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Ferro Content in Soil and Mustard Leave (*Brassica junjea*) Treated by Agricultural Waste on the Biosensitizer-Iron Photoreduction

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ABSTRACT

Atom absorption spectrophotometer (AAS) had been used to analyzed Ferro in the soil and in the green mustard leaf (*Brassica junjea*) treated with phenolics extract from the agricultural wastes of clove leaf (*Eugenia aromatica*), rice straw (*Oryza sativa*) and water hyacinth leaf (*Eichhornia crassipessolms*), in which the phenolics as the electron donor on the biosensitizer – iron photoreduction. Phenolics extract was obtained from varions of aquadest and 40; 60; 80% methanol. The solution without extract was used as sensitizer, while the extract without illumination was used as control. Green mustard was packed into medium polybag within it added by 2,000 mg kg^{-1}. Soil type as sample was volcanic soil in various categories, such as: soil-extract, soil NPK fertilizer extract, and soil control. Results of Ferro analysis in the clove leafs treated with 80% methanol indicated the highest increasing Fe^{2+} of 22.94 mg kg^{-1}. Rice straw treated with 60% methanol showed the highest increasing Fe^{2+} of 34.5 mg kg^{-1}. The water hyacinth leafs treated with 60% methanol obtained the highest increasing Fe^{2+} of 17.67 mg kg^{-1}. Fe^{2+} concentration at soil-clove leafs had the highest increasing of Fe^{2+} production for 5.6 mg kg^{-1}. Its concentration at soil NPK fertilizer extract water hyacinth leafs showed the highest increasing of Fe^{2+} production for 13.39 mg kg^{-1}. Highest concentration of Fe^{2+} in the green mustard at soil NPK fertilizer extract clove leafs was 176.37 mg kg^{-1}. Various concentrations and various soil categories resulted in the highest increasing Fe^{2+} concentration in each agricultural waste extract.

Keywords: Agricultural waste extract, ferro analysis, iron photoreduction, soil category

INTRODUCTION

Indonesia has been known for its abundant natural resources of flora and fauna. North Sulawesi has been enriched with great biodiversity and supporting environment for the growth and development of this flora and fauna. Biodiversity and supporting environment, therefore, must be appropriately managed and preserved. At North Sulawesi, the remnants of natural product or the last part of the flora living process, including unprocessed wood log or leaves waste, are just left for natural decomposition (Rorong 2012a; 2012b).

Many types of leaf are containing base substance or main source of phenolics. The phenolics can be recovered into biosensitizer material by the assist of sunlight through iron photoreduction process in the soil. This material may help plant growth and increase soil fertility. Biosensitizer can be prepared by extracting some leaf types and subjecting it to phytochemical analysis to produce phenolics, flavonoid and tannin compounds by using certain reagent and UV rays of sunlight (Suryanto 2010).

Previous research reported that phenolics compound is able to reduce the oxidized metal ion (Michalak 2006). Goodman and Cheshire (1982) have learned the reduction of molybdenum (Mo) ion by phenolics compound. Their result indicated that some MoO_4^{2-} ions in the solution is reduced by phenolics compound into Mo^{5+}. Indeed, MoO_4^{2-} and Mo^{5+} ions are absorbed by phenolics compound through ion exchange mechanism. Furthermore, it was found that phenolics compound can reduce V^{+5} into V^{+4} and also Hg^{+2} into Hg^0. Finally, Goodman and Cheshire (1982) concluded that the interaction of phenolics compound with the solving agent does not only reduce the anion species into cation, but also reduces cation into cation.

The effect of sunlight radiation on the speed of the reduction of manganese oxide (MnO_2) and iron oxide (Fe_2O_3) by phenolics compound, which is extracted from sea water and accelerated by sunlight, has been examined (Sunda *et al*. 1983). Waite and Morel (1984) have studied photo-reductive dissolution of iron oxide colloid in the natural water with or without dissolved phenolics compound. The result explains that the dissolved phenolics compound accelerates the reaction of the photo-reductive dissolution of iron oxide. According to Harborne (1987), organic component may function as metal chelating agent because one carboxyl cluster (-COOH) and two proximate hydroxyl clusters (-OH) have reacted with metal ion to produce a stabile complex. This potential is shown by the position of its hydroxyl cluster with the ability to capture free radical by chelating and stabilizing Fe.

According to Pizzi (1981), chromate (CrO_4^{-2}) and dichromate ($Cr_2O_7^{-2}$) ions are not only fixated quickly in the wood waste, but also helping to fixate the copper salts, similar to what has happened with Cu-Cr-Ar (CCA) in the wood preservation process. Wood impregnating treatment with chrome trioxide (Cr_2O_3) can improve the stability because of the characteristics of water resistance and water repellency. Any researches examining iron photo-reduction by the assist of phenolics compound as the electron donor seem failed to reveal this fact. Therefore, the author were interested to understand iron photo-reduction by using phenolics compound from the agriculture crop wastes, such as clove leaf, rice straw, and water hyacinth leafs, while the phenolics is used as the electron donor and also as biosensitizer.

The objective of research was to analyze Fe^{2+} concentration in the soil and in the green mustard leaf after treatment with phenolics extracted from the wastes of clove leaf, rice straw and water hyacinth leaf, when the capability to absorb UV rays is facilitating phenolics as the electron donor in the establishment of biosensitizer on the photoreduction $Fe^{3+} \rightarrow Fe^{2+}$ in the soil.

MATERIALS AND METHODS

Time and Research Site

Research was conducted for three months, precisely from July to September of 2011. It was located at Advance Chemical Laboratory, Faculty of Mathematical and Sciences, University of Sam Ratulangi Manado, and Chemical Laboratory of Researches and Industry Standarization Building in Manado.

Soil Sample and Preparation

Volcanic soil samples were collected from public plantation land in the proximity of Lokon Mount and Mahawu Mount at Paslaten Village, Tomohon City, North Sulawesi Province. The soil was dried by aeration, and then grounded and screened. Phenolics extract samples were obtained from clove leaf, rice straw and water hyacinth leafs. The materials were taken from plantation land at Papakelan Village and from Tondano Lake proximity in Minahasa Regency, North Sulawesi Province. The leafs samples were dried by aeration, blended, and extracted through maceration with aquadest and 40, 60 and 80% methanol solvents. Chemicals used for analysis include aquadest, CH_3OH, 50% Folin Ciocalteu reagent, 2% Na_2CO_3, 2% aluminum chloride, viscous HCl, HNO_3, C_2H_5OH, 4 % vanillin, and 0.07% 2.2 bipiridin (Suryanto 2008).

Extraction Procedure

Solvent extraction procedure through maceration was explained as follows. Leaf powder sample of 5 grams was extracted through maceration by mixing the solvents of 50 ml hot H_2O and 50 ml CH_3OH. The involved concentrations were 40, 60 and 80%. It was stored in the Erlenmeyer for 24 hours and screened. The filtrate was evaporated for 12 hours. It was then poured in the illuminated box at 5,000 Lux light intensity for 15 hours on the iron photoreduction process (Suryanto 2008). The samples included extracts of aquadest, and 40, 60 and 80% methanol. The solution

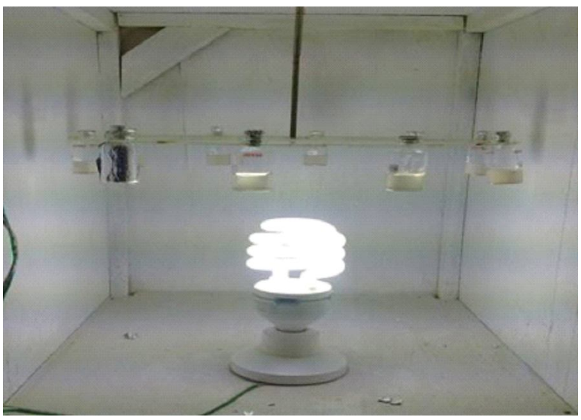

Figure 1. Illuminated box for photoreduction iron process.

without extract was employed as sensitizer while the non-illuminated extract was utilized as control in the illuminated box (Figure 1) for photoreduction iron process.

Data Analysis

Data were analyzed by statistic program SPSS version 13 to understand the obvious difference between treatments.

RESULTS AND DISCUSSION

Ferrous concentration recognized from photo-reduction process of clove leaf extract is shown in Figure 2. The samples included extract of aquadest, and 40, 60 and 80% methanol. The solution without extract was employed as sensitizer while the non-illuminated extract was utilized as control. The extract with 80% methanol solvent increased the production of Fe^{2+} ion to 22.94 mg kg^{-1} which was the highest compared to 22.56 mg kg^{-1} from the extract with 40% methanol solvent, 21.94 mg kg^{-1} from the extract with 60% methanol solvent, and 20.89 mg kg^{-1} from the extract with aquadest solvent. The solution without extract as sensitizer only produced Fe^{2+} for 6 mg kg^{-1}, while the non-illuminated extract produced 0.33 mg kg^{-1}.

Ferrous concentration produced through photo-reduction process of rice straw extract is illustrated in Figure 3. The samples were aquadest and 40, 60 and 80% methanol extracts. The solution without extract was functioned as sensitizer and the non-illuminated extract was used as control. The extract with 60% methanol solvent increased the production of Fe^{2+} ion to 34.5 mg kg^{-1}, which was the highest compared to 27 mg kg^{-1} with the aquadest extract, 25.28 mg kg^{-1} with 40% methanol solvent, and 10.61 mg kg^{-1} with 80% methanol solvent. The solution without extract as sensitizer only produced Fe^{2+} for 3.89 mg kg^{-1}, while the non-illuminated extract only attained to 1.06 mg kg^{-1}.

Ferrous produced through photo-reduction process against water hyacinth leafs extract is shown in Figure 4. The samples were aquadest extract, and 40, 60 and 80% methanol. The solution without extract was acted as sensitizer and the non-illuminated extract was used as control. Extract with 60% methanol solvent increased the production of Fe^{2+} ion for 17.67 mg kg^{-1} as the highest compared to 12.44 mg kg^{-1} from the extract with 40% methanol solvent, 2.94 mg kg^{-1} from the extract with aquadest, and 1.11 mg kg^{-1} from the extract with 80% methanol solvent. The solution without extract as sensitizer only produced Fe^{2+} ion of 5.67 mg kg^{-1}, while the non-illuminated extract only achieved at 0.06 mg kg^{-1}.

There was also obvious difference between Fe^{2+} contents produced by three solvents. After extraction, then clove leafs, rice straw and water hyacinth leafs were analyzed in the solution system containing Fe^{3+}. Some previous researchers reported that the phenolics compounds had ability to reduce the oxidized metal ion. Goodman and Cheshire (1982) had examined the reduction of molybdenum (Mo) ion by phenolics compounds. The result showed that some MoO_4^{2-} ions in the solution was reduced by phenolics compounds into Mo^{5+}. Indeed, MoO_4^{2-} and Mo^{5+} ions were absorbed by phenolics compounds through ion exchange mechanism.

According to Goodman and Cheshire (1982), phenolics compounds could reduce V(V) into V(IV) and Hg (II) into Hg(0). Goodman and Cheshire (1982) confirmed that interaction of phenolics compounds with the solving agent did not only reduce

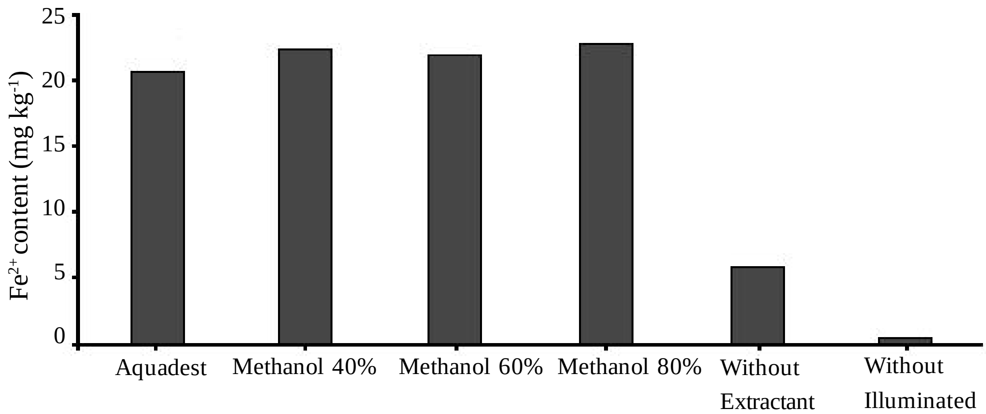

Figure 2. Ferro Concentration on the photoreduction result of clove leaves extract (*Eugenia aromatica*) with aquadest and 40, 60 and 80% methanol solvents in the illuminated box on the photoreduction iron process.

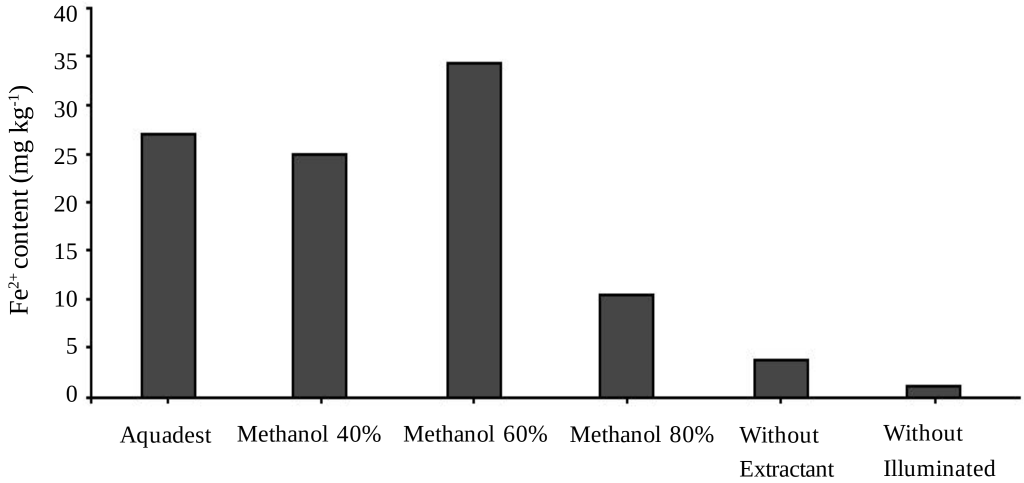

Figure 3. Ferrous concentration of Rice Straw with aquadest and 40, 60 and 80% methanol solvents in the illuminated box on the photoreduction iron process.

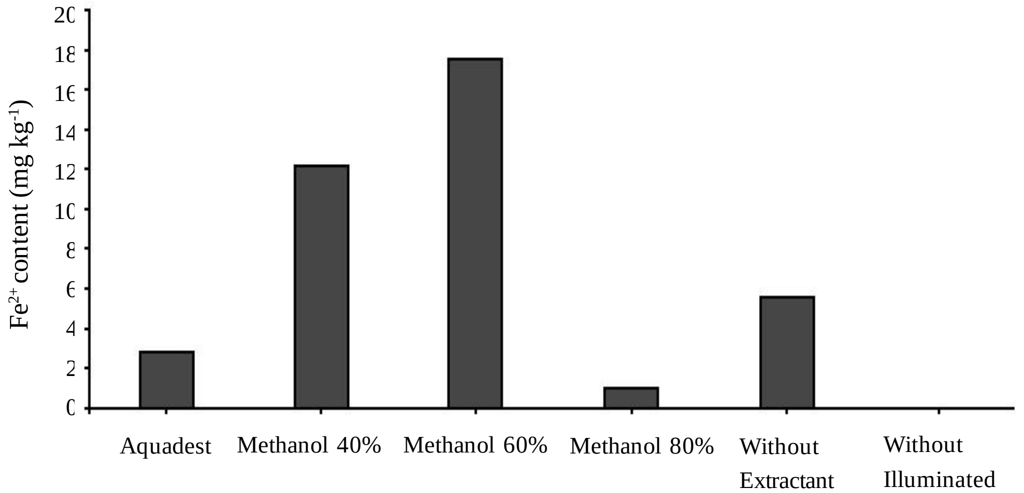

Figure 4. Ferrous concentration of water hyacinth leaves (*Eichhornia crassipessolms*) with aquadest and 40, 60 and 80% methanol solvents in the illuminated box on the photoreduction iron process.

the species from the anion into cation, but also reduce cation into cation.

Flores-Velez *et al.* (1995) had studied the specification of Cr (VI) in the phenolics compounds-contained soil by using polarographic method. Result of their study indicated that at acid condition (pH 2 and pH 4), Cr(VI) was reduced into Cr(III) by phenolics compounds. Skogerboe and Wilson (1981), who examined the reduction of Hg(II) by phenolics compounds, found that at low pH, phenolics compounds species was established as $-OH^+$. It was said that phenolics compounds needed to be protonized to improve its reducer characteristic. This result was consistent with Eary and Ray (1991) who studied the reduction of Cr(VI) in the sub-surface of the soil at various pH. The results showed that the reduction of Cr(VI) in the sub-surface of the soil could be faster at acid pH. According to Flores-Velez *et al.* (1995), the reduction reaction of Cr(VI) by phenolics compounds may be written as follows:

$$3 \text{ phenolics compounds}_{red} \longrightarrow SF_{ox} + 3mH^+ + 3e^-$$

$$HCrO_4^- + 3e^- + 7H^+ \longrightarrow Cr^{3+} + 4H_2O$$

$$3SF_{red} + HCrO_4^- + 7\,H^+ \longrightarrow 3SF_{ox} + 3mH^+ + Cr^{3+} + 4H_2O$$

Flores-Velez *et al.* (1995) obtained that to shift the balance of the product, thence the m rate must be bigger than 2 Cr(III) such that phenolics compounds were forming $(Cr(SF_{ox})n)^{3+}$. Wittbrodt and Palmer (1995) have researched the reduction of Cr(VI) into Cr(III) at dark condition using phenolics compounds as electron donor. The result showed that the speed of the reduction of Cr(VI) into Cr(III) depended on early concentration of Cr(VI), early concentration of phenolics compounds, pH of solution, and the

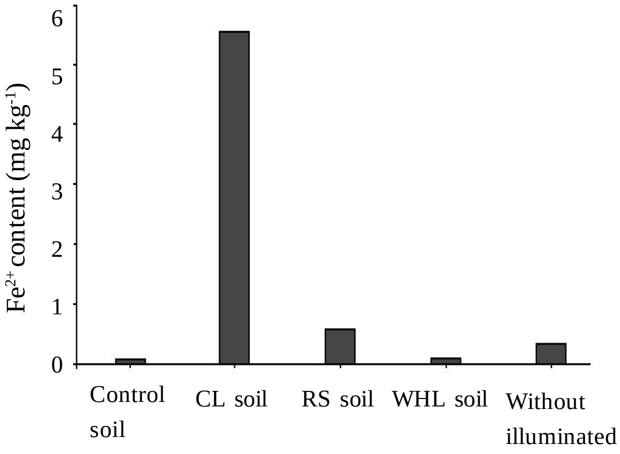

Figure 5. Ferrous concentration of the extract soil of clove leaves (CL) extracted with 80% methanol solvent, rice straw (RS) and water hyacinth leaves (WHL) extracted with 60% methanol solvent in the soil media in the illuminated box of photoreduction iron process.

changing number of phenolics compounds fraction which was oxidized during reaction.

Researches about the effect of sunlight radiation on the speed of the reduction of manganese oxide and iron oxide have been carried out. Result of Sunda *et al.* (1983) showed that the reduction of manganese oxide by phenolics compounds, which was extracted by sea water, could be accelerated by sunlight, also have observed the photoreductive dissolution of iron oxide colloid in the natural water with or without dissolved phenolics compounds. The result explains that dissolved phenolics compounds accelerates the reaction of the photo-reductive dissolution of iron oxide.

Ferrous concentration established through photo-reduction process of clove leaf, rice straw and water hyacinth leafs in the soil media is shown in Figure 5. The control was the soil untreated with extract and not illuminated. Soil extract containing clove leaf phytochemical increases Fe^{2+} production to 5.61 mg kg^{-1} which is the highest compared to rice straw with 0.61 mg kg^{-1} and water hyacinth leafs with 0.11 mg kg^{-1}. Soil extract only produced Fe^{2+} ion for 0.11 mg kg^{-1}, while the non-illuminated soil as control reached for 0.39 mg kg^{-1}.Ferri species from iron ammonium compounds (III) sulfate (yellowish clear) was reduced into Fe^{2+} after the addition of clove extract (bright yellow). It was confirmed by the change of the solution color into rather dark yellow. The change into darker color (like violet at glance) was more obvious after the solution was illuminated. If the result of photo-reduction process with extract addition was compared to extract soil water hyacinth leafs, very significant difference was found (Rorong and Suryanto 2010).

It seems that the presence of the light will improve the character of clove leaf extract as *sensitizer* in reducing Fe^{3+}. The reduction of Fe^{3+} into Fe^{2+} with phenolics compounds from clove leaf extract can be described in the following reaction:

$$Fe^{3+} + SF \rightleftharpoons SF\text{-}Fe^{3+}$$
$$SF\text{-}Fe^{3+} \xrightarrow{hv} Fe^{3+}\text{-}SF\bullet$$
$$Fe^{3+}\text{-}SF\bullet + e \longrightarrow Fe^{2+}\text{-}SF_{oks}$$
$$Fe^{2+}\text{-}SF_{oks} \longrightarrow SF_{oks} + Fe^{2+}$$

Note: FC (phenolics compounds)

After illumination, 2 mL quotes were taken and reacted with 0.07% 2.2 bipiridin. The orange-pink colored complex was produced and easily read by UV-Vis spectrophotometer at 520 nm wavelength.

This result contributed a very positive input to the use of clove leaf-based phenolics compounds as the reducer of Fe^{3+}. Meanwhile, Fe^{2+}-phenolics was the powerful chelate such that the iron could be protected from soil reaction and easily mobilized and absorbed by plant. For without bright extract, such activity was apparent even without clove extract. It indicated that only with light, Fe^{3+} was able to be reduced into Fe^{2+}. Such mechanism was confirmed because of the presence of Fe $(OH)^{2+}$ in the solution (Saragih 2002). Ferrousus hydroxide ($Fe(OH)^{2+}$) ion seems sensitive to the light and is able to absorb ultraviolet beam. The low efficiency of the reduced iron in the radiated solution containing Ferrous hydroxide is evident because of the reverse reaction between Fe^{2+} product-light and radical hydroxide. The reaction can be explained as follows:

$$Fe(OH)^{2+} \xrightarrow{hv} Fe^{2+} + \bullet OH$$

The difference of photo-reduction treatment with and without the addition of clove leaf extract means that the presence of extract in the Fe (III) solution will increase the efficiency of Fe (III) reduction significantly. The concentration of Fe^{2+} is increased along with the increase of extract concentration. Fe^{2+} content determined through photo-reduction process of clove leaf, rice straw and water hyacinth leafs in the soil media is shown in Figure 6. The soil without extract and illumination was used as control. Soil extract containing clove leaf phenolics showed the increase of Fe^{2+} production to 5.61 mg kg^{-1} which was the highest compared to rice straw extract with 0.61

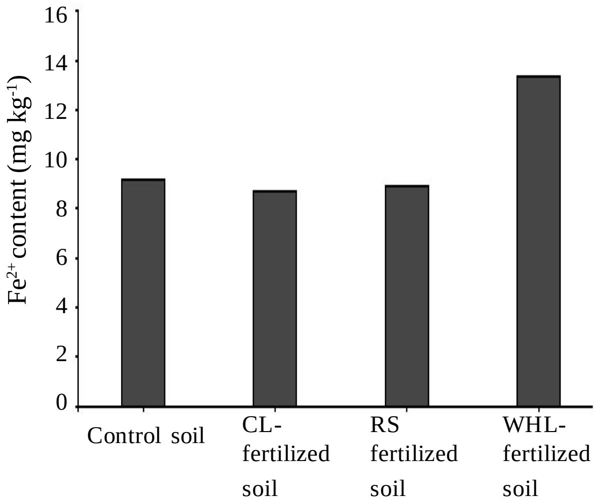

Figure 6. Ferrous concentration in green mustard of soil-fertilizer-extract of clove leaves (CL), rice straw (RS) and water hyacinth leafs (WHL) with 60% methanol in soil media and NPK fertilizer in the illuminated box on the photoreduction iron process.

mg kg^{-1} and water hyacinth leafs with 0.11 mg kg^{-1}. Soil extract only produced Fe^{2+} for 0.11 mg kg^{-1}, while the without illuminated soil extract as control achieved for 0.39 mg kg^{-1}.

Two reactions are very important in the soil, *i.e.* oxidation and reduction reactions. Oxidation is a process of losing the electron from a chemical compounds, from substance, or from atom and its radical. Reduction is the opposite, which is the adding of electron into the compounds (Stevenson 1994). Redox process represents a sustainable process in the soil. The electron donor is oxidized in this process, while the electron acceptor is reduced. In the classical example, atom or ion which is reduced is as follows:

$$Fe^{3+} + e \underset{\textit{Oxidation}}{\overset{\textit{Reduction}}{\rightleftharpoons}} Fe^{2+}$$

The increase of pH in the acid soil inundation may be caused by the increase of viscosity of OH^- ion due to the reduction of Ferrousus hydroxide ($Fe(OH)_3$) based on the following reaction:

$$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$$

At acid soil, micro substances such as iron, copper, zinc, and manganese are enormously provided but possibly poisoning the plant. In the soil, organic matter plays a role as the soil absorption complex. This complex absorbs cation, but it also absorbs anion in smaller rate. Metal ions in the clay and dry matters not only have an absorbing character, but also develop a complex compounds to wedge these ions such that its exchange or release in the soil solution is difficult. This event influences the soil fertility which is related to the release of fixated dry matter or the reduction of toxic matter solubility (Stevenson 1994).

The construction of complex compounds is built from the reaction of metal ion with ligand (an organic compounds to wedge the metal cation) through *electron pair sharing*. Result of this reaction is called as *metal coordination compounds*. Metal acts as the acceptor of electron pair, while ligand is the provider of electron pair. Metal ion acts as central ion, while organic ions are coordinated around it. Some organic ligands can bind metal ion even with more than one provider functional cluster (Brown 1969). This binding type can form a heterocyclic ring, called chelate. The process of forming the chelate ring is called as chelation. Chelation increases the mobility and the availability of cation. Interacting metal ion, either divalent or trivalent, with a functional cluster in the phenolics compounds with water medium at pH close to 7, may be available through one or more reaction mechanisms as follows (Saragih 2002):

The binding between transition metal and phenolics compounds begins at the site wh ere the strong binding is built through the formation of chelate structure. The weaker binding occurs after the strong sites are saturated. The concentration of metal ion and the ionic character in the binding between metal ion and phenolics compounds will increase (Suryanto *et al*. 2010).

Fe^{2+} concentration in the soil treated with phenolics extract was determined to acknowledge the effect of phenolics extract treatment on Fe^{2+} content. Result of Fe^{2+} and Fe^{3+} concentrations is shown in Figure 7.

For the soil without fertilizer, the highest Fe^{2+} concentration was found in the soil treated with clove leaf extract, with 3.7 mg kg^{-1} for Fe^{2+} and 8.23 mg kg^{-1} for Fe^{3+}. The lowest concentration was achieved in the extract soil of water hyacinth leafs with 2.17 mg kg^{-1} for Fe^{2+} and 4.82 mg kg^{-1} for Fe^{3+}. The data shown that Fe^{2+} and Fe^{3+} concentrations were increasing, in which in the beginning of treatment, Fe^{2+} concentration was 0.18 mg kg^{-1}, while Fe^{3+} concentration was 0.4 mg kg^{-1}. The addition of phenolics total extract in the soil influenced the increasing of Fe^{2+} concentration in the soil.

For soil treated with NPK fertilizer, the highest Fe^{2+} concentration was observed in the soil treated with water hyacinth leafs extract, with 2.62 mg kg^{-1} for Fe^{2+} and 5.84 mg kg^{-1} for Fe^{3+}. The lowest

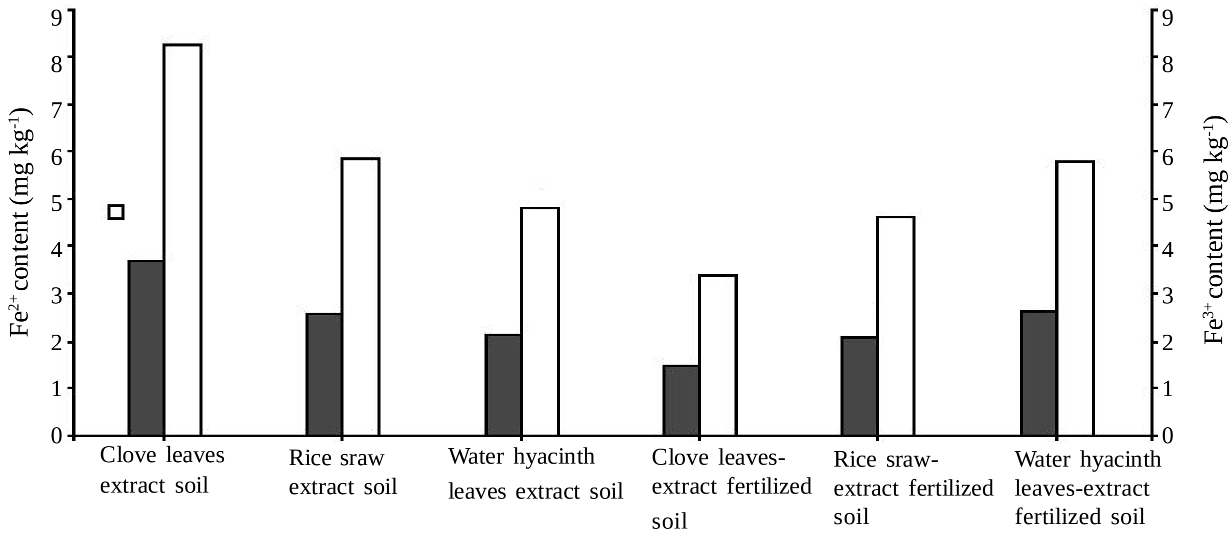

Figure 7. The comparison of Fe^{2+} and Fe^{3+} concentrations of the soil-extract and soil-fertilizer-extract of clove leafs, rice straw and water hyacinth leafs with 60% methanol in soil media on photoreduction iron process. ■ = Fe^{2+} and □ = Fe^{3+} concentrations.

Fe^{2+} concentration was found in the soil treated with clove leaf extract, with 1.55 mg kg^{-1} for Fe^{2+} and 3.46 for Fe^{3+}. The treatment between fertilizer and phenolics extract mix had an effect on the increasing of Fe^{2+} concentration in the soil.

To figure out whether there was an effect of phenolics extract treatment on the soil and green mustard, Figure 8 indicates Fe^{2+} concentration in the green mustard leaf treated with phenolics extract.

Figure 8 indicates Fe^{2+} concentration in green mustard. The highest Fe^{2+} concentration was obtained in the green mustard leaf in the soil mix treated with clove leaf extract, which the rate was 176.37 mg kg^{-1}. The lowest Fe^{2+} concentration was found as 98.95 mg kg^{-1} in the green mustard in the soil with fertilizer and water hyacinth leaf extract. Fe^{2+} concentration in the soil treataed with phenolics extract and fertilizer was not showing similar Fe^{2+} concentration. It may also due to the interaction between chemical compounds in the fertilizer and the phenolics extract added into soil mix. Fe^{2+} concentration in this soil treated with phenolics extract was higher than the control soil without phenolics extract or fertilizer.

The data indicated that phenolics extract had similar effect to those shown by the fertilized soil.

CONCLUSIONS

For clove leafs extract sample, 80% methanol solvent produced the highest increasing of Fe^{2+}

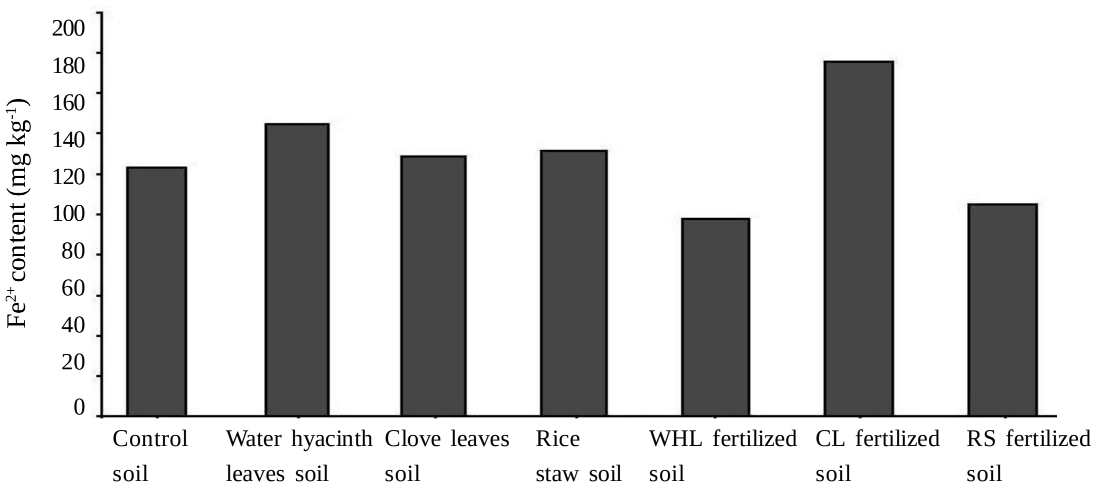

Figure 8. Ferrous concentration in the green mustard leaves with phenolics extract treatment.

production, followed by the extract with 40% and 60% methanol. For rice straw extract sample, 60% methanol solvent produced the highest increasing of Fe^{2+} production, compared to the extract with aquadest, and 40% and 60% methanol solvents. In the water hyacinth leafs extract sample, 60% methanol solvent showed the highest increasing of Fe^{2+} production, compared to 40% and 80% methanol solvents. Fe^{2+} concentration in the extract soil treated with clove leaf extract indicated the highest increasing, compared to extract soil with rice straw and water hyacinth leafs. Fe^{2+} concentration in the soil-fertilizer-extract treated with water hyacinth leafs showed the highest increasing, compared to fertilize soil extract clove leafs and rice straw. Fe^{2+} concentration in green mustard leaf showed the highest increasing under UV rays.

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