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# Synthesis and Characterization of Zero Valent Iron Prepared Using Green Synthesis Method

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## Abstract

This research was conducted to develop a green synthesis method for zero valent iron (ZVI) preparation. The ZVI was synthesized by reacting $FeCl_2$ with polyphenols extracted from kepok banana peels. This polyphenol extraction process was carried out using three different solvents, namely: water, chloroform, and ethyl acetate. GC-MS test showed three main phenolic compounds contained in the banana peel extract, namely: 2-Methoxy-4-vinylphenol, 4-Methoxy-2-vinylphenol, and 2-Methoxy-5-vinylphenol. The optimum composition of $FeCl_2$ and polyphenol was 3:2. FTIR data confirmed that the synthesized ZVI contains organic compounds having –OH and C=O groups which are assumed to be capping agents that can maintain stability. This has also been supported by the results of the EDX analysis where there are carbon atoms (C) and oxygen atoms (O) in ZVI. The ZVI particle size was uneven and form a compact solid. The largest particle size distribution of ZVI is in the range of 234.49 nm - 407.49 nm with the average size of ZVI beings 616.26 nm. The results of the XRD analysis have also confirmed the formation of a simple cubic ZVI with fine crystallite size of ca 26.64 nm.

*Keywords:* polyphenol, banana peel, extraction, zero-valent iron

## 1. Introduction

The usage of metal decontaminants to remediate water and soil has recently attracted much attention. Several metal decontaminants have begun to be synthesized and applied to restore water and soil downgrade due to pollution. One of the most interesting metal decontaminants to be developed is ZVI (Zero Valent Iron) [1] [2]. ZVI has the potential to adsorb heavy metals and transform organic compounds which pollute the water and soil. ZVI has great potential to remediate contaminated groundwater by chlorinated hydrocarbon compounds [3], nitrite and nitrate compounds [4], and radioactive waste [5]. ZVI is usually obtained by reducing $Fe^{2+}$ or $Fe^{3+}$ with $NaBH_4$ (sodium borohydride) as the reducing agent [6]. $Fe^{2+}$ ions can be produced by $FeSO_4.6H_2O$ or $FeCl_2.4H_2O$ compounds, while $Fe^{3+}$ can be obtained from $FeCl_3.7H_2O$. However, the function of $NaBH_4$ as a reductor still has several drawbacks, $NaBH_4$ is toxic, corrosive, flammable, and harmful to the environment. In addition, $NaBH_4$ is also an expensive chemical. Therefore, innovations are compulsory to look for other alternative materials that can be used to replace $NaBH_4$ which is more environmentally benign and inexpensive.

Recently, several attempts to replace $NaBH_4$ as a reductor for $Fe^{3+}$ or $Fe^{2+}$ based on green chemistry have been developed. One example of the method that has been applied is to replace $NaBH_4$ with polyphenolic compounds which are more environmentally benign and abundant. In addition, polyphenols can also produce ZVI which is more stable and not easily oxidized due to the nature of polyphenols as antioxidants. So far, several researchers have used green tea as a source of polyphenols to reduce $Fe^{3+}$ or $Fe^{2+}$ to $Fe^0$ [7]. Iron particles synthesized with polyphenols derived from green tea have been shown to degrade methylene blue (MB) and methyl orange (MO) dyes in aqueous media [8]. The synthesized product also proved to be more effective than iron particles synthesized with a borohydride solution.

Apart from green tea, polyphenols can also be obtained from parts of the banana plant (*Musa paradisiaca*) [9], such as peel waste. This banana peel waste can be used as a reducing agent for $Fe^{3+}$ or $Fe^{2+}$ to $Fe^0$. This is supported by statistical data on banana production in Indonesia which reached 8.18 million tons in 2020. This high banana production will be directly proportional to the number of banana peels in Indonesia.

In this study, polyphenols were extracted from the skin of the kepok banana (*Musa paradisiaca Normalis*) peels to be used as a reducing agent for $Fe^{2+}$ derived from $FeCl_2.4H_2O$. In addition, this study will also examine the volume ratio of polyphenols with $FeCl_2$ solution to produce ZVI optimally.

## 2. Materials and Method

Three main solvents, namely: water, chloroform, and ethyl acetate are used for extraction of polyphenols from 300 grams of kepok banana peels. The banana peel mixture was homogenized and heated at 900°C while stirring with a stirrer. The crushed banana peel was filtered with filter paper using vacuum filtration and the liquid extract was concentrated with a vacuum rotator evaporator at 700°C until reached 600 mL. The aqueous extract was dissolved in chloroform with a volume ratio of 1:1 and extracted. Then, the aqueous phase is separated from the organic phase and re-extracted with ethyl acetate (1:1). The ethyl acetate phase was evaporated using a rotary evaporator to obtain dry polyphenols. This dried extract was dissolved in water for later reaction with $FeCl_2$ solution. Then, the $FeCl_2.4H_2O$ solution was titrated with a polyphenol solution and stirred with a magnetic stirrer at a speed of 120 rpm. The volume ratio of $FeCl_2.4H_2O$ with polyphenols was varied with a composition ratio of 1:4, 2:3, 3:2, 4:1, and 1:1 to obtain the optimal composition. The extraction of banana peels obtained polyphenol extracts with a dry weight of 0.7234 grams from 300 grams or about 0.02% of the mass of banana peels. This is to previous research which also produced 0.02% polyphenol extract from wet banana peel mass [10]. Before being used as a reagent in the synthesis of ZVI, the extract obtained was examined qualitatively with $FeCl_3$ solution. The ZVI formed is indicated by the formation of a black suspension. The obtained samples were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX), X-ray Diffractometer (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and Particle Size Analyzer (PSA).

## 3. Results and Discussion

The GC-MS analysis of the banana peels extracts show three components of phenolic compounds contained in the banana peel extract, namely: (a) 2-Methoxy-4-vinylphenol, (b) 4-Methoxy-2-vinylphenol, and (c) 2-Methoxy-5-vinylphenol. These three components have the highest intensity in the GC-MS analysis compared to compounds from proteins that were detected by GC-MS. Therefore, it can be concluded that polyphenols have been successfully extracted from banana peels.

ZVI can be formed because $Fe^{2+}$ from the electrolyte solution is reduced by polyphenols to $Fe^0$. However, before electron transfer occurs between polyphenols and a solution of $Fe^{2+}$ ions, a chelate will be formed between Fe metal and polyphenolic compounds. After that, the $Fe^{2+}$ ion will accept the electrons that have been released by the polyphenol [12]. The reaction equation can be seen in Figure 1.

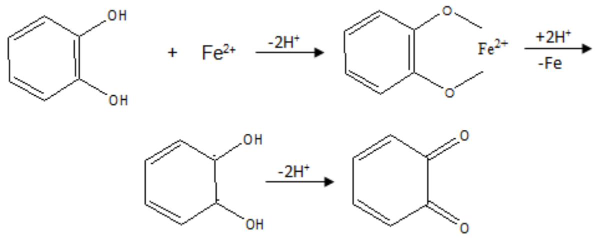


**Figure 1.** Mechanism of reaction of $Fe^0$ formation with polyphenol reducing agent

The AAS measurements in Table 1 show that the optimum composition of $FeCl_2$ and polyphenols for the synthesis of ZVI was at a ratio of 3:2. In this comparison, 77.5% $Fe^{2+}$ was reduced to $Fe^0$ by polyphenols from banana peels.

**Table 1.** Comparison of ZVI composition with polyphenols extracted from banana peels

| Volume $FeCl_2$ (mL) | Volume PP (mL) | Electrolyte concentration (ppm) | $C_0$ (ppm) | Ce (ppm) | $Fe^0$ (ppm) |
|---|---|---|---|---|---|
| 1 | 4 | 27394 | 5478.8 | 4636 | 842.8 |
| 2 | 3 | 27394 | 10957.6 | 6831 | 4126.6 |
| 2.5 | 2.5 | 27394 | 13697 | 9363 | 4334 |
| 3 | 2 | 27394 | 16436.4 | 9257 | 7179.4 |
| 4 | 1 | 27394 | 21915.2 | 15774 | 6141.2 |

The spectrum of FTIR analysis in Figure 2 depict a peak at a wavenumber of around 3406.11 $cm^{-1}$ which is the absorption area for the –OH functional group. The –OH functional group is derived from polyphenol compounds extracted from banana peels. Peaks at wavenumbers 2850.45 $cm^{-1}$ and 1623.17 $cm^{-1}$ which are signals for the C-H (alkane) and C=C functional groups. This group is also part of the polyphenol compounds extracted from banana peels. Then there are also peaks at wavenumbers 1585.03 $cm^{-1}$, 1063.47 $cm^{-1}$, and 835.48 $cm^{-1}$, each of which is an absorption region for the CC (benzene), CO, and =CH functional groups which are also derived from polyphenol compounds obtained from the extraction of banana peels. In addition, a peak at the wavenumber of 1759.88 $cm^{-1}$ which is the absorption area for the C=O functional group. This functional group indicate quinone compounds because of the oxidation of polyphenols by $Fe^{2+}$. From this information, it can be concluded that ZVI synthesized from banana peels has an organic composition. These organic compounds capped the synthesized ZVI particles [13]. With the capping agent, the stability of ZVI in the water medium can be maintained. This organic composition is also in accordance with the composition of the organic compounds extracted in this study.

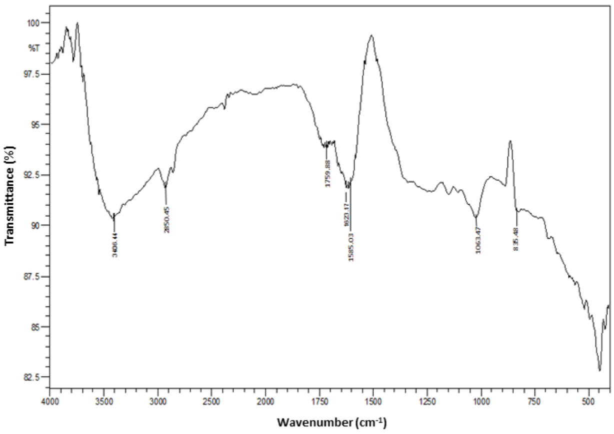


**Figure 2.** FTIR spectra of ZVI synthesized from $FeCl_2$ with polyphenols from kepok banana peels

The micrograph in Figure 3 shows the size of the ZVI synthesized with polyphenols ranging from 150 to 200 nm. Some particles also appear to be less than 100 nm in size, although there are not many of them. The particles formed are predominantly spherical in shape and some of them are agglomerated. The particles agglomerate because the interactions between the particles, make them stick together. The tiny particle size of the particles causes the surface area of the particles to increase [14]. This causes the particles to become more reactive. In addition, the atoms on the surface of the particle also affect the reactivity of a particle. In this case, the zero-charged Fe atom is the main constituent of the particles based on this experiment. Under normal conditions, Fe will be stable at the +3 oxidation state. Therefore, Fe with an oxidation number of 0 is unstable which makes it more reactive [15].

The graphs and tables of the ZVI analysis with EDX in Figure 4 depict the total Fe atoms that make up the ZVI particles are about 15.99% of the total mass. Meanwhile, the other constituent components include carbon atoms (C) at 46.25%, oxygen atoms (O) at 34.57%, and chlorine atoms (Cl) at 03.19%. The large content of carbon (C) and oxygen (O) atoms in ZVI is due to the presence of polyphenolic compounds that participate in capping ZVI particles, while chlorine (Cl) atoms are residues of the reactant ($FeCl_2$) which are carried away by ZVI particles.

From the XRD spectra in Figure 5, it can be seen that the peak with the highest intensity is at 2θ ~45° which is a typical peak for zero-valent iron ($Fe^0$) according to JCPDS (00-006-0696). Apart from 2θ ~45°, there is also another peak at 2θ 65.80°; 83.19°, and 99.87° with lower intensity. These values are also typical peaks for zero-valent iron with a simple cubic structure as indicated in JCPDS card 36-1351.

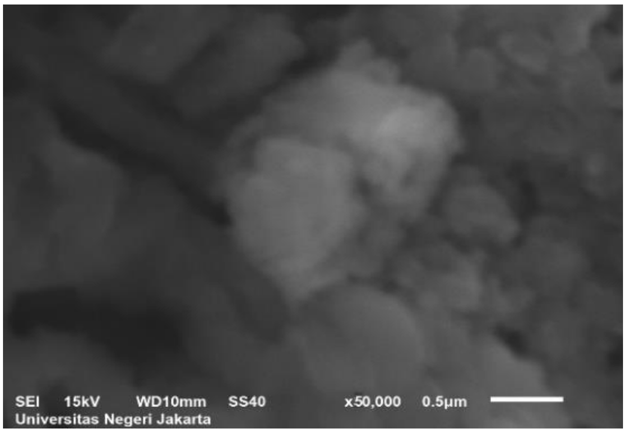


**Figure 3.** SEM micrograph of synthesized ZVI particles with banana peel polyphenols

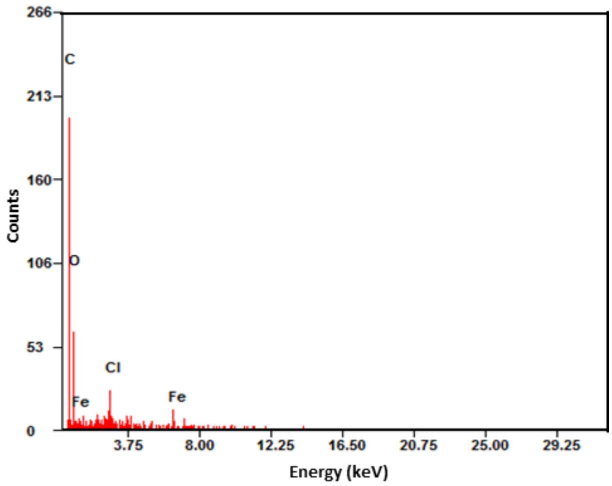


**Figure 4.** EDX spectrum of ZVI analysis synthesized with polyphenols from banana peel extract

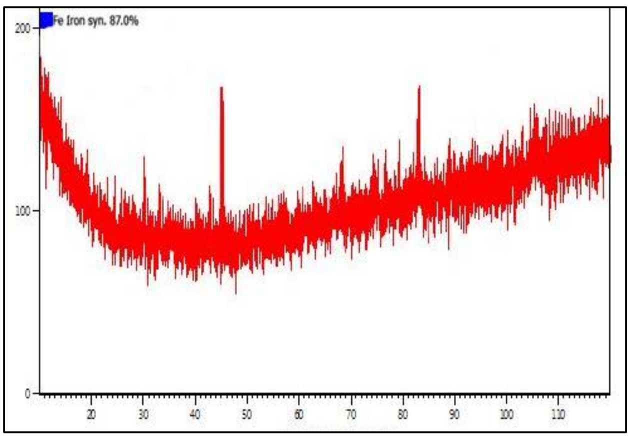


**Figure 5.** XRD diffractogram of ZVI synthesized from $FeCl_2$ with polyphenols from kepok banana peels

The average crystal size can be calculated using the Debye-Scherrer equation as shown in Equation 1 [16]:

$$D = \frac{K.\lambda}{\beta.cos\theta} \qquad (1)$$

D: The crystal size
K: Scherrer constant (0.98)
λ: X-ray wavelength (1.41874 Å)
β: FWHM in radians
θ: Bragg diffraction angle
From the calculations, the average crystal size value of ZVI synthesized was 26.64 nm.

The result of PSA analysis in Figure 6 shows that the largest particle size distribution is at sizes above 100 nm. From the graph, it can also be seen that the largest particle size distribution is in the range of 234.49 nm to 407.49 nm. It can be concluded that the average particle size of the synthesized ZVI data is still on the sub-micron order. This is probably because the ZVI particles have started to agglomerate a lot. From the table, it can be shown that the first 10% of the total number of all particles has a size below 1479.50 nm. Then the first 50% of the total particles have a size below 4074.88 nm and the first 90% of the total particles have a particle size below 8513.64 nm.

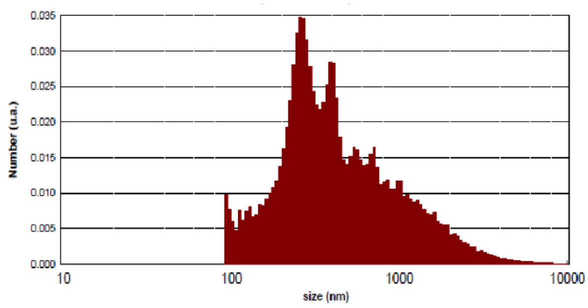


**Figure 6.** The results of the measurement of the particle size distribution of ZVI synthesized using PSA

## 4. Conclusions

Zero valent iron (ZVI) can be prepared using polyphenols extracted from kepok banana peels using three different solvents, namely: water, chloroform, and ethyl acetate. The FTIR analysis showed that in ZVI there was a composition of organic compounds having –OH and C=O groups derived from polyphenolic compounds extracted from banana peels which were suspected as capping agents for ZVI. The ZVI SEM micrograph showed that the ZVI particle size was uneven, ranging from 150 to 200 nm. However, some ZVI particles are less than 100 nm in size. The results of the EDX analysis for ZVI synthesized with polyphenols from banana peels, yielded 15.99% Fe mass percent of the total mass. The XRD analysis explained that the particles synthesized in this study were true ZVI characterized by the presence of a typical peak for ZVI, namely at a value of 2θ=45° and the average crystal size of ZVI was 26.64 nm. The results of the PSA analysis with the largest particle size distribution were in the range of 234.49 nm - 407.49 nm with an average ZVI size of 616.26 nm.

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