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Synthesis and Characterization of Zero-Valent Iron Using Polyphenols Extracted from Kepok Banana Peel (*Musa paradisiaca Normalis*)

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Abstract

This study aims to synthesize zero-valent iron (ZVI) with green-chemistry method. Synthesis was performed by reducing Fe^{2+} ion using polyphenol extract. The extract was obtained from banana peel that abundant in Indonesia and contain high of polyphenols. Synthesis of ZVI was carried out by reacting polyphenol extract to $FeSO_4$ solution with different composition 1:4, 2:3, 1:1, 3:2, 4:1, and 4.5:0.5. The gas chromatography-mass spectroscopy spectrum confirmed the existence of polyphenols in the banana feel extract from the observed peaks assigned to 2-methoxy-4-vinylphenol, 4 methoxy-2-vinylphenol, and 2-methoxy-5-vinylphenol. Based on the atomic absorbtion spectroscopy data, the best composition for ZVI's synthesis was 4:1 (polyphenol extract : $FeSO_4$ solution). The fourier transform infrared spectroscopy spectrum shows that there was –OH group indicating a present of polyphenol in the synthesized ZVI. The energy dispersive X-ray spectroscopy shows that the sample contain of Fe, C, O, S, Ca, Cu, and Na. The X-ray diffraction analysis exhibit crystalline phase of a simple cubic structure of the synthesized ZVI. This results shows that the ZVI was successfully synthesized using environmentally benign reducing agent extracted from the banana peel.

Keywords: zero-valent iron, polyphenol, banana peel

1. Introduction

Recently, many studies have been carried out to produce decontaminant metal compounds to remediate the environment. One of the decontaminant compounds developed is zero-valent iron (ZVI) [1]. ZVI is an iron particle that has a typical core-shell structure, the core consists of zero valent iron and the outer part is a shell consisting of a mixture of iron oxides (II) and (III) [2]. ZVI has attracted because of its potential applications as an adsorbent for various environmental contaminants, such as heavy metals, chlorinated hydrocarbons, pesticides, and nitrates [3]. ZVI also has a high surface area with great reactivity on the surface, compared to bulk iron [4]. Because of this advantages, a lot of technology has been utilized to remove heavy metals from water using ZVI. However, previous studies aimed to synthesize ZVI were costly and harmful to the environment [5]. One of the dangers is the formation of toxic by product in the form of boric acid and explosive H_2 gas when ZVI is synthesized using the reductant $NaBH_4$ [6].

In order to produce environmentally benign ZVI and lower production costs, a ZVI synthesis technique was developed using reducing agents from plant extracts, such as polyphenols [5]. Polyphenols were chosen because they have potential as metal chelators, radical scavengers and absorbers, chain reaction breakers, and capping agents, where these properties are needed for an adsorbent such as ZVI. One source of plants that contain lots of polyphenols is banana peel [7]. Dried banana peel contains 907 mg/100 g polyphenols, while dried banana pulp contains only 2.09 mg/100 g polyphenols [8]. In addition, banana peel is often considered as waste, so that it has not been used optimally [9]. The use of banana peels as a source for ZVI synthesis is also supported by the abundance of banana plants in Indonesia [10]. In this study, ZVI particles were synthesized using polyphenol extracted the kepok banana peel.

2. Materials and Method

2.1 Extraction of Polyphenols from Kepok Banana Peels

The banana peel was cut into small pieces and boiled in water to deactivate the polyphenoloxidase enzyme [11]. The mixture of water and banana peel was blended, and then stirred and heated at 90 ˚C for 2 hours. The mixture was then filtered. The filtrate was extracted using water and chloroform solution. From this step, the aqueous phase was obtained. This phase was then re-extracted with a mixture of water-ethyl acetate, and shaken for 30 minutes. From this step, the organic phase was obtained. This phase was then evaporated at a temperature of 50 ˚C until dry. Dried polyphenols were dissolved in 35 mL of distilled water.

2.2 Synthesis of ZVI

Synthesis of ZVI was carried out by mixing $FeSO_4$ solution with polyphenol extract. The volume ratio of $FeSO_4$: polyphenol was 1:4, 2:3, 1:1, 3:2, 4:1, and 4.5:0.5. The ZVI precipitate in the form of a suspension was then filtered with Whatman No. 42 filter paper. The precipitate obtained was then dried in a desiccator for a night.

2.3 Characterization of ZVI

The synthesized ZVI was then characterized by fourier transform infrared spectroscopy (FTIR, Shimadzu IR-Prestige 21) to determine the functional group, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX, JSM-651OLA JEOL) to determine the morphology and elemental composition, X-ray diffraction (XRD, PANalytical Empyrean) to determine the structural characteristics, and particle size analyzer (PSA, Vasco PSA 2010 Particulate Systems) to determine the ZVI particles size.

3. Results and Discussion

3.1 Extraction of Polyphenols from Kepok Banana Peels

From 300 grams of banana peel used, the dry polyphenols obtained was 0.7234 grams or about 0.02% of the mass of banana peels. This is in accordance with previous experiments which also produced 0.02% polyphenols from the mass of banana peels [11]. This extract was firstly tested qualitatively with $FeCl_3$ solution. From the results of this qualitative test, a dark green solution is formed which indicates the presence of polyphenolic compounds in the sample [12]. These polyphenolic compounds may exist in the free form or in the form of glycosides.

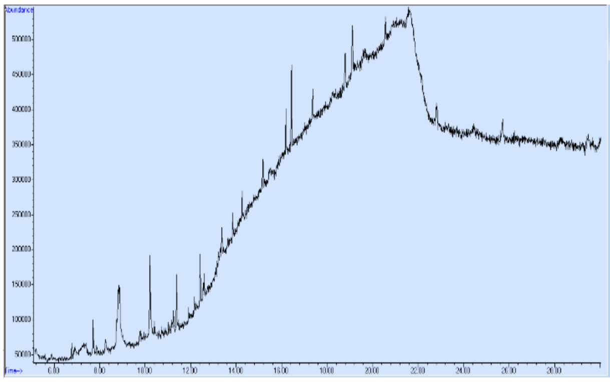
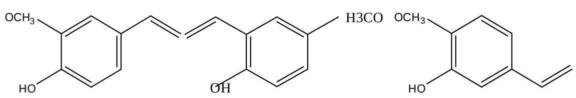


Figure 1. GC-MS analysis graph

From the results of the GC-MS analysis as shown in Figure 1, there are three peaks at the longest retention time. These indicate that the three components of the phenol compound with the highest intensity were 2-methoxy-4-vinylphenol, 4-methoxy-2-vinylphenol, and 2-methoxy-5-vinylphenol, as shown in Figure 2. Based on these, banana peel extracted in this study contains polyphenols which will be used to reduce Fe^{2+} compounds from $FeSO_4$. In addition, there are other compounds such as 1,2-benzendicarbolic acid, dipropyl ester, 2-p-nitrophenyl-1,3,4-oxidiazole-1,3,4-on-5, and 1,1,1,3,5,5,5-heptamethyltrisiloxane. However, some of the compounds above were not expected, and exist in a very small amount as indicated by the retention time in the short graph.



(a) (b) (c)

Figure 2. Monomer structure of polyphenolic compounds extracted from banana peels. (a) 2-methoxy-4-vinylphenol, (b) 4-methoxy-2-vinylphenol, and (c) 2-methoxy-5-vinylphenol.

3.2 Synthesis of ZVI with Kepok Banana Peel Extract

The ZVI synthesis was carried out by reacting $FeSO_4$ directly into the polyphenol extract. The reaction between polyphenols and $FeSO_4$ was indicated by the formation of a black precipitate dispersed in the solution. ZVI can be formed due to the presence of Fe^{2+} ions from the electrolyte solution which acts as a reactant, reduced by polyphenols to Fe(0). The H^+ ion present in polyphenols acts to reduce Fe^{2+} ions, resulting in the exchange and handover of electrons to the C atom that binds to OH, which makes it a radical. Because of these, a resonance occurs which causes the formation of a carbonyl group (C=O) in polyphenols. Characterization with AAS produced data as shown in Table 1.

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

Volume of $FeSO_4$ (mL)	Volume of PP (mL)	C_0	Residue (ppm)	Amount of reacting Fe (ppm)
1.0	4.0	5909	5897	12
2.0	3.0	11819	5492	6327
2.5	2.5	14773	6311	8462
3.0	2.0	17728	6445	11283
4.0	1.0	23638	7880	15758
4.5	0.5	26592	12885	13707

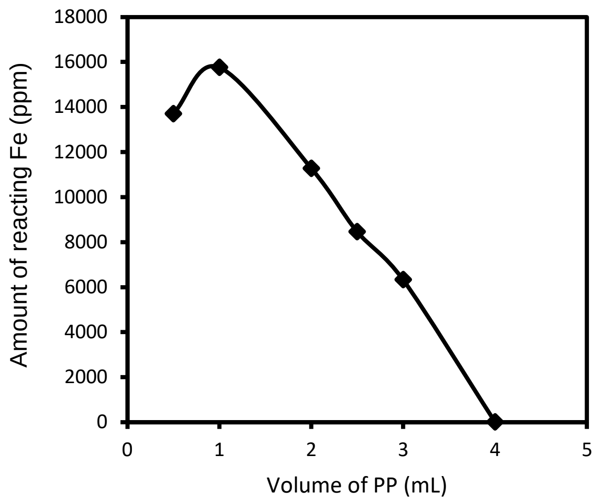


Figure 3. Curve of the relationship between the volume of polyphenols and amount of reacting Fe.

From the AAS data in Figure 3, it can be concluded that the optimal composition of ZVI synthesis between polyphenols and $FeSO_4$ was 1:4. This can be seen from the graphs and tables, when the ratio of PP volume is 1, the amount of Fe reacted shows the highest value of 15758 ppm.

3.3 ZVI Characterization

Figure 4 shows the FTIR spectrum of the ZVI indicating a main peak at wave number 3567.50 cm^{-1} related to –OH functional group derived from polyphenols extracted from banana peels. There were peaks at 2921.32 and 1617.38 cm^{-1} assigned to C-H functional group and signal of the C=C functional group, respectively. These two signals were also detected, because they were a group of extracted polyphenols. Meanwhile, the peaks at 1416.78, 1144.80, and 839.07 cm^{-1} were related to C-C (benzene), C-O, and =C-H functional groups, respectively. The signals detected in the FTIR data above strengthen the data generated from the GC-MS test, where the structure of the polyphenol compounds detected in GC-MS contains functional groups –OH, CH, C=C, CC (benzene), CO, and =CH. In addition, there was a peak at 1751.45 cm^{-1} which related to C=O functional group come from the quinone that surrounds ZVI. The sample contained quinones derived from polyphenols that had reacted with $FeSO_4$.

The SEM micrograph of ZVI is shown in Figure 5, while the EDX spectrum is depicted in Figure 6. Based on micrograph, ZVI obtained in this work is similar to previous study [13]. From the EDX data, it is known that the relative weight of the Fe component contained in the synthesized ZVI sample was 11.99%. Then, there was a very high spectrum of C and O atoms, with relative weights of 53.68% and 29.05%, respectively. This is in accordance with the FTIR data, that there are a large number of C=O groups of quinone compounds present in ZVI samples, where quinones are the result of polyphenol oxidation reactions. This can be attributed to the relative molecular mass of Fe, which was 56 g/mol, while the polyphenol monomers in this study, such as 2-methoxy 4-vinylphenol were 150 g/mol. Based on this, the possible ratio of relative weight between Fe and quinone is 1:3. However, from the EDX data obtained, the ratio of the relative weight of Fe to C and O is 1:8, so the possible relative mass of polyphenols obtained in this study is 448 g/mol. S atoms were also detected in this EDX analysis, because the ZVI came from the reduction of Fe^{2+} ions from $FeSO_4$ compounds. So that there were a few S atoms that might have precipitated in the analyzed sample. There were also several other atoms, such as Ca, Cu, and Na which were detected in the sample. Based on the literature, banana peels contain Ca 715 mg/100 grams of sample [14], while Na and Cu atoms come from the latex of banana peels that also precipitate [15].

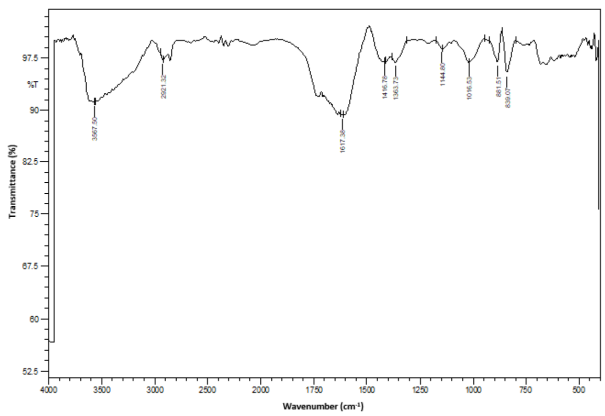


Figure 4. FTIR spectra of ZVI

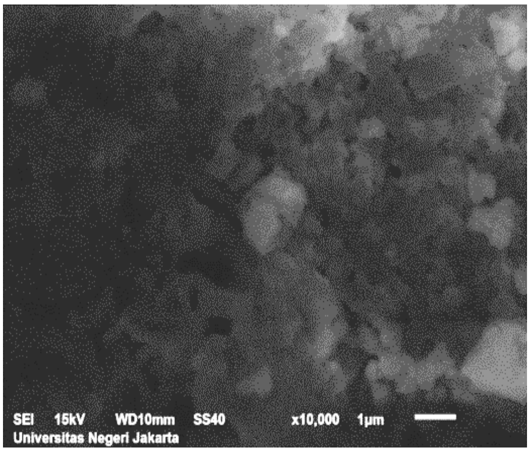


Figure 5. Micrograph of ZVI

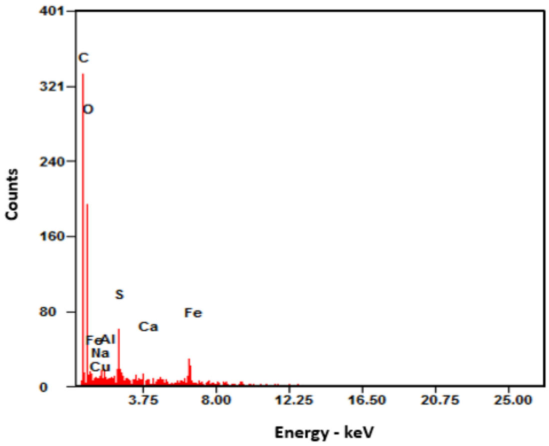


Figure 6. EDX spectrum of ZVI

Table 2. Elemental composition of ZVI

Elements	Wt%
C	53.68
O	29.05
Ca	00.34
Cu	00.55
Na	00.48
S	03.20
Fe	11.99

Based on the ZVI sample diffractogram in Figure 7, there are 6 main peaks, namely at 2ϴ 18.28˚, 30.03˚, 45.84˚, 65.80˚, 83.50˚, and 100.71˚. These peaks represent the crystal form that has the highest intensity in the sample. The highest peak is at a value of 2ϴ 45.84˚. From the XRD data, it can also be seen that the crystal plane of the synthesized ZVI particles is a simple cube. According to previous studies, the main peak of ZVI is at 2ϴ values around 40-56 nm [4]. This is in accordance with the data obtained in the study.

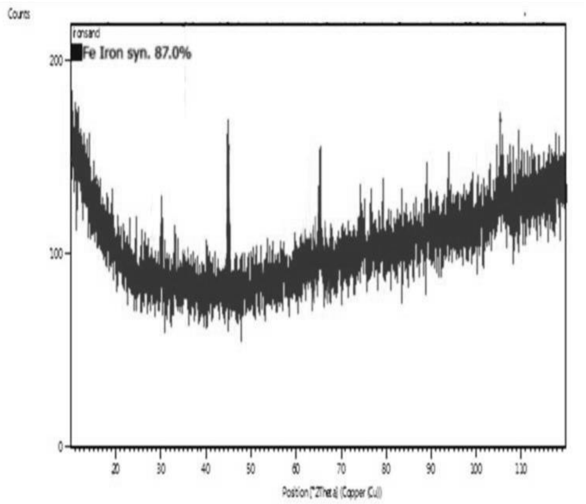


Figure 7. Diffractogram of ZVI

Figure 8 shows of the particle size measurement of the ZVI suspension. Based on the presented size distribution data, it is known that the largest particle size in the first 10% of particles in the sample (Dv10) was 1950.36 nm, the largest particle size in the first 50% particles in the sample (Dv50) was 4899.09 nm, and the largest particle in the first 90% of the particles in the sample (Dv90) was 8914.09 nm. The average size of all particles (Z average) was 524.09 nm. These data indicate that the particles detected from the sample are micro-sized. By connecting the XRD data, it can be seen that the sample was a micro-sized particle composed of nano-sized crystals.

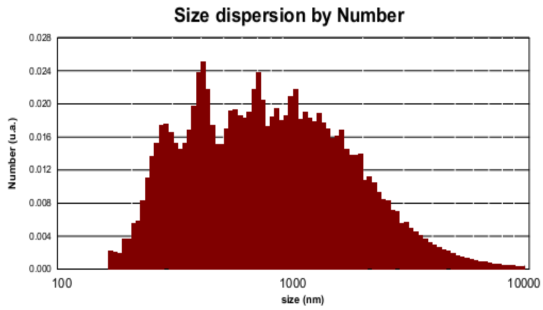


Figure 8. PSA analysis of ZVI

4. Conclusions

Based on this study, it can be concluded that the polyphenols obtained from the kepok banana peel extract can be used as a reducing agent for Fe^{2+} ions contained in $FeSO_4$ to Fe(0). The polyphenolic extract of kepok banana peel contained include 2-methoxy-4-vinylphenol, 4-methoxy-2-vinylphenol, and 2-methoxy-5-vinylphenol. The optimum composition between polyphenols and $FeSO_4$ for ZVI synthesis was 1:4. The synthesis of ZVI with the optimal composition resulted in ZVI with spherical morphology covered by polyphenols as a capping agent as evidenced by the presence of a relative weight of C of 53.68% and O of 29.05%. The synthesized ZVI is found to simple cubic structure with the average particle size is 524.09 nm.

Acknowledgements

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