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Synthesis of Nanoscale Zero-Valent Iron with Polyphenol Extract from Cloves (*Syzygium aromaticum*) Through a Stepwise Reaction and Adsorption Test on Pb(II)

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Abstract

Polyphenols from clove extract (*Syzygium aromaticum*) were successfully used as reducing agents to synthesize nanoscale zero-valent iron (nZVI). Optimization of nZVI synthesis was carried out by reacting polyphenols and $FeSO_4$ at a composition of 0.25:4.75, 1:4, 2:3, and 3:2. The particle size analyzer showed that the smaller particle size distribution was obtained at nZVI 0.25:4.75, with values of D10 = 85.1 nm, D50 = 122 nm, and D90 = 175 nm. The results of the Pb(II) removal test showed that nZVI 0.25:4.75 had a fairly high percentage of Pb(II) removal, which was 96,4852% at 60 minutes. The smaller particle size of nZVI 0.25:4.75 compared to other samples is an important factor affecting the adsorption activity of Pb(II) in an aqueous medium.

Keywords: nZVI, polyphenols, clove extract, metal Pb(II), adsorption

1. Introduction

Rapid population growth and industrial development causes a lot of toxic waste materials to be dumped into the environment. These waste materials can later pollute the environment in amounts that are difficult to control precisely [1]. In Indonesia, pollutant materials can come from household waste, companies, mining, industry, agriculture, and others. One of the many pollutants that is interesting to study is heavy metals that encourage the emergence of environmental change issues, especially related to environmental pollution by toxic heavy metals [2]. The concentration level of heavy metals is divided according to the level of pollution, such heavy pollution, moderate pollution, and not polluted [3]. One of the heavy metals that can pollute the environment is lead (Pb) [4] that generally comes from motor vehicles emission, tin mines, plastic factories, paint factories, and printing. The presence of Pb in water needs special attention because this metal can adversely affect organisms in the water and accumulates in the food chain. If food contaminated with Pb is consumed by humans, it can cause hypertension [5], anemia [6], infertility [7], damage to the central nervous system [8] and impaired kidney function [9].

In previous studies, several methods have been used to reduce the concentration of metal contaminants in waste-water, including precipitation [10], ion exchange [11], filtration [12], and adsorption [13]. Adsorption is the most widely used method because it is economical and simple. In adsorption, one of the most important factor is the adsorbent. In recent years, the use of zero-valence iron (nZVI) nanoparticles adsorbent to remove various contaminants in water has been great interest to study [14–16].

nZVI is obtained by reducing trivalent iron with the reducing agent $NaBH_4$. However, the synthesis of nZVI using $NaBH_4$ leaves byproducts of toxic boric acid and explosive H_2 gas. In addition, synthesis using this method tends to cause particles to corrode due to the washing process [17]. To obtain nZVI with lower production costs and be environmentally friendly, a synthesis method for nZVI was developed by reducing Fe^{2+} to Fe^0 using a polyphenol reductant. Currently, nZVI synthesis is carried out using polyphenols derived from extracts of green tea and eucalyptus leaf, lemon, grapes, and sorghum. The advantages of nZVI synthesis using polyphenols are that it does not produce toxic by-products, lower production costs, and polyphenols do not need to be washed from nZVI so that the particles are not oxidizing by air [18].

In addition to the materials previously mentioned, clove is one of the plants that produces phenolic compounds such as flavonoids, hydroxybenzoic acid, hydroxycinamic acid and hydroxyphenyl propens. Eugenol is the main bioactive compound in clove, with a concentration of 9381.70 to 14650.00 mg per 100 g of fresh plant material [19]. In addition, gallic acid is also found in a higher concentration (783.50 mg/100 g fresh weight). Apart from that, another phenolic acids found in cloves are caffeic, elagic, ferulic, and salicylic acids. Flavonoids such as kaempferol, quercetin and their derivatives (glycosylation) are also found in cloves in lower concentrations [20]. So it is estimated that clove extract can be used to synthesize nZVI. Therefore, in this study, nZVI will be synthesized with polyphenol extract from cloves (*Syzygium aromaticum*) through a stepwise reaction and adsorption test for Pb(II).

2. Materials and Method

2.1 Materials

The materials used in this study were $FeSO_4.7H_2O$, clove plant of Zanzibar variety (from Sinjai Regency, South Sulawesi), distilled water, concentrated HCl, 1,10-ortho phenanthroline, $Pb(NO_3)_2$, and concentrated HNO_3.

2.2 Extraction of polyphenols from cloves stems

The dry clove stems were washed and baked in an oven at 50 °C for 5 hours. 20 g of the dried sample was boiled in 250 mL of distilled water and stirred at 300 rpm for 120 minutes at a temperature of 40 °C to 50 °C. After that, the mixture was filtered with Whatman paper number 42.

2.3 Synthesis of nanoscale zero valent iron (nZVI)

The synthesis of nZVI was carried out by mixing polyphenols into 0.1 M $FeSO_4$ solution with the compositions of 0.25:4.75, 1:4, 2:3, and 3:2 mL. The mixing process was carried out by dripping polyphenols into the Fe solution using a calibrated pipette (1 mL polyphenol equal to 40 drops). Then, the solution was stirred for an hour at 250 rpm and stored in a glass bottle.

2.3 Characterization of nZVI

Polyphenol extracts from cloves were characterized using a fourier transform infrared spectroscope (FTIR) to determine organic functional groups. Meanwhile, the synthesized nZVI suspensions with various compositions were characterized by UV-Vis to determine the most optimum iron content (in volume), which can react with polyphenols to form nZVI. Before being tested with UV-Vis, nZVI was pre-complexed with 1,10-ortho-phenanthroline until form an stable orange-red color. In addition, particle size analyzer (PSA) is used to determine the size distribution of the nZVI particles formed.

2.4 Test of nZVI adsorption activity on Pb(II)

The adsorption process was carried out by mixing $Pb(NO_3)_2$ with nZVI, then stirred at 150 rpm for 10, 30, 60, 120, and 180 minutes. After the adsorption process is complete, the adsorbent that has absorbed ions from the feed solution is separated with the help of the Whatman paper, then the filtrate is taken and the remaining Pb^{2+} ion content is analyzed using atomic absorption spectroscopy (AAS).

3. Results and Discussion

3.1 Extraction of polyphenols from cloves

The FTIR spectra of clove extract are shown in Fig. 1. The band at 3676.02 cm^{-1} , would be due to the vibration of O-H (phenolic) group. Strong bands at 3109.25 cm^{-1} would be related to an aromatic ring. Band at 1710.86 cm^{-1} indicated C=O (carbonyl) group. Band at 1516.05 cm^{-1} would be related to stretching aromatic ring C=C bond. Band at 1371.39 cm^{-1} would be related to C-H bond. Strong band at 1604.77 cm^{-1} assigned alkene C=C bond. Band at 1257.59 cm^{-1} related to C-O group (ether). While the sharp peak at 1067 cm^{-1} represents C-O [21]. The presence of functional groups in the FTIR spectrum would be suspected to represent the presence of eugenol compounds in the sample. Eugenol compounds have the molecular formula $C_{10}H_{12}O_2$, which contains several functional groups, such as allyl ($-CH_2-CH=CH_2$), phenol (-OH), and methoxy ($-OCH_3$). In the spectrum, not all of the resulting bands indicate the presence of eugenol. The band at 1710.86 cm^{-1} is a C=O (carbonyl) group, whereas in the eugenol compound there is no carbonyl group. This indicates the presence of other phenolic compounds or eugenol derivatives contained in the extract clove.

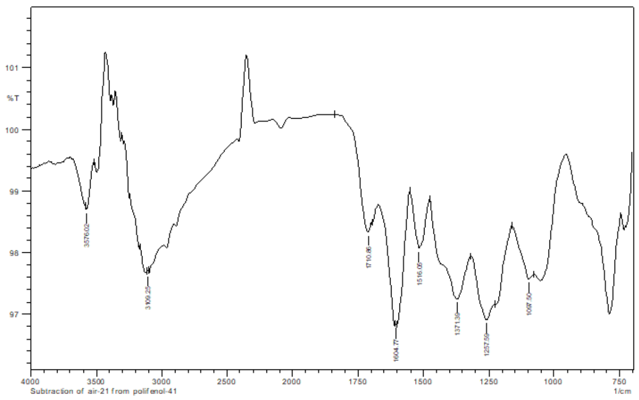

Figure 1. FTIR spectra of clove extract.

3.2 Polyphenols of extract clove and $FeSO_4$ composition optimization in nZVI synthesis

Based on the UV-Vis results, the maximum wavelength obtained is 509 nm with an absorbance value of 1.09. The results obtained are similar to the reference which states that the iron complex has a maximum absorption value at a wavelength of 510 nm [22]. Furthermore, the four nZVI solutions were measured for their absorbance values. The comparison curve between clove extract (mL) and reactant Fe (ppm) is shown in Fig. 2.

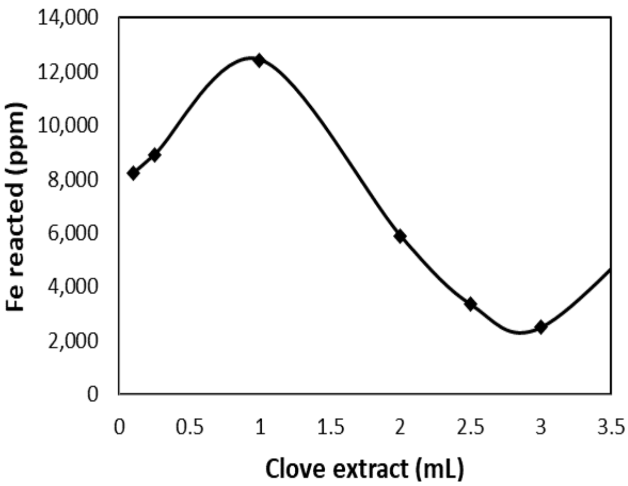

Figure 2. Volume comparison curve of clove extract with concentration of reactant Fe.

The curve states the optimum concentration of reactant Fe occurs at a volume ratio of 1:4. Characterization using PSA to determine the particle size distribution produces data as shown in Table 1. From these data it can be seen that nZVI 0.25:4.75 has the smallest particle size among the other compositions, with D10 = 85.1 nm, D50 = 122 nm, and D90 = 175 nm. The above results show that the synthesized iron particles are on the nanometer scale so that they can be called nanoscale zero valent iron (nZVI). According to the reference, to obtain nanoparticles of uniform size, nuclei formation must be carried out at the same time, so that the nuclei will have the same state. From these results, it was concluded that the synthesis of nZVI through a stepwise reaction resulted in an inhomogeneous particle size.

Table 1. Size distribution of nZVI on variation in composition.

D %	Composition of clove extract : Fe (mL)			
	0.25:4.75	1:4	2:3	3:2
D10	85.1 nm	124 nm	155 nm	124 nm
D50	122 nm	170 nm	269 nm	291 nm
D90	175 nm	250 nm	426 nm	624 nm

3.3 Adsorption test on Pb(II)

The Pb(II) adsorption process used two ratios of clove extract : Fe in the nZVI synthesis, namely 0.25:4.75 and 1:4. The selection of this composition was based on the results obtained previously, in which the clove extract : Fe ratio 0.25:4.75 resulted in the smallest particle size and the 1:4 composition resulted in the optimum level of reacted Fe. The AAS test results in Fig. 3 show the comparison of the percentage removal of Pb from the two nZVIs.

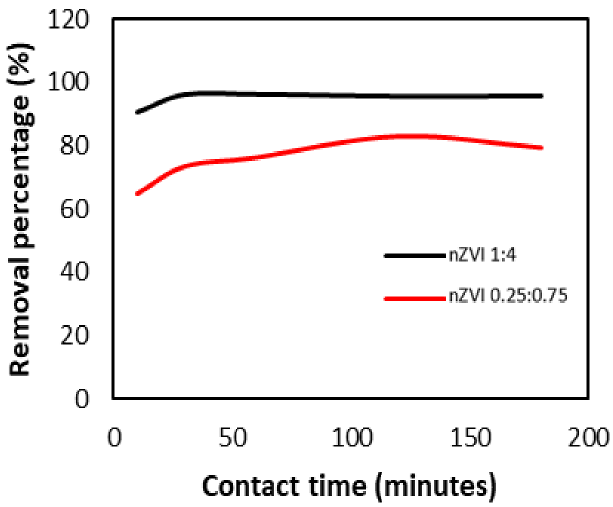

Figure 3. Graph of nZVI removal percentage in comparison of clove extract:Fe 1:4 and 0.25:4.75.

The data above indicates that nZVI has a fairly high percentage of removal. This suggests that nZVI from polyphenolic extracts can act as an adsorbent in the Pb(II) adsorption process. The optimum contact time for nZVI at composition 1:4 occurred at 120 minutes, which was 82.57%, while the optimum contact time at composition 0.25:4.75 occurred at 60 minutes with a percentage removal value of 96.49%. It is clear that the percentage value of Pb(II) removal using nZVI at a composition of 0.25:4.75 is greater than when using nZVI at a composition of 1:4. In addition, after being tested for 180 minutes, nZVI 0.25:0.75 still has a relatively constant adsorption activity, while nZVI 1:4 has decreased adsorption activity. This is because at nZVI 0.25:4.75 the particle size is smaller, so the particle surface area is larger. This larger surface area is responsible for the more maximal Pb(II) reduction. The small particle size leads to increased reactivity and large surface area per unit mass, making it useful in the remediation of harmful contaminants [23–25].

4. Conclusion

Clove extract was successfully used as a reducing agent in the synthesis of nZVI. The optimum reacted Fe content was produced at nZVI 1:4, while the smallest particle size distribution was produced at nZVI 0.25:4.75. The results Pb(II) removal test showed that nZVI 0.25:4.75 had a better removal ability than nZVI 1:4. The optimum reaction time required for Pb(II) adsorption by nZVI 0.25:4.75 is 60 minutes with a removal percentage of 96.4852%. The smaller particle size of nZVI 0.25:4.75 is an important factor affecting the effectiveness of its adsorption on Pb(II) metal in an aqueous medium.

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