

## Removal of Zinc by Nano-scale Zero Valent Iron in Groundwater

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**Abstract.** Groundwater has long been identified as potential alternative of clean water supply due to its reliable quantity. However, pollution of groundwater due to anthropogenic factor still remains a challenging issue. To date, nano-scale zero valent iron (nZVI) has received great attention for its capability to treat various contaminants including chlorinated organics and metals. This study investigate Zinc (Zn) removal in aqueous solution by nano-scale zerovalent iron (nZVI). The characteristics study of the synthesized nZVI particles were investigated by its particle size and surface morphology using Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). SEM and TEM analyses verified that the particles size of synthesized nZVI were 71nm ( $< 100$  nm). Structure of nZVI congregate to each other and a thin layer of oxide layer formed on the outer part of the nZVI particle. In the batch study, removal kinetic of Zn increased from 0.14 to 0.18  $\text{mins}^{-1}$  as the concentration of Zn increased from 0.1 to 0.5 ppm. However, the removal kinetic decreased from 0.162 to 0.148  $\text{mins}^{-1}$  as the amount of nZVI was increased from 0.25 mg/L to 2.50 mg/L. At pH 7, removal kinetic reached 0.157  $\text{mins}^{-1}$ . However as the pH suspension decreases to pH 6.5, the removal kinetics decreased significantly to 0.144  $\text{mins}^{-1}$ . The same behaviour was observed at pH 9 where the removal kinetics was decreased to 0.117  $\text{mins}^{-1}$ . Removal kinetic of Zn significantly decreased at basic condition due to the formation of passivation layer which decreased the density of reactive surface area (e.g.,  $\text{Fe}^0$  and  $\text{Fe}^{2+}$ ) on the surface of nZVI. Experimental results from this study can provide basic knowledge of effectiveness of Zn removal mechanisms by nZVI at different environment conditions and provide potential remediation technology for the treatment of toxic heavy metals in groundwater.

### Introduction

Industrial, agricultural, mining and waste disposal are the anthropogenic activities have the potential to leach heavy metals (e.g., cadmium, lead and zinc) into groundwater [1]. Heavy metals are toxic contaminants and can give serious effect to biodiversity and human health. The close relation between the soil and corresponding groundwater contamination causes the toxic metals in the contaminated soils to seep through the fissured and faulted zones, leading to groundwater pollution [1]. There is an increased concern in Malaysia regarding the environmental impacts of groundwater contamination by the bioavailability and leaching of toxic heavy metals in soil and groundwater. The government takes serious efforts to remediate the contaminated groundwater to achieve cleaner soil and potable groundwater.

Zinc (Zn) is one of heavy metals that is naturally available in the environment. The concentration of Zn in uncontaminated water is in a range of  $10^{-10}$  to  $10^{-6}$  M [2]. However human activities such as mining or steel production activities cause serious Zn contamination to surface and groundwater. Excessive amount of Zn uptake may cause human deficiencies such as dermatitis, diarrhea, alopecia, mental disturbance and intercurrent infections [3]. Therefore efforts on elucidating Zn contamination and its remediation initiatives in groundwater should be given serious attention.

Remediation technologies of contaminated groundwater have emerge on utilizing nanoscale zero valent iron (nZVI) in the removal of heavy metals such as Cd, Ni, Zn, As and Cr [4,5,6]. nZVI

offers an advantage to groundwater remediation due to its unique properties of high surface reactivity and enormous reactive surface area [7]. Due to its nano size, nZVI application can be relatively easy to transport and inject effectively into contaminated groundwater. With its high reactive surface area, nZVI provide high potential contaminant removal and degradation through reduction and adsorption [8].

### Materials and Methods

**List of Chemicals.** Chemical utilized for this study include, sodium borohydride ( $\text{NaBH}_4$ ) (99%, Aldrich), iron chloride ( $\text{FeCl}_3$ ) (98%, Aldrich), acetone (99%, Merck) for nZVI synthesis, MOPS,  $\text{pK}_a = 7.2$  for pH 6.5 to 7.9 and hydrochloric acid (HCL) (0.1 M, Merck) for preparing buffer solution. Standard stock solution of Zn, (1000 ppm, Merck), Zinco Ver 5 reagent powder pillow and cyclohexanone was utilized for Zn determination. Deaerated deionized water (DDW) was prepared using ultra pure water (18  $\Omega\cdot\text{cm}$ ) purged by  $\text{N}_2$ . Anaerobic chamber was maintained purged with 95%  $\text{N}_2$  and 5%  $\text{H}_2$ . All reagents and solutions used in the experiments was prepares using DDW.

**Synthesize of nZVI.** Synthesis of nZVI were performed by using sodium borohydride ( $\text{NaBH}_4$ ) (0.9 mM, 1000 mL) and iron chloride ( $\text{FeCl}_3$ ) (0.11 mM, 1000 mL), followed the method proposed by Wang and Zhang [9]. The  $\text{NaBH}_4$  functions as a reducing agent in order to reduce  $\text{FeCl}_3$  to produce nZVI. Both chemicals were mixed by dropping  $\text{NaBH}_4$  solution into  $\text{FeCl}_3$  solution continuously while stirring the mixture well. Fe (III) will be reduced to Fe (0) by hydrogen generated during the reaction. Black iron particles was formed and separated from the solution by centrifuge at 3000rpm at 10min. The nZVI were washed twice with DDW and once with ethanol before dried and stored in an aerobic chamber.

**Batch Experiments.** Batch experiments were conducted to determine removal kinetic of Zn by nZVI. To investigate the effectiveness of Zn removal by nZVI, experiments were conducted in 40 mL amber glass vials sealed with three layered septum system. The three layered septum consist of rubber septum, aluminum foil and parafilm. MOPS buffer solution (50 mM) was prepared using MOPS sodium salt and DDW. pH of buffer solution was adjusted from pH 9 to pH 7 using 0.1 M HCL acid. Exact amount of nZVI 0.05g was weighted and transferred to each vials and MOPS buffer solution (50 mM) was poured into each vials without headspace to keep the pH suspension constant at 7. Zn with concentration of 0.30 ppm was then introduced into each vial and to initiate reaction between nZVI and Zn. Vials were then rapidly capped, mounted on a tumble mixer, and rotated at 7 rpm at room temperature ( $25 \pm 0.5^\circ\text{C}$ ) for 30 minutes. All the experimental works were conducted in an anaerobic chamber. Samples and controls were prepared in duplicate. The removal of Zn was determined by measuring aqueous concentration of Zn in the nZVI suspension at each sampling time. At sampling time of every 10 minutes, samples were taken out of the anaerobic chamber, centrifuged for 5 min at 5000 rpm, and then aliquots of aqueous solution were collected to measure the Zn concentration. Concentration of Zn was determined by HACH Spectrometer DR5000, Method 8009. Batch kinetic experiments were conducted to investigate effect of concentrations of Zn and nZVI, and pH on the removal of Zn by nZVI. Three different concentrations of Zn (0.1 ppm, 0.3 ppm and 0.5 ppm) were prepared by diluting Zn standard stock solution (1000 ppm, Merck) in DDW. Initial concentration of nZVI was set at 1 mg/L at pH 7. Samples were prepared by following the same way as the batch test described above. To investigate effect of nZVI on the removal of Zn by nZVI at pH 7, three different concentrations of nZVI (0.01 g, 0.05 g and 0.10 g) were weighted and transferred into vials. Initial concentration of Zn was set at 0.3 ppm at pH 7. To study effect of pH on the removal Zn by nZVI, 50 mM MOPS buffer and 0.1 M HCL were used to adjust and keep the pH values constant at 6.5, 7 and 9. Initial Zn and nZVI concentrations were set at 0.3 ppm and 1 mg/L, respectively. Samples were prepared by following the same way as the batch test described above.

## Analytical procedures

**Characterization of nZVI.** The characteristics study of the synthesized nZVI particles were investigated by its particle size and surface morphology using Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). nZVI sample were dried in anaerobic condition for 24 hours. It was carefully packed under anaerobic condition to avoid its surface oxidation prior to analysis.

**Zinc Concentration.** Concentration of Zn was determined using HACH Spectrometer DR5000, following Method 8009. Aliquots of aqueous solution collected from samples and controls were transferred to 20 ml mixing cylinder and Zinco Ver 5 Reagent Powder Pillow and cyclohexanone were added for Zn determination.

## Result and Discussion

**Characterization Study of nZVI.** Fig. 1 shows the particle size and morphology of synthesized nZVI using SEM. The resulting image of nZVI shows that the size of nZVI was approximately 71nm and it was aggregated to each other due the strong dipole-dipole magnetic of individual particles [4]. Size of nZVI was also measured using TEM (Fig. 1 (b) and (c)). Fig. 1(b) and (c) show that size of synthesized nZVI was 20 nm and 60 nm, respectively. These results strongly confirmed that synthesized nZVI in this study was in nano-scales (<100 nm). This experimental result is consistent with the previous study reported by Efcan [10].

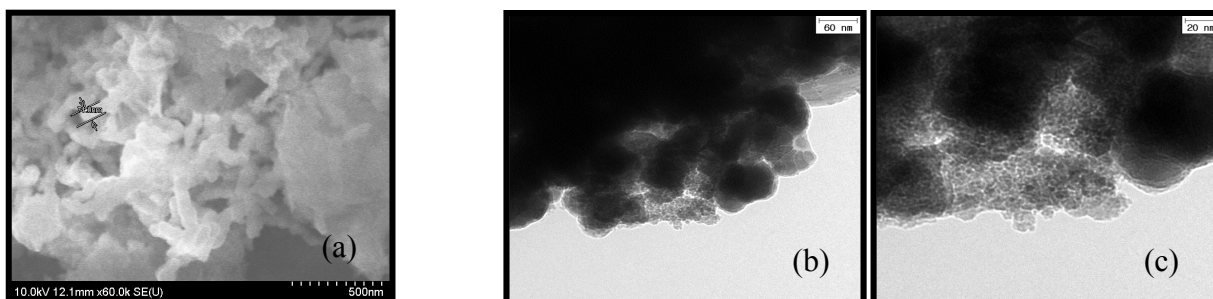


Fig 1(a): SEM image of nZVI

Figure 1 (b) and (c): TEM image of nZVI

**Removal of Zn by nZVI.** Fig. 2 shows the removal of Zn by nZVI at pH 7. Based on the result obtained, the removal of Zn is observed immediately at the first 10 minutes of reaction time. At 20 minutes reaction time, Zn was completely removed. The removal kinetic of Zn removal by nZVI at pH 7 was  $0.157 \text{ min}^{-1}$ . This experimental result indicates that nZVI is capable to remove Zn at natural pH. Result suggests that redox reaction between nZVI and Zn probably occur around pH 7. Similar observation was reported by Khatoun et al [11].

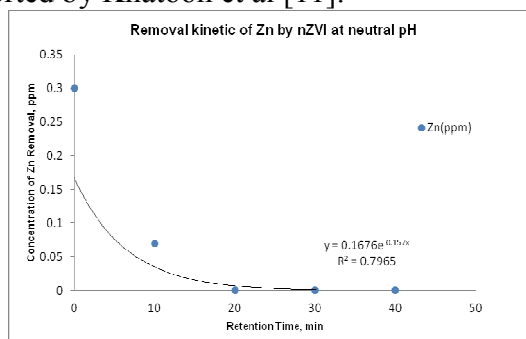


Figure 2. Removal of Zn by nZVI. (Initial condition nZVI=0.05 g; Zn= 0.30 ppm; pH 7).

**Effect of Zinc Concentration on Removal of Zinc by nZVI.** Fig. 3(a) and (b) show removal kinetic of Zn at different concentration of Zn (0.1 ppm, 0.3 ppm and 0.5 ppm) at pH 7. It was observed that at concentration of 0.1 ppm, 90% of Zn concentration was removed at the first 10 minutes and totally removed on the following sampling time. At 0.3 ppm Zn concentration, Zn was completely removed at 20 minutes followed by concentration of Zn at 0.5 ppm which was

completely removed at 30 minutes reaction time. This result shows that higher Zn concentration requires longer reaction time to be entirely removed. Similar behavior of Zn removal by nZVI was observed in previous studies where contact time significantly influence the percent removal of Zn [11,12,13]. The removal kinetic rate of Zn at 0.5 ppm of Zn concentration was  $0.18 \text{ mins}^{-1}$ , which is 1.15 time greater than removal kinetic rate of Zn at 0.3 ppm of Zn concentration ( $k = 0.157 \text{ mins}^{-1}$ ). While the removal kinetic rate of Zn at 0.1 ppm of Zn concentration ( $k = 0.115 \text{ mins}^{-1}$ ) was 1.06 time lower than the removal kinetic rate of Zn at 0.3 ppm of Zn concentration. Removal kinetic rate of Zn was significantly increased as concentration of Zn increased from 0.1 ppm to 0.5 ppm. These experimental results indicate that removal kinetic rate of Zn by nZVI was significantly controlled by concentration of Zn in this system. Results suggest that 0.05 g of nZVI provides sufficient reactive surface to completely remove 0.1 to 0.5 ppm of Zn at pH 7 in this study. The results from this study are consistent with the experimental results reported by Khatoon et al [11].

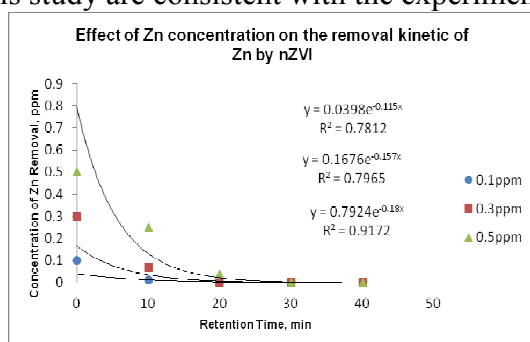


Figure 3(a): Effect of Zn concentration on the removal kinetic of Zn by nZVI at pH 7.

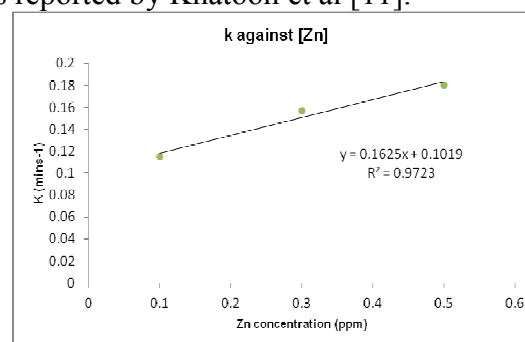


Figure 3(b): Removal kinetic rate value ( $k$ ) of Zn by nZVI at different concentration of Zn (pH 7, [nZVI] = 0.001 g/L)

**Effects of nZVI Concentration on Removal of Zn by nZVI.** Fig. 4 (a) shows removal kinetic of Zn by nZVI at different concentration of nZVI at neutral pH. Zn was completely removed by different concentrations of nZVI (0.01 g, 0.05 g and 0.10 g) in 30 mins. This result indicates that even at low concentration of nZVI 0.25 mg/L (0.01g) was sufficient to remove 0.3 ppm of Zn at neutral pH. However, result presented contradicts with results reported by Liang et al. and Kržišnik et al. where efficiency of Zn removal significantly increased with the increased of nZVI loading [12,13]. Fig. 4 (b) illustrates removal kinetic rate of Zn by nZVI at different concentration of nZVI. Removal kinetic rate of Zn was significantly decreased as concentration of nZVI increased from 0.25 mg/L, 1.25 mg/L and 2.50 mg/L. The removal kinetic rate of Zn with 0.25 mg/L of nZVI was  $0.162 \text{ mins}^{-1}$ , which is 1.03 time greater than removal kinetic rate of Zn at 1.25 mg/L of nZVI ( $k = 0.157 \text{ mins}^{-1}$ ). While the removal kinetic rate of Zn at 2.50 mg/L of nZVI ( $k = 0.148 \text{ mins}^{-1}$ ) was 1.06 time lower than removal kinetic rate of Zn at 1.25 mg/L of nZVI. This result indicates that removal kinetic rate of Zn was not dependent on the concentration of nZVI in this system. This was probably occurred due to the agglomeration of nZVI particles itself at high concentration of nZVI. Literatures have reported that agglomeration of nZVI may decrease reactive surface area on the nZVI surface. Due to this reason, electron transfer from the reactive surface of nZVI to Zn was inhibited and  $\text{Zn}^{2+}$  could not be reduced to Zn [14,15]. The results from this study is consistent with the experimental results reported in the previous study [12,13].

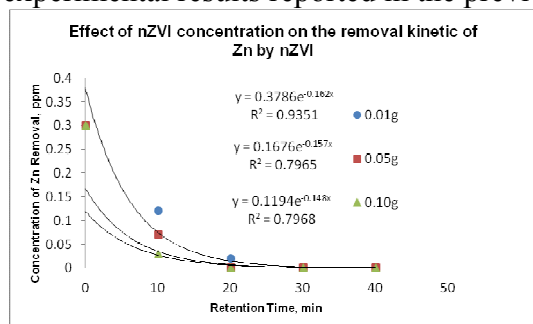


Figure 4(a): Graph effect of nZVI concentration on the removal kinetic of Zn by nZVI

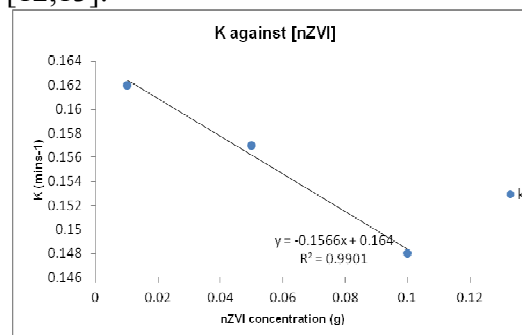


Figure 4(b): Removal kinetic rate value ( $k$ ) of Zn by nZVI at different concentration of nZVI (pH 7, [Zn]=0.3ppm)

**Effects of pH on Zn removal by nZVI.** Fig. 5 (a) shows removal kinetic of Zn by nZVI at different pH. Zn was completely removed by nZVI at pH 6.5, 7 and 9 in 40 mins. There was not significant different of the removal of Zn by nZVI at pH 6.5 and 7. However, removal of Zn by nZVI was slower at pH 9 than that at pH 6.5 and 7. This result indicates that removal of Zn by nZVI was significantly influenced by pH condition in this system. Similar result was observed by Kržišnik et al where highest Zn removal was obtained at pH 7 [13]. In neutral pH range, strong magnetic forces enhanced the particles aggregation, thus increasing the potential of contaminant removal efficiency [13, 16]. Fig. 5 (b) illustrates removal kinetic rate of Zn by nZVI at different pH. Removal kinetic rate of Zn was significantly decreased as pH increased from neutral to alkaline conditions. However, the removal kinetic of Zn by nZVI was slightly increased at pH 7. The removal kinetic rate of Zn at pH 7 was  $0.157 \text{ mins}^{-1}$ , which is 1.3 time greater than removal kinetic of Zn at pH 9 ( $k = 0.117 \text{ mins}^{-1}$ ). While the removal kinetic rate of Zn at pH 6.5 ( $k = 0.144 \text{ mins}^{-1}$ ) was 1.1 time lower than at pH 7. This results indicate that fast removal kinetic of nZVI occurred at pH 7, suggesting that nZVI particles may have high density of reactive surface on its surface at this condition. This result is consistent with the study reported by Efekan [10]. Literatures have reported that formation of passivation layer on the surface of nZVI at high pH condition probably decrease the removal efficiency of Zn by nZVI [11,12]. The formation of passivation layer decreases the density of reactive surface area (e.g.,  $\text{Fe}^0$  and  $\text{Fe}^{2+}$ ) on the surface of nZVI [11]. While, the kinetic removal was slightly increased at pH 7 probably because the density of reactive surface area was sufficient to enhance removal of Zn by nZVI [11,12]. This result suggests that pH value is an important factor to be considered during the reduction process between Zn and nZVI. The results from this study is consistent with the experimental results reported in the previous study [12,13].

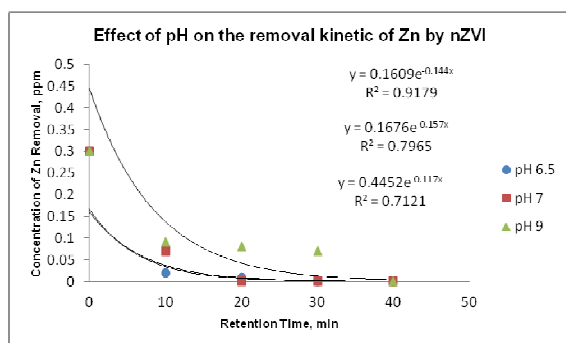


Figure 5(a): Graph effect of pH on the removal kinetic of Zn by nZVI

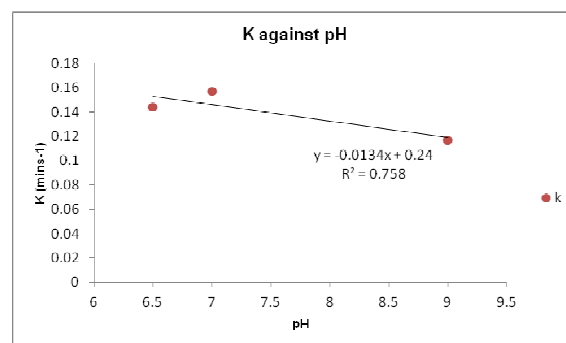


Figure 5(b): Removal kinetic rate value ( $k$ ) of Zn by nZVI at different pH ([nZVI] = 0.001 g/L, [Zn] = 0.3ppm)

## Conclusion

Results from this study shown significant finding on the removal of Zn by nZVI in an anaerobic condition. The optimum condition for removal of Zn by nZVI was identified in this study ([Zn] : 0.3 ppm, [nZVI]: 0.25 mg/L, pH 7). Finding from this study provides significant fundamental knowledge on the characteristic of removal of Zn by nZVI at different environment conditions. Thus, this finding can be proposed as a potential remediation method to remove Zn in groundwater. This study is very significant to Department of Environmental Malaysia because finding from this study could be implemented to achieve sustainable development in remediation technology of groundwater in Malaysia.

## Acknowledgment

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