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Green preparation of nanoscale zero-valent iron using clove extracts as adsorbent for lead removal

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Abstract. This paper reports our studies on the synthesis of nanoscale zero-valent iron (nZVI) for lead ions (Pb(II)) adsorbent. The nZVI was prepared using clove (*Syzygium aromaticum*) extracts as an environmentally-friendly reducing agent. Fourier transform infra-red spectroscopy (FTIR) studies indicate that eugenol is the main fraction found in the extracts used in this work. Dynamic light scattering (DLS) measurements show that relatively small particles with narrow size distribution were obtained by dropping the reducing agent gradually into the iron sulphate solution. The batch experiments showed that the as-prepared nZVI exhibits very high removal efficiency of Pb(II). The optimum adsorption time was reached differently for the adsorbent with different size distribution. The highest value is 96%, which was achieved at the adsorption time of 30 minutes by using CT-nZVI.

1. Introduction

Lead has been known as one of the heavy metals utilised in various applications, such as batteries, coatings, and photographic materials, and in the automotive, aviation, steel, and paint industries. As an example, in the later application, lead is commonly used in the form of PbCO_3 and Pb(OH)_2 to speed up the paint drying process, protect corrosion-coated surfaces and extend the paint life from damage [1,2]. However, the widespread use of lead has caused environmental problems along with increasing the levels of these harmful metal pollutants in aquatic environments [3,4]. This condition is hazardous for the ecosystem and human health. The accumulation of lead in the human body can cause hypertension [5], anaemia [6], infertility [7], central nervous system damage [8] and impaired renal function [6,9]. Several studies have been conducted as an effort to remediate lead-polluted water. The studies that have been undertaken include using zeolite compounds, such as chabazite and clinoptilolite [10]. Other remediation efforts are reported using a permeable reactive barrier (PRB) stabilised with apatite [11,12]. However, these methods require a high cost to remediate water over a large area. To reduce costs, we can use activated carbon as an adsorbent [13], but activated carbon is not suitable for groundwater remediation.

Over the past few years, nZVI has been developed as one of the promising materials for overcoming various types of pollutants in aquatic environments, one of which is heavy-metal ions. Previous studies have proven that nZVI may remediate water from inorganic contaminants, such as Pb(II), As(III), As(V), [3,14] and Cr (VI) [15–17]. Remediation of metal ions using nZVI is a chemisorption process. In this process, the positively charged metal ions will be adsorbed on the nZVI surface, which tends to release electrons. After the adsorption process occurs, the metal ions, which were initially dissolved in water, will be reduced by nZVI and precipitated, whereas nZVI will be oxidized to FeOOH and also precipitated [4]. In this case, nZVI can precipitate lead through redox reactions because Fe(II) has a



more negative standard reduction potential value compared to Pb(II). The standard reduction value shows the tendency of the element to be reduced, and the higher the standard reduction potential value of an element, the easier it is to be reduced.

For this reason, various synthesis methods have been investigated to fabricate nZVI as an adsorbent. Generally, nZVI can be synthesised in either top-down or bottom-up techniques. In the top-down method, nZVI is obtained mechanically by breaking larger iron particles into nanoscale iron particles using mechanical milling [18]. In the bottom-up method, nZVI is usually obtained through the wet chemistry pathway by reducing divalent iron (Fe^{2+}) or trivalent iron (Fe^{3+}) with the NaBH_4 as a reducing agent [19,20]. With this technique, the nZVI particle size is more comfortably to be controlled through reaction conditions and additive additions. However, NaBH_4 is a harmful chemical because it is toxic, corrosive and flammable. Plant extracts, such as green tea, an alternative and environmentally-friendly natural reducing agent, can be used as a substitute for NaBH_4 [21,22]. Utilization of plant extracts as reducers is based on their polyphenol content, which is believed to reduce iron ions to zero-valent iron (Fe^0). So, the high polyphenol content is expected to increase the productivity of the nZVI synthesis process. In Indonesia, one local plant largely available with a high content of polyphenol is the clove flower (*Syzygium Aromaticum*). In this study, clove extract was used as a reducing agent in a green synthesis approach of nZVI. Based on batch experiments, the obtained nZVI was found to have high Pb(II) removal efficiency.

2. Experimental Methods

The cloves sample was cut into small cuboid-sizes measuring $\pm 2.5 \times 2.5$ cm. The clove pieces were rinsed several times by using tap water and then distilled water. Subsequently, the clove pieces were dried in an oven at 500°C for five hours. Two grams of the dried sample was boiled in 25 mL of distilled water and stirred for 120 min at a temperature of $\pm 45^\circ\text{C}$ to inactivate the enzyme polyphenol oxidase. The filtrate was then filtered using Whatman paper number 42 to obtain a clear extract, and the extracts obtained were analysed using FTIR. The nZVI synthesis was performed by reacting the cloves extract (PP) with a 0.1 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution in a 0.01 M HCl solvent. The reaction was carried out with a PP:Fe volume ratio of 1:4. The clove extract was added either directly at the start of the reaction to obtain a C-nZVI sample or gradually over an hour of reaction time to produce a CT-nZVI. During the reaction, the mixture was stirred at 250 rpm for one hour. The resulting black powder was then characterised using an X-ray diffractometer (XRD).

To investigate the Pb(II) removal efficiency, we tested the adsorption performance of nZVI using the batch method. The batch experiment was conducted using a 200 ppm $\text{Pb}(\text{NO}_3)_2$ solution. The adsorption process was performed by adding 5 ml of the dispersed nZVI into 25 ml of the Pb(II) solution and using a shaker at 150 rpm with contact times of 10, 30, 60, 120 and 180 minutes. After the adsorption process was completed, the filtrate was separated from the adsorbent and was measured using an atomic absorption spectrometer (AAS) to determine the remaining Pb(II) ion content.

3. Results and Discussion

Figure 1 shows FTIR spectrum from the clove extracts. The polyphenol was indicated by a number of peaks observed at wavenumbers of 3576, 3108, 1604, 1516, 1257 cm^{-1} . The stretching peak of the phenolic functional group was observed at 3576 cm^{-1} . The stretching peak from the C-H bond on the aromatic ring appeared at 3108 cm^{-1} . C=C bonding in the alkene and aromatic ring appeared as sharp peaks at 1604 and 1516 cm^{-1} , respectively. The presence of C-O (ether) in the functional group was observed from the peak at 1257 cm^{-1} . In addition, there was a peak at 1097 cm^{-1} indicating a =C-H bond from the alkene. The adsorption peaks lead to the presence of eugenol content in clove extracts [23,24]. In addition to these peaks, at the wave number of 1710 cm^{-1} , there was a peak derived from the carbonyl group (C=O), whereas the eugenol structure has no carbonyl group. This peak indicates the presence of other secondary metabolites of the polyphenols contained in the clove extracts. The substance is thought to be tannin and acetyl eugenol that has a molecular structure in the presence of the carbonyl group since

both structures are reported as the second most massive secondary metabolite substances other than eugenols in the clove extracts [24,25].

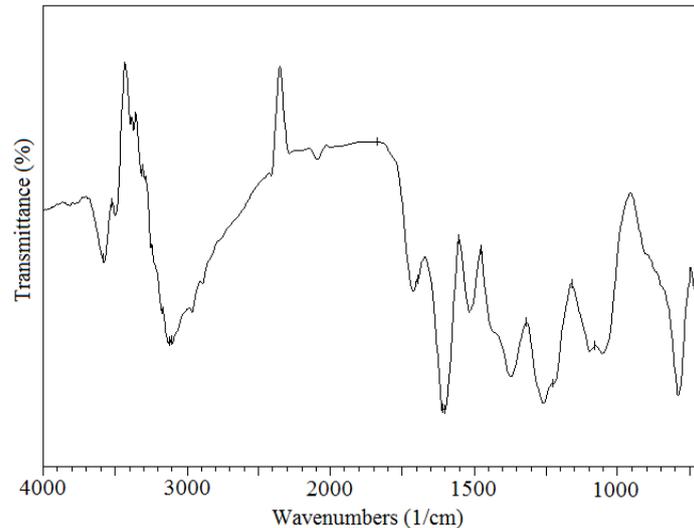


Figure 1. FTIR spectrum of the clove extract

Figure 2 shows a diffraction pattern of CT-nZVI synthesised with the clove extracts. The formation of Fe^0 is indicated by a sharp diffraction peak at 2θ 44.89° correspond to (110) plane of Fe. This result is confirmed by the XRD pattern database PDF card number 00-006-0696. Other diffraction peaks are derived from iron oxide, such as Fe_2O_3 and Fe_3O_4 , which generally grown on the surface of the nZVI particles. The very high peak intensity at 2θ 44.89° compared to other diffraction peaks indicated that Fe^0 exists as a main phase in the prepared nZVI. The formation of Fe^0 using plant extracts is believed to be the role of the polyphenol contained therein. The results of the nZVI particle size distribution measurements performed using the dynamic light scattering PSA is shown on the form of the histogram in Figure 3. The histogram indicates that the synthesised nZVI are polydisperse. From the figures, it is seen that CT-nZVI has a narrower size distribution with Dv10, Dv 50 and Dv90 values of 170 nm, 147 nm and 422 nm, respectively, compared to C-nZVI with Dv10, Dv 50 and Dv90 values of 113 nm, 170 nm and 250 nm, respectively.

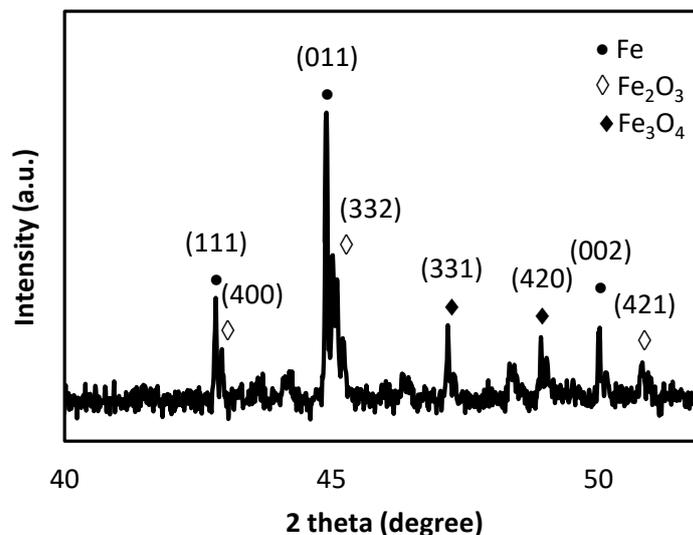


Figure 2. The diffraction pattern of the synthesised nZVI

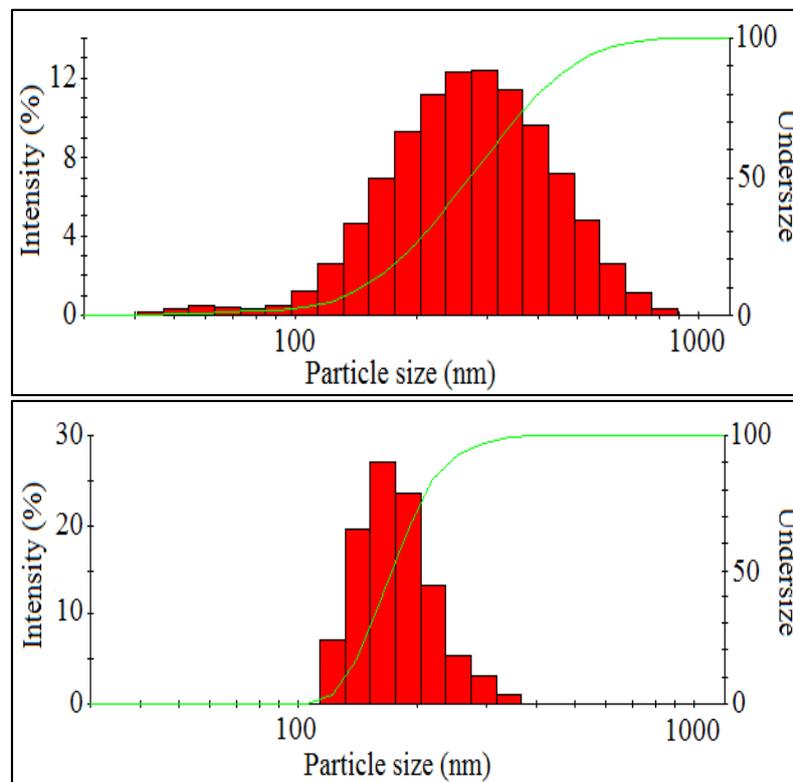


Figure 3. Particles size distribution of C-nZVI (a) and CT-nZVI (b).

The adsorption ability of nZVI for Pb(II) removal was investigated using batch adsorption experiments. The removal efficiency (R) of Pb(II) was calculated using the following equation [14],

$$R = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \quad (1)$$

where C_0 is the initial concentration and C_t is the final concentration of Pb(II) in the aqueous solution. Figure 4 shows the effect of adsorption time on the removal of Pb(II) by both C-nZVI and CT-nZVI. It is seen that the removal efficiency value of CT-nZVI is higher than that of C-nZVI at all adsorption time tested. The smaller particles size with the narrower size distribution of CT-nZVI could be a convincing reason for this fact since small particles have a high surface area of the adsorbent. In Figure 4, we could also notice the changes in the removal percentage of lead, as an effect of the adsorption time for C-nZVI and CT-nZVI, are dissimilar. For C-nZVI adsorbent, the percentage of removal increases with the increase of adsorption time from 63% at 10 minutes to 86% at 120 minutes. In this case, the rise of the contact period should give enough time for the adsorbent to capture the lead ions. However, at the longer adsorption time (180 minutes), the percentage removal is found to decrease to 79%. This result indicates dissolution of a small number of the adsorbed lead occurred. In the case of CT-nZVI, the increase of the removal percentage values only takes place until the adsorption time of 30 minutes has passed, at which time the removal percentage reaches 96%. The value was then found to steady at longer adsorption times. We can assume that the adsorbent has been saturated at 30 minutes of the contact time, which indicates that the lead adsorption occurred more rapidly than that of C-nZVI. The lead adsorption takes place through the chemisorption process, in which the ions adsorbed on the surface of nZVI that donated electron to reduce the lead ion [4] having more positive reduction potential ($E^\circ = -0,13$ V) compared to iron ion ($E^\circ = -0,44$ V). Therefore, the rapid adsorption processes by CT-nZVI should be attributed to the fine particle of the adsorbent, which provided a larger adsorption site [12,24] than that of C-nZVI.

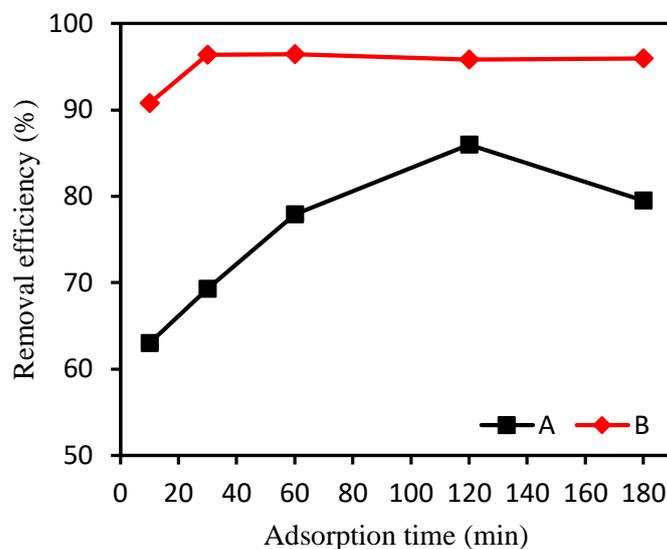


Figure 4. The removal efficiency of lead for C-nZVI and CT-nZVI at different adsorption times.

4. Conclusion

The use of clove extracts as a green reducer agent for the preparation of nZVI was investigated. Narrow size distribution of the small particles of nZVI was obtained by dropping the extracts into the iron sulphate solution rather than adding it all at once. The as-prepared nZVI demonstrated its ability to adsorb Pb(II) from the aqueous solution. The removal efficiency of Pb(II) depended on the adsorption time and adsorbent particles size distribution. In this work, by using CT-nZVI, the highest removal efficiency values with a relatively short adsorption time was achieved. The smaller particles size of CT-nZVI that should have a large surface area is a critical factor in increasing the adsorbent capacity and also speeding up the adsorption process.

5. Acknowledgement

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6. References

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