

SPECTROSCOPIC STUDIES OF THE IRON NANOPARTICLES (Fe-NPs) DERIVED FROM EUCALYPTUS LEAVES EXTRACT AND ULTRASONIC WAVE ASSISTED METHOD

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Abstract

This study aimed to investigate the characteristics of iron nanoparticles (Fe-NPs) synthesized using a green synthesis and ultrasonic wave irradiation. According to the availability of eucalyptus leaves in northeastern Thailand and many studies on non-chemical extract, the eucalyptus leaves extract was applied as a reducing reagent. The Fe-NPs were synthesized by mixing the eucalyptus leaves extract and 0.1 M FeSO₄ aqueous solution with an applied ultrasonic wave at a constant power of 1,000 W with a frequency of 20 kHz. The properties of the synthesized sample were characterized by various techniques such as field emission scanning electron microscope (FESEM), transmission electron microscope (TEM), Fourier transform infrared (FT-IR), and X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS). X-ray absorption spectroscopy (XAS) was also used to measure the oxidation state of the material. The mean diameter of the iron nanoparticles (Fe-NPs) derived from eucalyptus leaves extract and ultrasonic wave (Fe-NPs-EL-UL) 1,000 W was 29±5 nm, smaller than that of the iron nanoparticles (Fe-NPs) derived from eucalyptus leaves extract (Fe-NPs-EL). FT-IR analysis confirmed the covering of oxidized polyphenols on the surface of Fe-NPs. The surface chemical compositions and chemical states of the element of the synthesized sample were analyzed by XPS. The characteristic peak of Fe⁰ at around 706 eV was not detected. However, XRD showed amorphous material and XAS indicated the presence of Fe₂O₃ (Hematite).

Keywords: Iron nanoparticles, eucalyptus leaves extract, ultrasonic wave, green synthesis, X-ray Absorption Spectroscopy, X-Ray Photoemission Spectroscopy

Introduction

Nowadays, many research groups have synthesized iron nanoparticles. There are many forms of iron nanoparticles such as Magnetite, hematite, and zerovalent iron (Petcharoen *et al.*, 2012; Jamei *et al.*, 2014; El Aal *et al.*, 2019). Metal particles play a key

role in groundwater treatment and soil remediation such as removal of trichloroethylene (TCE) by nanoscale zero-valent iron (nZVI) (Kim *et al.*, 2010), hematite for adsorbing heavy metals (Pb, Co, Ni, Cd, and Cu) from aqueous solution (El Aal

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et al., 2019) and remediation of soil contaminated with petroleum using biochar supported nano iron activated persulfate (Zhang *et al.*, 2020).

The utilization of nano-particles has some advantages such as greater specific surface area (smaller particle size), and reducing the usage dose compared with the use of macro-particles (Schrack *et al.*, 2002). The ultrasonic-assisted method can be used in the synthesis of nZVI for the enhancement of the synthesis. The particle size reduction using ultrasonic irradiation was first recommended by Tao *et al.*, 1999. Jamei *et al.*, 2014 synthesized nano zero-valent iron particles using sodium borohydride (NaBH_4) and ultrasonic power 1,000 W with a frequency of 20 kHz. nZVI synthesized using ultrasonic obtained higher specific surface area with smaller particle size (10 nm) than those without using ultrasonic (34 nm).

Even though sodium borohydride is highly reactive reducing agents, its toxicity remains, which can cause harmful impacts on the animal lives, plants, and environment. Some experiments have shown a possible reduction of metal ions to zero-valent metallic particles using green chemicals as an alternative reducing agent instead of sodium borohydride, such as green tea (Shahwan *et al.*, 2011; Ahmmad *et al.*, 2013), grape leaves (Luo *et al.*, 2014), aloe vera (Phumying *et al.*, 2013) and eucalyptus (Wang *et al.*, 2014a; Wang *et al.*, 2014b; Liu *et al.*, 2018). The extract has developed as replacements for commonly used reducing agents. These plant extracts act as both covering and dispersing agents because they contain polyphenols compounds, and they are non-toxic and biodegradable. Consequently, this study focuses on using eucalyptus leaves extract because of their availability in the northeastern of Thailand. The purpose of the eucalyptus plantation is to make paper using stems. Therefore, the leaf is a waste that is not used.

Nonetheless, only XRD and XPS techniques were used to characterize the green synthesis of zero-valent iron by many researchers. But these techniques might be limited to identify the details of the oxidation state since the organic constituents in the extract cover on the synthesized iron particles surface. For this reason, the XAS technique could be used to analyze the oxidation state and the surrounding structure of atoms due to its deeper penetrating power. Therefore, this work pointed to highlight the results from XAS analysis.

This paper aimed to elaborate on iron nanoparticle synthesis by using eucalyptus leaves extract and a constant ultrasonic power 1000 W with frequency 20 kHz. The materials were characterized using field emission scanning electron microscope (FESEM), transmission electron microscope (TEM), Fourier transform infrared (FT-IR), and X-ray

diffraction (XRD) spectrophotometer. Besides, X-ray photoelectron spectroscopy (XPS) and the X-ray absorption spectroscopy (XAS) technique from Synchrotron Light Research Institute, Thailand were used to confirm the oxidation state of iron nanoparticles.

Materials and Methods

Materials

Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, MW: 278.01), purchased from CARLO ERBA, was analytical reagent grade and used immediately after purchased. Ethanol 99%, purchased from CARLO ERBA. Eucalyptus leaves were from a eucalyptus plantation in Surin, Thailand. Deionized water (DI) was used in all experiments.

Fe-NPs Synthesis

Eucalyptus leaves (EL) were washed thoroughly with tap water many times and continued with DI water, then dried using an oven at 60°C for 48 h. The eucalyptus leaves extract was prepared by the boiling method. 60 g of dry eucalyptus leaves were boiled in 1 liter of DI water for 1 hour and lastly vacuum-filtered with GF/C filters. After that, a solution of FeSO_4 (0.1 M) 250 mL was added to 500 mL of the extract (a volume ratio of 1:2), stirred for 30 min on an agitator at 800 rpm. The constant ultrasonic power of 100 W and 1,000 W with a frequency of 20 kHz were used during the experiments as shown in Table 1. All experiments were controlled at a room temperature. However, due to the existence of the ultrasonic waves, solution temperature increased during the reaction. The solution temperature after the synthesis was in the range of 25-31°C. After mixing of FeSO_4 solution and the eucalyptus extract, the appearance of black color was gradually seen, specified the reduction of Fe^{2+} ions. After the synthesis, the mixture was vacuum-filtered to separate the nanoparticles and rinsed with ethanol for three times. The obtained samples were gently blown with nitrogen gas in the wrapping of aluminum foil and dried in a hot air oven at 50°C for 12 h. The samples were kept in a nitrogen atmosphere before use.

Table 1. Atomic concentration of Fe-NPs

Samples	Atomic Concentration %		
	C	O	Fe
Euca extract 0.1 M Fe(Fe-NPs-EL)	69.04	29.34	1.62
Euca extract + Ultrasonic 1000W 0.1 M Fe (Fe-NPs-EL-UL 1000 W)	61.43	35.96	2.61

Characterizations

Morphological characteristics of Fe-NPs were studied using a field emission scanning electron microscope (FESEM) (Carl Zeiss Model Auriga). The transmission electron microscope (TEM) images of the sample were measured using JEOL, JSM-2010. Composition analysis of Fe-NPs by X-ray diffraction (XRD) patterns was completed on a Bruker, D2 Phaser with a high-power CuK α 1 radioactive source ($\lambda = 0.154$ nm) at 40 kV and 40 mA. All samples were scanned from 10° to 80° 2θ . Fourier transform infrared spectrophotometer (FT-IR) was performed on a Bruker Tensor 27; infrared rang 4,000-400 cm^{-1} . X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) spectra were measured at the SUT-NANOTEC-SLRI XAS and beamline (BL5.2) (electron energy of 1.2 GeV; bending magnet; beam current 80-150 mA; $1.1\text{-}1.7 \times 10^{11}$ photon. S^{-1}) and BL5.3 XPS machine (PHI5000 VersaProbe II, ULVAC-PHI) at the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand

Results and Discussion

Morphologies By Field Emission Scanning Electron Microscope (FESEM) And Transmission Electron Microscope (TEM)

Morphological characteristics of synthesized Fe-NPs were investigated using a field emission scanning electron microscope (FESEM) as shown in Figure 1. The results of Fe-NPs-EL denoted in Figures 1(a) and 1(b) and of Fe-NPs-EL-UL 1000W denoted in Figures 1(c) and 1(d). It can be seen that the green synthesized iron exhibits agglomerated iron particles. The approximated mean dimension of Fe-NPs-EL was 95 ± 5 nm (100 particles counted), while that of Fe-NPs-EL-UL 1,000 W was 29 ± 5 nm (130 particle counted). However, compared to the conventionally synthesized Fe-NPs using sodium borohydride, there were fewer aggregates in the green synthesized nano-particles, which was ascribed to the eucalyptus leaves extract which contained polyphenols acting as the capping agents. (Wang *et al.*, 2014a). While Jamei *et al.*, 2014 showed a synthesis of nano zero-valent iron particles using NaBH_4 and 1,000 W ultrasonic power with a constant frequency of 20 kHz, the spherical iron nanoparticles of Fe-NPs (particle size less than 100 nm) were obtained. The morphology of Fe-NPs varied significantly when the high-power ultrasonic was applied.

From Figure 2, TEM images of iron nanoparticles synthesized with eucalyptus leaf extract combined with ultrasonic waves. (Fe-NPs-EL-UL 1,000 W), the size of the nanoparticle is approximately 60 nm.

The shape of the iron nanoparticles Fe-NPs-EL-UL 1,000 W is like a non-spherical. Each particle adheres to a cluster as shown in the FESEM photograph (Figure 1(c) and 1(d)).

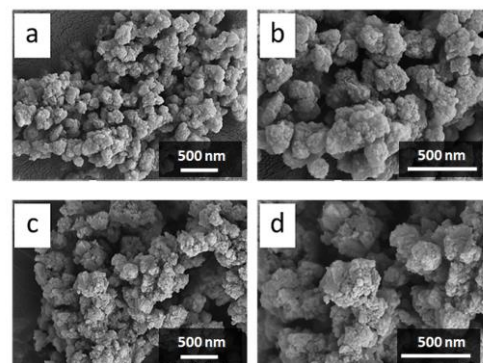


Figure 1. FESEM images of Fe-NPs-EL with a) 30000X and b) 60000X and Fe-NPs-EL-UL 1,000 W with c) 30000X, and d) 60000X

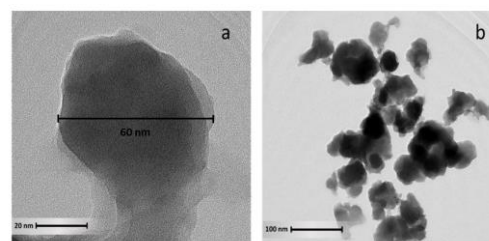


Figure 2. TEM images of Fe-NPs-EL-UL 1,000 W

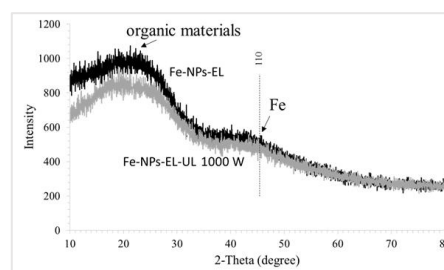


Figure 3. XRD patterns of Fe-NPs-EL and Fe-NPs-EL-UL 1,000 W

X-Ray Diffractometer (XRD) Analysis

Figure 3 shows XRD patterns of Fe-NPs-EL and Fe-NPs-EL-UL 1,000 W. The patterns are incomplete in distinctive diffraction peaks, indicating that the synthesized Fe-NPs-EL and Fe-NPs-EL-UL 1,000 W are amorphous. The broad swelling peak at $2\theta = 20\text{-}25^\circ$ is identified as organic constituents adsorbed from eucalyptus leaves extract as stabilizing agents. Similar results were also found in

the studied of Wang and his group, where iron nanoparticles were synthesized using eucalyptus leaves extract (Wang *et al.*, 2014a; 2014b). Similar results can be found from studies using green tea (Hoag *et al.*, 2009), sorghum bran a (Njagi *et al.*, 2011), and Terminalia chebula (Kumar *et al.*, 2013). Moreover, the magnitude of the peak of Fe-NPs-EL was slightly different with Fe-NPs-EL-UL 1,000 W, indicated the organic content of Fe-NPs-EL-UL 1,000 W was lower than Fe-NPs-EL. This happened as a result of the amount of organic substance covered on the particle surface that can be reduced after ultrasonic applied. Jamei *et al.* (2014) synthesized nano zero-valent iron using NaBH₄ and ultrasonic power 1,000 W with a constant frequency of 20 kHz. Fe peak of the sample using ultrasonic waves is higher than without ultrasonic waves. It may be described by the fact that the ultrasonic wave generates many central jets, causes to enhance mixing of Fe particles, and reduce organic compounds on the surface of Fe particles.

Fourier-transform Infrared (FT-IR) Analysis

The FT-IR bands for eucalyptus leaf extract, Fe-NPs-EL, and Fe-NPs-EL-UL 1,000 W were presented in Figure 4. The intense band at 3,292 cm⁻¹, 3,371 cm⁻¹, and 3,375 cm⁻¹ were assigned to O-H stretching vibration fitting to polyphenols (Kumar *et al.*, 2013; Wang *et al.*, 2014a; 2014b;). The FTIR spectrum of eucalyptus leaf extract (Figure 4(a)) showed the characteristic peak at 1,606 cm⁻¹ corresponding to C=C stretching vibration in the aromatic ring of phenolic compounds (Zhuang *et al.*, 2015). The C-H and CH₂ vibration of aliphatic hydrocarbons were indicated with the bands at 2,932 cm⁻¹, and the band at 1,711 cm⁻¹ was specified as carbonyl groups from the reduction of saturated aliphatic acid (Vázquez *et al.*, 2008). After Fe-NPs synthesis, the FTIR spectrum of Fe-NPs-EL (Figure 4(b)) and Fe-NPs-EL-UL 1,000 W (Figure 4(c)) showed O-H stretching vibrations at 3,371 cm⁻¹ and

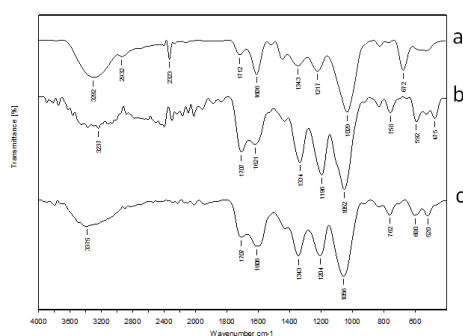


Figure 4. FTIR bands for eucalyptus leaf extract (a), Fe-NPs-EL (b), and Fe-NPs-EL-UL 1,000 W (c)

3,375 cm⁻¹, respectively. Moreover, the C-N stretching vibrations occurred at 1,052 cm⁻¹ and 1,056 cm⁻¹ for Fe-NPs-EL and Fe-NPs-EL-UL 1,000 W, respectively. For Fe-NPs-EL sample, the intensity of these peaks decreased, because the phenols molecules in the extract were involved in the reduction of Fe²⁺ (Huang *et al.*, 2015). This confirms the covering of oxidized polyphenols on the surface of Fe-NPs which helps in their sustained stability (Kumar *et al.*, 2013). The band centered at 592 cm⁻¹ and 600 cm⁻¹, respectively, denoted to Fe-O.

X-ray Photoemission Spectroscopy (XPS) Analysis

XPS was measured to verify the chemical states of the elements which were existing on the surface of Fe-NPs as shown in Figure 5. XPS spectra of Fe-NPs-EL and Fe-NPs-EL-UL 1,000 W: In Figure 5, the peaks of Fe2p_{3/2} at 711.0 eV and 713.6 eV were given to Fe (II) and Fe (III), respectively, in the iron oxide structure, and the peak at 717.1 eV was ascribed to satellite peak. This indicates the presence of Fe₂O₃ on the sample surface (Lv *et al.*, 2015). Also, the characteristic peak of Fe⁰ at about 706 eV was not observed, which is attributed to the covering and trace amounts of Fe⁰ in Fe-NPs. XPS spectrum was deconvoluted into four signals as C-C (284.8 eV), C-O (286.0eV), C=O (287.5eV), O-C=O (289.5 eV), respectively (Luo *et al.*, 2016). XPS spectra fitted to three peaks which contributed to O=C-O (532 eV), -OH (533.6 eV), C-O (534.9 eV), respectively (Luo *et al.*, 2016). The peaks in Fe2p_{3/2} and O1s endorsed that the surface of Fe-NPs was

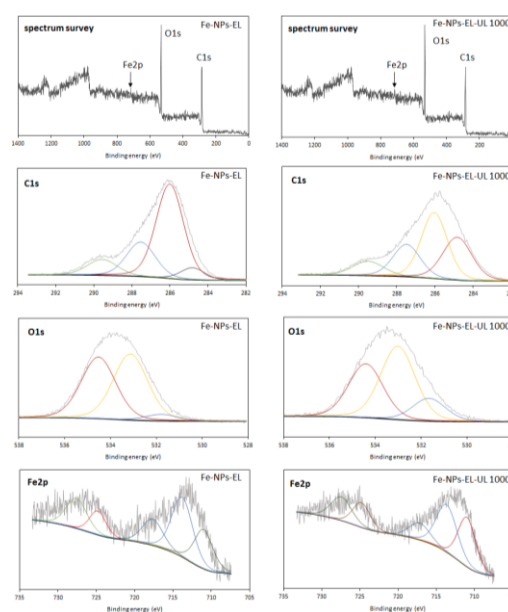


Figure 5. FTIR bands for eucalyptus leaf extract (a), Fe-NPs-EL (b), and Fe-NPs-EL-UL 1,000 W (c)

covered by an oxide layer. The results of XRD analysis were also confirmed by XPS spectra. Table 1 shows the atomic concentration of iron (analyzed using XPS Multipak program), comparing between Fe-NPs-EL and Fe-NPs-EL-UL 1,000 W. The atomic concentration of Fe in Fe-NPs-EL-UL 1,000 W significantly increased from 1.62% to 2.61% and the atomic concentration of C in Fe-NPs-EL-UL 1,000 W decreased from 69.04% to 61.43%. This is because the compounds from eucalyptus leaf extract can be reduced after ultrasonic was applied. However, XPS spectra did not identify species of iron, therefore, the species of iron was identified by XAS as the following section.

X-ray Absorption Spectroscopy (XAS) Analysis

The XAS technique is used for studying the structure of matter at the atomic level. This technique can analyze the oxidation state and the atoms' surrounding structure. Therefore, it is used to analyze the oxidation state of iron in which the surface is covered with a layer of biomolecules. Figure 6 shows the XAS spectra of the synthesized samples compared with the standards. The species of Fe-NPs-EL and Fe-NPs-EL-UL 1,000 W were evaluated against standard Fe (Fe foil), FeO, Fe₂O₃, Fe₃O₄ having oxidation states Fe⁰, Fe⁺², Fe⁺³, and Fe^{+2/+3}, respectively. The XAS results indicated the synthesized sample fitting with Fe₂O₃ (Hematite).

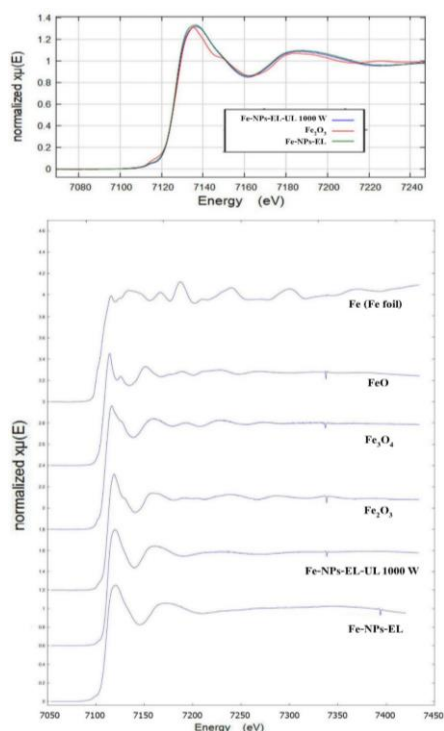


Figure 6. XAS Spectra of different iron sources

These could confirm the results that synthesis using eucalyptus leaves extract and the ultrasonic wave irradiation of iron nanoparticles (Fe-NPs) is hematite.

Conclusions

Green synthesis of iron nanoparticles can be performed using eucalyptus extract as stabilizing agents. Characteristics of Fe-NPs-EL and Fe-NPs-EL-UL 1,000 W are differences in size and shape as proved by FESEM and TEM. The use of 1,000 W constant ultrasonic power with a frequency of 20 kHz to assist in the synthesis will generate smaller particles. It could be explained by the fact that the ultrasonic wave generates many central jets, causes to enhance mixing of Fe particles, and reduce organic compounds on the surface of Fe particles. Also, the XAS technique indicated that the Fe-NPs synthesis using eucalyptus leaves extract is hematite form.

Acknowledgments

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