

Synthesis of Lignin-Modified Nanoscale Zerovalent Iron Applied to Arsenic RemovalPhoomipat Jungcharoen¹, Denis O' Carroll², Jin Anotai^{3*}, Tanapon Phenrat^{4*}¹*Chulalongkorn University, Bangkok, Thailand*²*The University of New South Wales, Kensington, Sydney, Australia*³*King Mongkut's University of Technology Thonburi, Thailand*⁴*Naresuan University, Phitsanulok, Thailand***Abstract**

Nanoscale zerovalent iron (NZVI) plays a significant role on environmental remediation including removal of arsenic from groundwater and drinking water. This study investigates the synthesis and characterization of nZVI derived from lignin containing wastewater from paper and pulp industry. The two resulting nZVI types including lignin-modified nZVI (L-nZVI) and pulp-modified nZVI (P-nZVI), were then used for arsenic removal by comparing with and bare-nZVI (B-nZVI). We found the modified nanoparticles were characterized using TEM, SEM-EDX, and BET. The specific surface areas of P-nZVI (49.3602 m²/g) was much greater than L-nZVI (7.6126m²/g) presumably due to a lot of polymers. B-nZVI, L-nZVI, and P-nZVI could remove 1 mg/L of arsenic with the removal efficiency of 88.79, 88.66 %, and 90.79%, respectively at an initial pH of 7. The enhanced arsenic removal efficiency by P-nZVI was attributed to the highest specific surface area.

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Keywords— Lignin, Pulp and Paper Wastewater, Nanoscale Zerovalent Iron (nZVI), Drinking Water, Arsenic

Introduction

Arsenic is one of the toxic elements in environment [10]. It may be released from both natural and anthropogenic sources. The effect of arsenic on human health and drinking water contamination as well as groundwater contamination has become a global environmental issue. Approaches for arsenic removal from drinking water are adsorption [8], coagulation [9], ion exchange [1], and biological process [4]. Recently researchers have focused on nano zerovalent iron (or nZVI) for rapid removal of arsenic in groundwater.

nZVI gains more and more attention from researchers and practitioners recently due to its highly reactivity, cost effectiveness, and potential to treat a various range of contaminants [7]. Due to its small size, the proportion of atoms at the surface increases significantly compared to bulk or micron-sized particles. nZVI has also been used to remediate metals or metalloid contaminants such as arsenic in groundwater [3, 6]. However, nZVI has weaknesses consisting of a lack of stability and limited mobility in subsurface due to particle agglomeration. In [2] Cirtiu et al. (2011) demonstrated that polymers or polyelectrolytes which are carboxymethylcellulose(CMC), polystyrenesulfonate (PSS), polyacrylamide (PAM),and polyacrylic acid (PAA) can increase nZVI colloidal stability in the water and enhance nZVI mobility in porous media. The functional groups in these polymers provide steric repulsions which decrease nZVI agglomeration.

Pulp and paper wastewater is highly polluted because of enormous quantity of lignin compounds. The presence of lignin in the wastewater contributes to strong color and high COD. Additionally, lignin compounds are macromolecules which theoretically should enhance nZVI dispersion stability and mobility in subsurface. Therefore, this study focuses on nZVI to removal lignin compounds from pulp and paper wastewater to obtain lignin-modified nZVI as a by-product of pulp and paper wastewater treatment. Two kinds of lignin containing wastewater were used in this study. First, synthetic lignin contaminated water was used to obtain lignin-modified nZVI (L-nZVI). Secondary, real pulp and paper wastewater was used to obtain pulp-modified nZVI (P-nZVI). Then, this study compared the efficiency of arsenic removal both bare nZVI, L-nZVI, and P-nZVI. Particle characterizations were performed and mechanistic explanation for enhanced arsenic removal using P-nZVI was proposed.

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Methodology

Materials

All chemicals including $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, NaBH_4 , NaOH , HCl , and HNO_3 were reagent grade and obtained from Ajax Company, Australia. Alkali lignin (Sigma-Aldrich) NaAsO_2 (Merck Company). Pulp wastewater (untreated) was obtained from SCG-PAPER, Wangsala, Thailand.

Synthesis of bare and modified- nZVI

All nZVI formulas were synthesized using the borohydride method. Addition of 0.1 M FeSO_4 into 500 mL of DI water (Bare- nZVI), 1 g/L Lignin (L-nZVI), and pulp wastewater (P-nZVI) was stirred for 30 seconds by dropwise addition of 0.1 M NaBH_4 aqueous solution with peristatic pump. After an addition of NaBH_4 solution, the mixture was stirred for an additional 20 minutes. Then, various forms of nZVI were separated by a small magnet.

Batch Experiments for Arsenic Removal

Arsenic removal was carried out using polypropylene bottle 1 L containing 400 mL of 1 mg/L of total arsenic solution at room temperature. Arsenic solutions were prepared by dilution of 0.05 M NaAsO_2 at initial of pH 7⁺ 0.06 immediately before use.

This study compared arsenic removal efficiency of Bare nZVI, L-nZVI, and P-nZVI. In each set of experiments, 0.4 g freshly prepared nZVI was added to each bottle containing 400 mL of 1 mg/L total arsenic solution and covering bottle with aluminum foil and rotated end over end in rotator at 30 rpm for 2.5, 5, 15, 30, and 60 min. For 2.5 minutes was sonicated by ultrasonicator at 20 kHz. And then the samples were collected by small magnet and measured ORP and pH immediately. All samples were analyzed for arsenic concentration using graphite atomic absorption spectrometer. All experiments were achieved at least by duplicated.

Characterization of nZVI

The morphological and surface characteristics of Bare nZVI, L-nZVI, and P-nZVI were investigated by transmission electron microscopy (TEM) and scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDX). The specific surface area of L-nZVI and P-nZVI was measured by BET analysis.

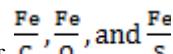
Results and Discussion

Characterization of nZVI

Figure 1. illustrates TEM images of nZVI particles in scale 20 nm at 360 kX magnification. Bare nZVI particles are amorphous particle with Fe core and outer shell namely iron hydroxides. These particles are spherical particles ranging diameters from 34 to 57 nm. The morphology of Bare nZVI was similar to another study [12]. On the other hand, the morphologies of L-nZVI and P-nZVI were altered by polymer coating.

Figure 2. illustrates SEM images of L-nZVI and P-nZVI. The surface of L-nZVI was neat and slim, whereas that of P-nZVI was rough.

Energy Dispersive X-ray analysis revealed peaks of Fe, O, C, and S in Figure 3. The elemental components between L-nZVI and P-nZVI were similar, whereas P-nZVI showed other components including Si and Cl. These components may be from bleaching of pulp wastewater such as Na_2SiO_3 .



The ratios of components were investigated by EDX and composed of $\frac{\text{Fe}}{\text{C}}$, $\frac{\text{Fe}}{\text{O}}$, and $\frac{\text{Fe}}{\text{S}}$ shown in Table 1 and Figure 4. The results demonstrated that organic compounds are the source of carbon and oxygen originates from carbon dioxide and hydrocarbon in the air and water. However, sulphide from ferrous sulfate is lower than other compounds. Obviously, the proportion of these chemical is almost similar to iron particles.

Figure 5. demonstrates the specific surface area of P-nZVI quantified by BET was $49.36 \text{ m}^2/\text{g}$, which is greater than L-nZVI that was $7.61 \text{ m}^2/\text{g}$. Pulp wastewater has a lot of polymers including lignin and starch, while alkali lignin consists of lignin only. Moreover, suspended solids of pulp wastewater and pure alkali lignin were 111 mg/L, and 0 mg/L, respectively. The sorption of hetero-macromolecules could lead to the greater specific surface area of P-nZVI in comparison to L-nZVI. Consequently, P-nZVI can enhance arsenic removal more than that of L-nZVI.

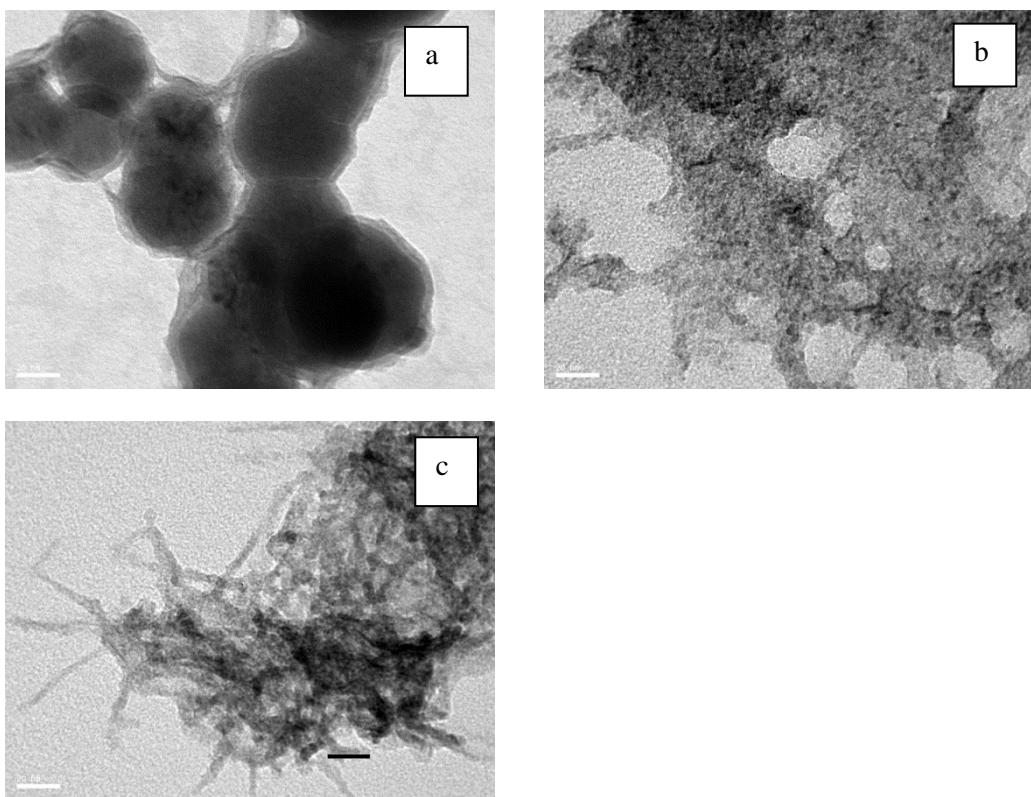


Figure 1: Representative TEM images of (a) B-nZVI, (b) L-nZVI, and (c) P-nZVI

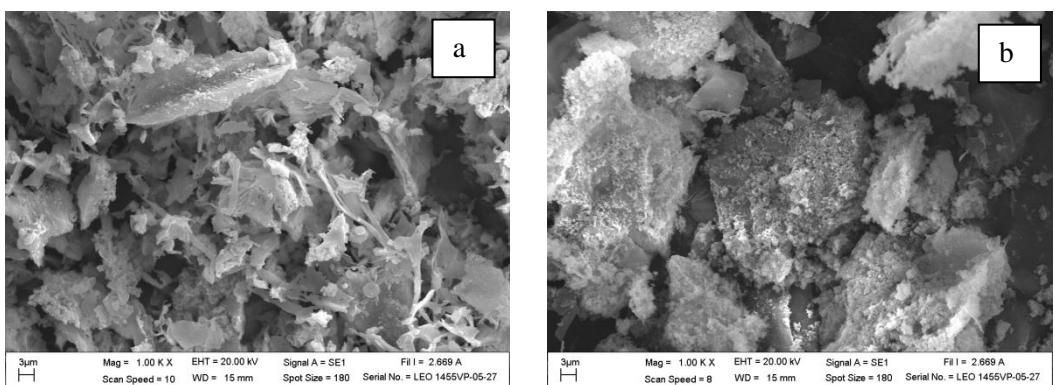


Figure 2: SEM images of (a) L-nZVI, and (b) P-nZVI.

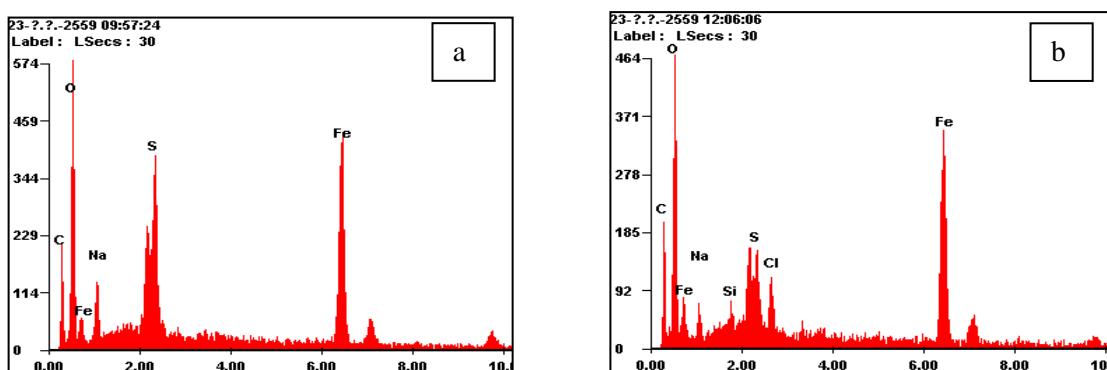


Figure 3: EDX analyses of (a) L-nZVI, and (b) P-nZVI.

Table 1:
Effect of L-nZVI and P-nZVI on Atomic Percentage Ratios by EDX

Ratios of component	At%	
	L-nZVI	P-nZVI
Fe/C	0.218457	0.208676
Fe/O	0.309574	0.290831
Fe/S	2.329545	5.342105

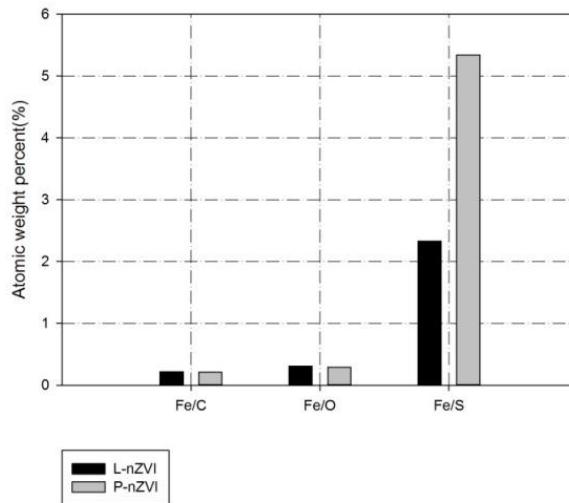


Figure 4: Effect of L-nZVI and P-nZVI on atomic percentage ratios

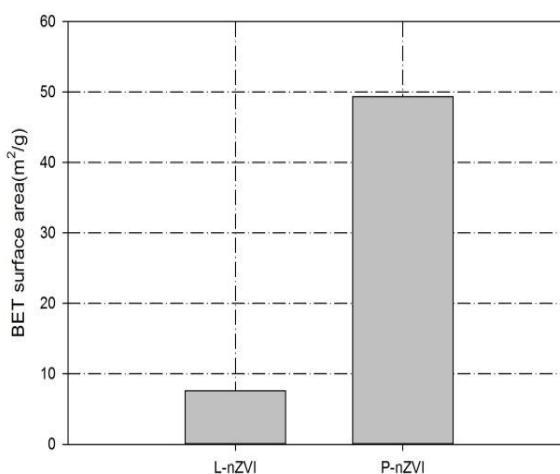


Figure 5: Effect of L-nZVI and P-nZVI on specific surface area.

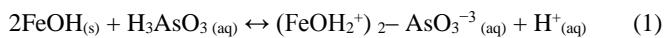
Effect of various forms nZVI on pH, ORP, and arsenic removal

Figure 6 (a), (b) and (c). illustrate the effect of Bare nZVI, L-nZVL, and P-nZVI on pH, ORP as well as arsenic removal of the sample having initial arsenic concentration of 1 mg/L, pH of 7 ± 0.06 , and ORP values of 143.5 ± 47.38 .

Figure 6 (a) and (b) reveal the decrease of pH and the increase of ORP respectively, for all nZVI evaluated in this study. This trend agrees with the slow depletion of the nZVI similar to results reported previously [5]. As can be seen in Equation. 1, ferric oxide reacts with arsenite species that generated proton, decreasing the pH of the system.

In almost all of Bare nZVI, L-nZVI and P-nZVI the pH values decreased essentially from 7 to 5.49, 4.82, and 4.62, respectively. However, with increasing time, ORP values of Bare nZVI, L-nZVI and P-nZVI were escalated similarly and approximately from 144 to 69, 213, and 192.5 respectively.

Arsenic removal by ZVI involves formation of Fe(II) and Fe(III) corrosion products on the surface of iron owing to oxidation. The various corrosion products are a mixture of amorphous Fe (III) hydroxide or oxide, maghemite and magnetite. These products are capable of As (III) and As (V) sorption by surface complexation [13]. According to pH and ORP, the predominant arsenic species in all nZVI reactors should be H_3AsO_3 . Thus, arsenic removal mechanism is the inner-sphere and outer -sphere complexation between ferric hydroxide surface and arsenite species as suggested by [11], and also shows in Equation (1) and (2) and (3), respectively.



As can be seen in Figure 6 (c), total arsenic removal efficiency by B-nZVI, L-nZVI, and P-nZVI were 88.79, 88.66, and 90.79%, respectively within 5 minutes. Interestingly, when time increased to 60 min, the arsenic removal efficiency decreased to 82.07, 1.15, and 65.87% for Bare nZVI, L-nZVI, and P-nZVI respectively. This finding suggests that the solution chemistry of the batch experiment might change because the experiment was opened to the atmosphere. Consequently, dissolved oxygen may increase and oxidize nZVI particle resulting in the decrease of arsenic removal efficiency using nZVI.

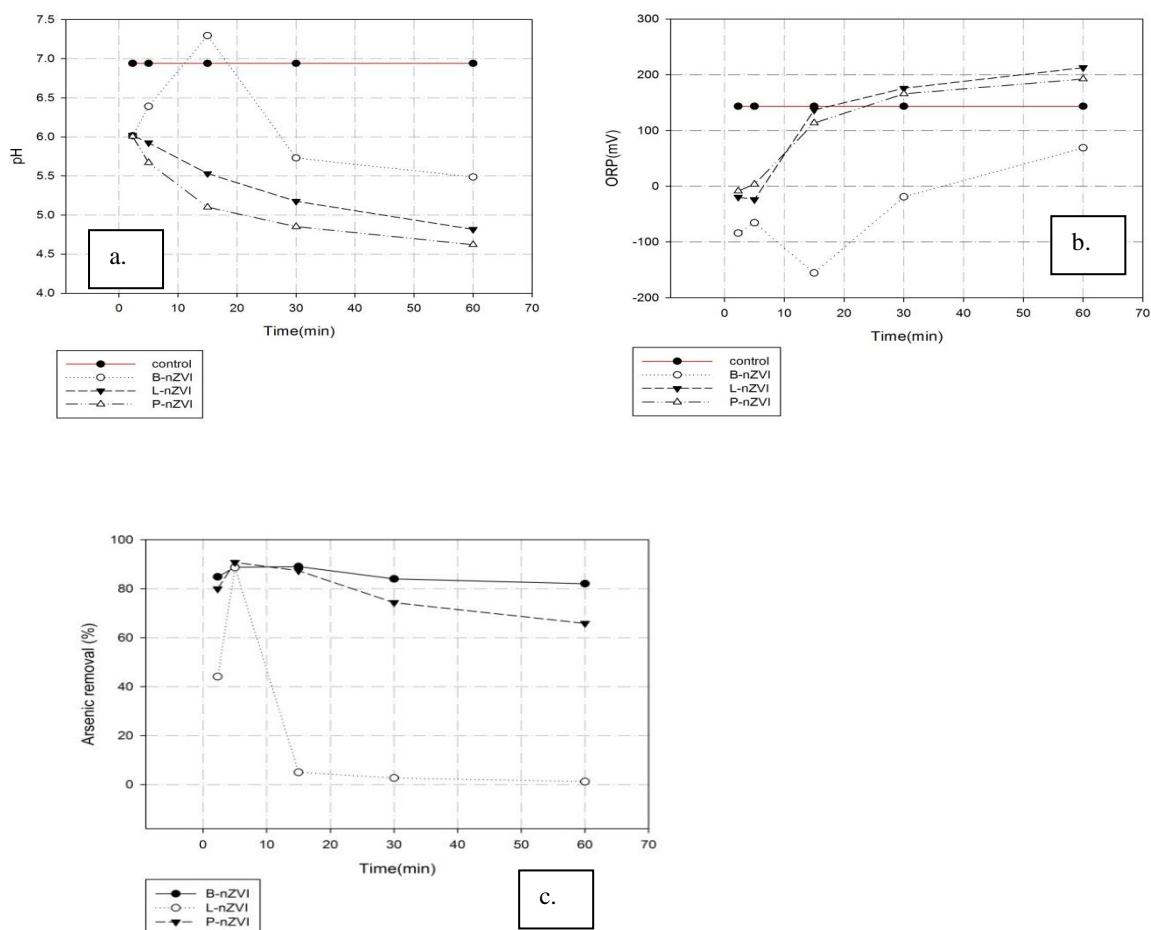


Figure 6: Effect of various forms nZVI on (a) pH, (b) ORP, and (c) Arsenic removal

$$\text{Total arsenic} = 1\text{mg/L}, \text{pH of } 7 \pm 0.06, \text{ and ORP values of } 143.5 \pm 47.38.$$

Conclusion

Various forms of nZVI including Bare nZVI, L-nZVI, and P-nZVI at 1g/L and pH 7 had potential to remove total arsenic in 1 mg/L within 5 minutes. Nevertheless, P-nZVI is the best suggesting that pulp wastewater can be effectively modified nZVI. The pulp wastewater stabilized nanoparticle is the most efficiency for arsenic removal presumably because of the highest specific surface area.

Acknowledgment

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