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Effect of Temperature and Feeding Time in Zero-Valent Iron (ZVI) Synthesis with Polyphenol Extracts of Kepok Banana Peels

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Abstract

In this research, zero-valent iron (ZVI) was synthesized from kapok banana peels extracts as reducing agent. The fourier transform infrared spectrum showed a clear peak at a wavenumber of 600 cm^{-1} that could be assigned to Fe-O bond. XRD measurement results prove that ZVI has been successfully formed. The resulting ZVI particles are spherical granules with heterogeneous sizes and close together or agglomerating. Based on the results, it was found that the optimum ratio between $FeSO_4$ and polyphenols for ZVI preparation is 4 : 1. Based on the particle size distribution analysis, it was shown that the optimum feeding temperature and time for ZVI synthesis were 25°C and 30 minutes, respectively.

Keywords: Bottom-up, iron, polyphenol, temperature, feeding time

1. Introduction

Zero-valent iron (Fe^0 or ZVI) [1] has potential in a variety of applications, such as a reactive and effective porous barrier agent (PBR) to remediate water from waste contaminants [2], being able to degrade halogenated organic contaminants such as chlorinated hydrocarbons, pesticides, nitrates, as well as inorganic contaminants such as heavy metals [3] and as adsorbents of heavy metals. ZVI can be prepared by reduction method using a reducing agent $NaBH_4$ [4]. However, $NaBH_4$ is known as harmful and environmentally damaging [4]. Therefore, the use and development of natural reducing agent of synthesis can be a solution to reduce the impact of environmental damage experienced. This reducing agent can be produced from the extraction of plants, fruits, or waste from plants and fruits. Natural reductors that can be produced from plant extraction are polyphenols [5]. One plant source that contains polyphenols is banana peel which is a waste from bananas [6]. In this study, ZVI synthesis ZVI was prepared using kapok peel extracts as reducing agent. The feeding time and reaction temperature were varied to optimaze the fromation of fine ZVI particles.

2. Research Methods

2.1 Extraction of polyphenols

The banana peel is cut into small cubes and weighed 300 grams. Prepared 900 mL aquadest with a temperature of 80° - 90°C, then inserted the banana skin and boiled for 5 minutes in a waterbath shaker (comparison of banana skin mass with water mass 1:3). This serves to inactivate the polyphenoloxide enzymes in banana peels [9]. The mixture of aquadest and banana peels is then mashed with a blender until homogeneous, and reheated at the same temperature for 2 hours. Crushed banana peels are then filtered with a filter cloth and continued with Whatman filter paper no.1 using vacuum filtration. The filtering results as a result of isolation are further extracted to obtain polyphenols.

The isolation results were extracted with chloroform (1:1 ratio of filtrate and chloroform volume) then stirred with shakers for 30 minutes. Stirring results in the form of two phases of solution, inserted into a split funnel and silenced until the mixture is separate. Then, separated between the water phase and the chloroform phase, the water phase is taken to be further extracted with ethyl acetate (Ratio of filtrate with ethyl acetate 1:1). Next, stirring again with a shaker for 30 minutes. Stirring of two phases of solution, inserted into a split funnel and silenced until the mixture is separate. Then, separated between the water phase and the ethyl acetate phase, the ethyl acetate phase is taken. This phase of ethyl acetate is then dried in the evaporator to dry, after dry added 35 mL aquadest and obtained polyphenols with a volume of 35 mL.

2.2 ZVI Synthesis

ZVI synthesis is done by mixing $FeSO_4$ solution with banana peel extract in a small sample bottle with a comparison of polyphenols: $FeSO_4$ (1:4). After the mixing process is done stirring with magnetic stirrer 250 rpm for 60 minutes so that the reaction occurs optimally. Stirring results as a result of synthesis with optimal composition are then used to determine the effect of temperature and feeding time on the distribution of ZVI particle size of the synthesis. Furthermore, the resulting ZVI is in the form of suspension, filtered with whatman filter paper No.42 with a pore size of 0.2 µm. The obtained solids are dried in a vacuum for one night.

2.3 Effect of Temperature and Feeding Time in ZVI Synthesis

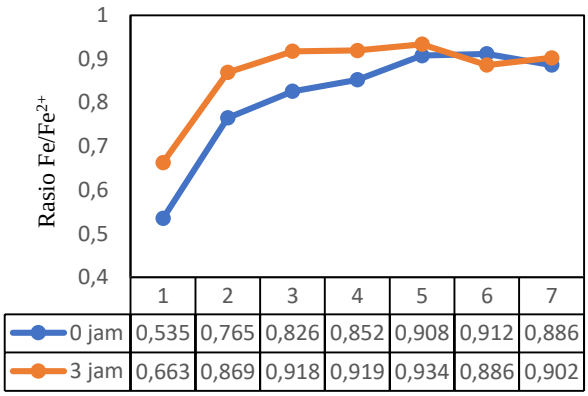
The effect of temperature in synthesis is determined in the same way as ZVI synthesis, but water baths are used to regulate temperature at reaction with the ratio of $FeSO_4$ to optimal polyphenols. The reactions were performed at 0,10, and 25°C, respectively, feeding times varied from 0 minutes, 30 minutes, and 60 minutes of polyphenol testing. Then ZVI synthesis in the form of colloidal phase is characterized with PSA and filtered with whatman filter paper No.42 with a pore size of 0.2 µm. The obtained solids are then dried in a vacuum for a night.

2.4 ZVI Characterization

The results of ZVI synthesis are then characterized by a UV-Vis Spectrophotometer to determine the concentration of Fe^{2+} ions that react with polyphenols, PSA to find out the size of the distribution of ZVI particles produced, SEM to determine the morphology of ZVI, EDX to find out the composition of the sample constituent atoms, FTIR to find the functional groups in ZVI, and XRD to determine the properties and morphology of the resulting ZVI crystals.

3. Results and Discussions

Based on analysis of the UV-Vis spectrophotometer of optimum composition obtained, the ratio of the number of Fe^{2+} ions reacting with polyphenols at some variation in the composition ratio between $FeSO_4$ solution 0.5 M with polyphenols is 1-(1:4), 2-(2:3), 3-(2.5:2.5), 4-(3:2), 5-(4:1), 6-(4.5:0.5) and 7-(4.75:0.25) shown in **Figure 1.**



	1	2	3	4	5	6	7
0 jam	0,535	0,765	0,826	0,852	0,908	0,912	0,886
3 jam	0,663	0,869	0,918	0,919	0,934	0,886	0,902

Figure 1. Fe^{2+} ratio relationship curve that reacts to the ratio of Fe^{2+} ions and polyphenols

Figure 1. In reaction time from 0 hours to 3 hours, the ratio of the number of Fe^{2+} ions reacting (ppm) with polyphenols was greater and there was an increase from the initial ratio in the ratio of $FeSO_4$ and polyphenol composition at a ratio of 4: 1. This shows that the Fe^{2+} ion reacts optimally to the comparison.

Furthermore, ZVI is produced with a composition ratio of 1: 4, FTIR measurements are taken. The results of FTIR analysis show that the formation of Fe atoms as a result of the synthesis of Fe^{2+} ions by polyphenols shown in **Figure 2.**

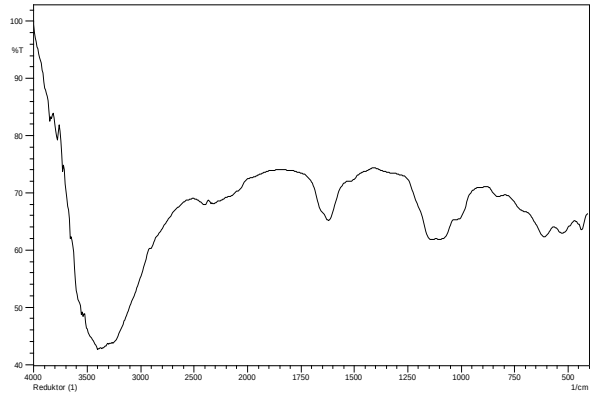


Figure 2. Results of FTIR ZVI analysis on composition comparison of 4: 1

Based on **Figure 2.** It can be known that the peak appears in the wavenumber 600 cm^{-1} is a fingerprint region

that shows the presence of Fe-O bonds, namely in compounds resulting from polyphenol reactions with $FeSO_4$. The bond between the Fe and O atoms indicates that the presence of Fe is formed from the synthesis in accordance with the purpose of the synthesis. But F-O also shows that Fe has oxidized which is closely related to the corrosion process in iron. The high activeness of Fe in ZVI and this spontaneous corrosion process are the main factors that cause ZVI to oxidize very easily [2].

Then the resulting ZVI will be studied the influence of temperature and feeding time on the distribution of particle size. PSA analysis results show that the optimum temperature of ZVI synthesis based on the distribution of particle size at a smaller range value, shown in **Figure 3.**

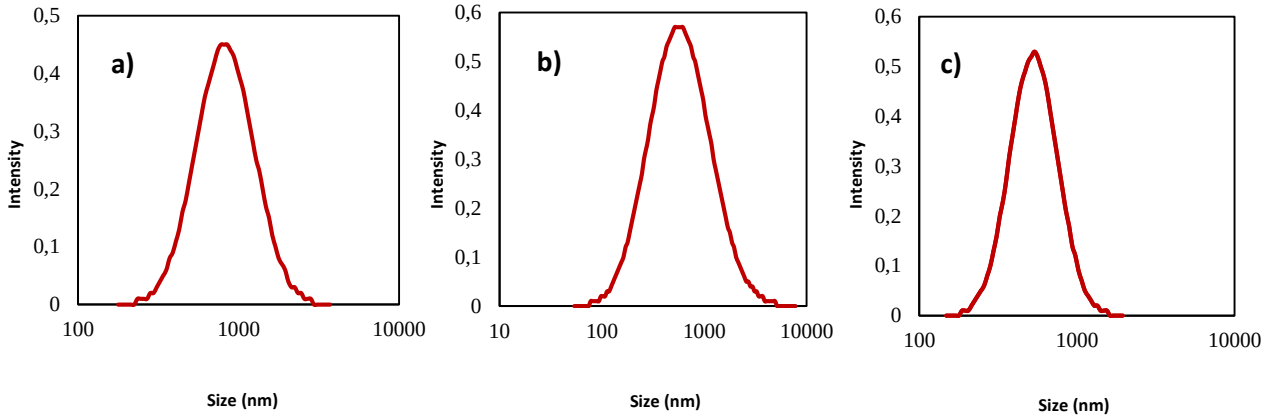


Figure 3. Graph of PSA particle size distribution based on intensity to effect of reaction temperature a) 0 °C; b) 10 °C; c) 25 °C

Based on **Figure 3.** The ZVI particle size distribution at a reaction temperature of 25 °C has a particle size distribution in the range of 150 - 1900 nm which shows a smaller particle size distribution range value compared to the range of particle size distribution values produced at reaction temperatures of 0 °C and 10 °C. The resulting PDI is also smaller than the reaction temperature of 0°C and 10°C. So it can be concluded that the reaction temperature affects the distribution of the resulting particle size. The optimum temperature for ZVI synthesis is 25 °C (room temperature).

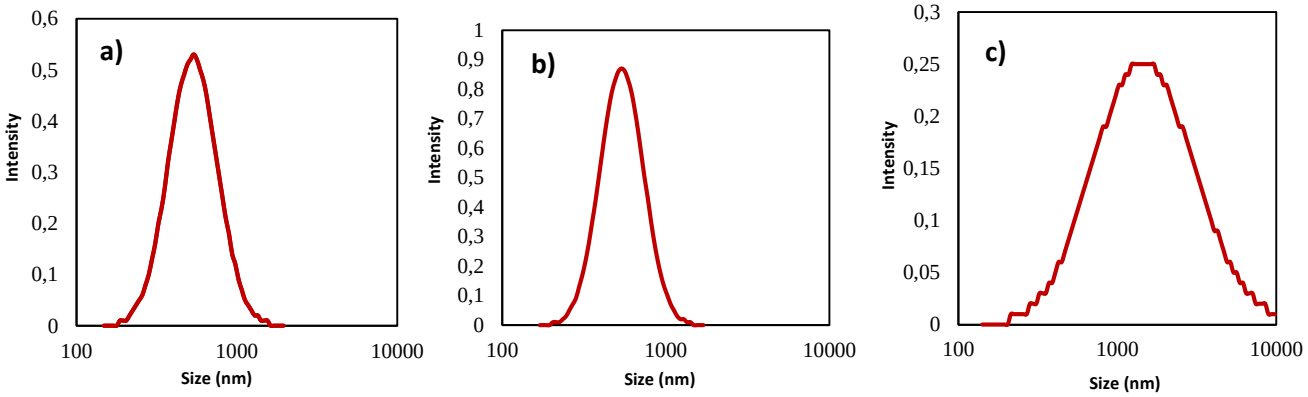


Figure 4. Graph of PSA particle size distribution based on intensity to the effect of feeding time a) 0 minutes; b) 30 minutes; c) 60 minutes

Furthermore, the results of PSA analysis on ZVI which varied feeding time during synthesis, showed the distribution of particle size shown in **Figure 4.** Based on the image it is seen that at feeding time 30 minutes has a distribution of particle size at a much smaller range than the distribution of particle size at feeding time 0 hours and 1 hour. This suggests that nucleation processes are going better, resulting in nuclei that are growing with a relatively more homogeneous size distribution [10]. The resulting PDI value is smaller than the particles synthesized at feeding time of 0 hours and 1 hour. The results showed that the optimum reaction feeding time occurred at a total time of 30 minutes. In addition, the reduction ability factor of polyphenols also plays a role where the ability of strong reducing or causes rapid reactions and forms smaller particles while the ability of weak reducing or causes slow-running reactions and relatively produced larger particles [11].

The next ZVI synthesis is carried out under both optimum conditions, namely a temperature of 25 °C and a

feeding time of 30 minutes. Based on the results of the analysis of surface morphology and its constituent atomic components from SEM-EDX shown in **Figure 5.** This suggests that the resulting ZVI has a diameter of about 1 µm from the entire ZVI particle produced, and that the surface structure is like a collection of small spherical grains of a size that is still very heterogeneous and attached to each other or agglomerated. This can be due to the surface interaction of ZVI particles formed as a resulting reactivation effect [10]. EDX showed that the relative

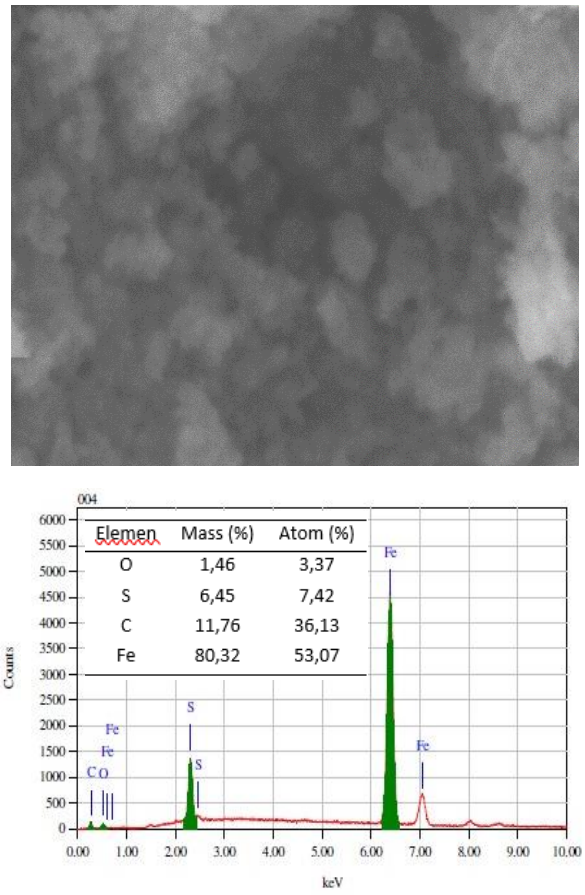


Figure 5. SEM-EDX ZVI characterization results

weight of Fe components contained in the ZVI sample was synthesized by 80.32% with a Fe atom of about 53.07%. This shows that Fe formed from the result of the Fe^{2+} ion reduction reaction from $FeSO_4$ salt is quite a lot. Then there is the O atom with a relative mass of 1.46 and a % of atoms of 3.37%. The large number of O atoms detected indicates that the ZVI formed has oxidized where the corrosion reaction in iron takes place spontaneously and it also shows that the resulting ZVI is highly reactive [12].

XRD crystallography analysis shows that there are several crystal phases of the resulting ZVI, which can be seen in the XDR ZVI difractogram shown in **Figure 6.**

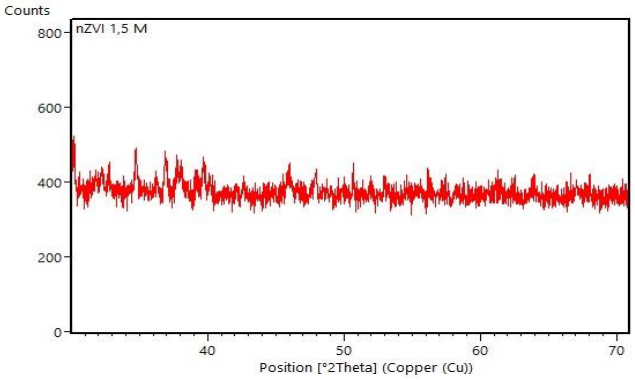


Figure 6. XRD difractogram of ZVI sample

Fitting results show the presence of peaks of Fe and maghemit (FeO) atoms. Based on the position of 2 theta per peak formed, the percentage of Fe and maghemit phases is 3.7% and 96.3%, of all, of 3.7% and 96.3%, of each. The percentage of iron oxide is due to the high activeness of ZVI synthesis so it is very easy to oxidize.

4. Conclusion

It can be concluded that kapok peel extract can be used as reductor agent in ZVI preparation. The data analysis results showed that the ratio of the optimum composition of $FeSO_4$ salts and polyphenols is (4:1). The distribution of particle size indicates that the optimum reaction temperature and optimum feeding time in the reaction process are at a reaction temperature of 25°C and a feeding time of 30 minutes. The ZVI surface structure obtained is shaped like a collection of small spherical grains with a size that is still very heterogeneous and attached to each other or agglomerated. The peaks formed in the XRD spectrum showed a percentage of Fe and maghemit phases of 3.7% and 96.3%, of 3%, and 96.3%, of them, million, in total.

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