnetic saturation (emu/g)	Magnetic Remanent (emu/g)	Coercivity field (Tesla)
NiE	-	1.88	0.36	-	-
NiEN	13.22	1.81	1.66	-	0.015
NiENK	15.86	1.65	34.26	14.6	0.015
NiN	21.31	1.96	52.90	21.5	0.010

Fig.-4: DRS UV-Vis Absorption Spectra of (a) NiE, (b) NiEN, (c) NiENK, and (d) NiN Samples

Fig.-5: Binding Energy of NiFe₂O₄ sample

Fig 6. FTIR spectra of NiFe, NiFeN, NiFeNK and NiFe samples

Fig.-7: Photocatalytic Activity of Sample on the Degradation of (a) Direct Yellow 27 and (b) Batik Waste Dyes

Catalytic Activity Evaluation

The photocatalytic degradation activity of the samples was evaluated on Direct Yellow 27 and batik waste dyes under sunlight irradiation as shown in Fig.-7. The graph in Fig.-7a shows that the degradation of Direct Yellow 27 without a catalyst reached 10 % after 2 h. In the presence of a NiEN catalyst, there was an almost six-fold increase in the degradation of the Direct Yellow 27 dye (57%). The calcined NiENK catalyst was even more effective with 95% of the Direct Yellow 27 dye and 84% of the batik waste dye degraded after 2 h. As a semiconductor, spinel ferrite has valence band electrons that can be excited into the conduction band when exposed to light. These electrons then react with H^+ from water molecules resulting in the production of O_2^- ions. These O_2^- ions react with H^+ from other water molecules forming OH radicals which photodegrade the dyes under sunlight. The higher activity of NiENK is likely to be due to the lower amount of agglomeration within the catalyst increasing the formation of OH radicals in the solution.

CONCLUSION

Magnetic spinel ferrites of $NiFe_2O_4$ were successfully synthesized in an economical and environmentally friendly procedure using *Hibiscus rosa-sinensis* extract as a capping agent. When this synthesis was conducted in the presence of NaOH the spinel ferrites had a high crystallinity index. Subsequent calcination increased the size of the crystallites, crystallinity and magnetic saturation while decreasing the bandgap energy. These calcined spinel ferrites had excellent photocatalytic degradative activity on both Direct Yellow 27 and batik waste dyes. Furthermore, their high magnetic saturation facilitates extraction from a liquid making them practical and retrievable tools for the removal of waste dye from water.

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