ENHANCEMENT OF REDUCTIVE DECHLORINATION OF TETRACHLOROETHENE BY INTERACTION BETWEEN NANO-SIZED ZERO VALENT IRON AND VITAMIN B_{12}: EFFECT OF PHYSICOCHEMICAL FACTOR

Amir.A, Lee W.

Department of Civil and Environmental Engineering, Korea Advanced Institute of Science and Technology, 335 Gwahangno, Yuseong-gu, Daejeon 305-701, Korea

Abstract

This study presents an experiments which characterizes reductive dechlorination of tetrachloroethene (PCE) by interaction between nano-sized zero valent iron and vitamin B_{12} (nZVI-Vitamin B_{12}), and effect of physicochemical factor (pH, vitamin B_{12} and nZVI concentration) in this system. Characterization study of interaction between nZVI and vitamin B_{12} showed an enhanced reduction rate of PCE. Removal of PCE by nZVI-Vitamin B_{12} was 78% in 6 hours at pH 8. The reduction kinetic of PCE was 20 times faster than that by nZVI. The predominant cobalt species present under the reaction condition was cobalamin (II) (vitamin B_{12r}), as confirmed by color observation analysis. Reduction of PCE increased with increasing pH due to the formation of vitamin $B_{12r.}$ PCE reduction kinetic was accelerated by increasing the concentration of vitamin B_{12} and nZVI. The experimental results about interaction between vitamin B_{12} and nZVI could provide fundamental knowledge of interaction between soil-bacteria and nano materials to develop advanced remediation technologies to treat the soil and groundwater contaminated with chlorinated organic compounds.

Introduction

Chlorinated ethenes are one of main pollutants found in the contaminated soil and groundwater. These compounds have been used intensively over the last century, and large amount have been released to the environment. They are known to be very toxic, carcinogenic, mutagenic, and very persistent in environment [1-6]. Reductive dehalogenation of chlorinated ethenes can be catalyzed by metallocoenzymes [7]. One of metallocoenzymes, vitamin B_{12}, is produced by anaerobic bacteria and contains a corrin ring coordinated with cobalt atom. The common commercial available form of vitamin B_{12} is cyanacobalamin. Vitamin B_{12} in a form oxidation state Co^{3+} can be reduced to Co^{2+} (vitamin B_{12r}) and Co^{1+} (.vitamin B_{12s}). Previous studies have reported that vitamin B_{12r} and vitamin B_{12s} can be significantly involved in the reductive dechlorination of CT, TCE, and PCE [11-13]. A reductant source such as nZVI is needed to provide sufficient electron for the reduction of vitamin B_{12} in anoxic condition. nZVI has been known as one of the strongest reductants (E^0 = -0.41V) due to its high specific area and mobility through saturated aquifer [8, 14]. Its reactivity, however, easily decreases due to formation of iron oxide or hydroxide over its surface under environmental conditions (e.g., pH). This phenomenon has been reported as a major problem of field application [9]. To get over this problem, an engineered catalysis process is needed to improve the reactivity of nZVI. The objective of this study is to characterize the reductive dechlorination of PCE by interaction between nano-sized zero-valent iron and vitamin B_{12} to enhance dechlorination of PCE. Experiment was also conducted to investigate the effect of physicochemical factors including pH and vitamin B_{12} and nZVI concentrations on the reductive dechlorination of PCE.

Material and Methods

Materials. Chemical used in this study were $FeCl_3.6H_20$ (98%, Aldrich), NaBH4 (98%, Aldrich), Tetrachloroethene (≥99.9%, Aldrich), Acetone (≥99.8%, MERK), Methanol (≥99.9%, MERK), 1,2-Dibromopropane (97%, Aldrich), Cyanocobalamin (III) (vitamin B_{12}- 99%,Aldrich). Buffer used were 2-(N-morpholino)-ethanesulfonic acid (MES, Sigma), 3-(N-morpholino)propanesulfonic acid (MOPs, Sigma), Trizma Hydrochloride, reagent grade (99%, Sigma). Redox titration, Tris(hydroxymethyl)amino-methane,(99.8%). All chemicals are ACS reagent grade. Deionized water was purified to obtain 18 MΩ cm ultra pure water using a ELGA PURELAB Classic system.

Synthesis of Nano-sized Zero Iron. nZVI was synthesized by reducing 0.11 M $FeCl_3 \cdot 6H_2O$ with 0.9 M $NaBH_4$ solution, modifying Wang's method [14]. nZVI was washed with water three times, followed by washing with acetone. Dried particles were stored in an anaerobic chamber (5% H_2 in N_2 atmosphere, Coy) to avoid air contact.

Batch experiments. Amber vials (24mL) sealed with three layered septum system (Teflon-lined rubber septum, lead foil, and teflon) were used as batch reactors. Aqueous reagent mixture (24 mL) containing pH buffer (50mM), nZVI (0.01-0.5g), vitamin B12 (5ηM - 5μM) were transferred to the reactor. All samples used in this research were prepared in an anaerobic chamber at 25°C. Control samples were prepared to check the potential loss by volatilization and adsorption in the batch reactor. All samples were prepared in duplicate. The dechlorination of PCE was initiated by injection of a methanolic PCE stock solution (100μL) to the reactor. Samples were then mixed by tumbler at 7rpm.

Analytical methods. The analyses for PCE was performed with a Hewlett Packard 5890 gas chromatograph (GC) equipped with an electron capture detector (ECD) and a HP-5 column (30 m x 0.32 mm x 0.25 μm). The temperature of injector and detector was 175 and 200 °C, respectively and oven temperature was isothermal at 80 °C. Peak areas for PCE and internal standard were compared to a standard calibration curve to quantify the concentration of PCE in aqueous solution.

Result and discussion

1. Kinetic Study. As a benchmark for the reduction dechlorination of tetrachloroethene (PCE) by nZVI- vitamin B_{12}, we conducted a characterization of the dechlorination of PCE. The reduction of vitamin B_{12} by nZVI was checked by color observation. Figure 1 shows reductive dechlorination of PCE by nZVI-vitamin B_{12} at pH 8. Compared to the reductive dechlorination of PCE by nZVI, that by nZVI-vitamin B_{12} was 20 times faster. Removal of PCE by nZVI-Vitamin B_{12} was 78% within 6 hours. This result demonstrates that interaction between nZVI and vitamin B_{12} could enhance the dechlorination of PCE. The predominant cobalt species present under the reaction condition was cobalamin (II) (vitamin B_{12r}), which was confirmed by the color observation method.

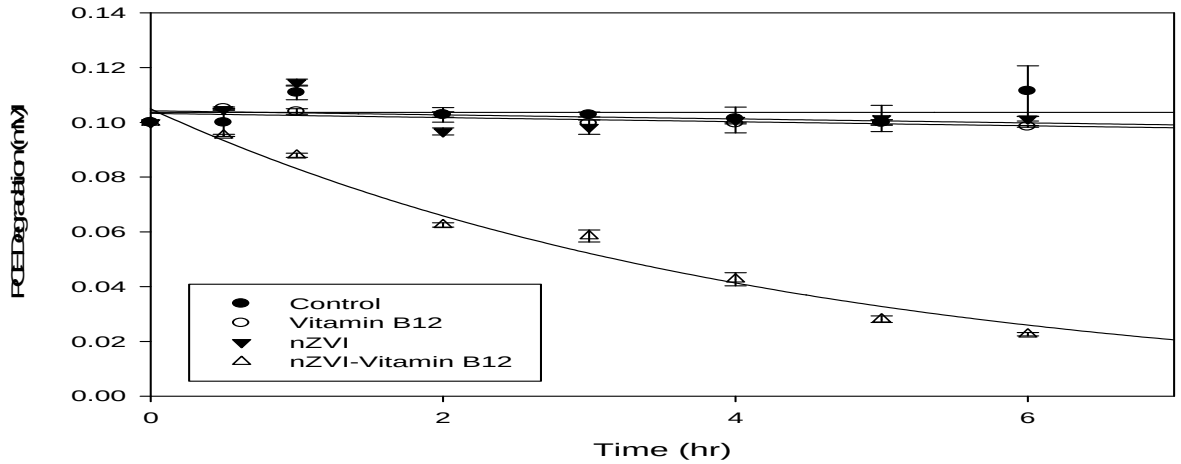

Figure 1. Reduction of PCE by 0.05g nZVI with 0.5mM Vitamin B_{12} at pH 8.

2. Effect of pH. To investigate the effect of pH on the interaction between nZVI and vitamin B_{12}, the dechlorination kinetics of PCE was examined under different pHs using a series of buffers. Figure 2 shows the reductive dechlorination of PCE by nZVI-vitamin B_{12} at different pH where the dechlorination kinetics of PCE was very fast at pH 8-9. Chiu and Reinhard reported similar trend in the reductive dechlorination of carbon tetrachloride by interaction between vitamin B_{12} and titanium (III) citrate. At low pH, dechlorination of PCE by nZVI-vitamin B_{12} showed a similar trend which could be observed in the reductive dechlorination of PCE by nZVI. No significant enhancement was observed in the reductive dechlorination of PCE by nZVI-vitamin B_{12} at low pH. The reactivity of nZVI has been strongly influenced by pH and decreased as the pH increased [12].

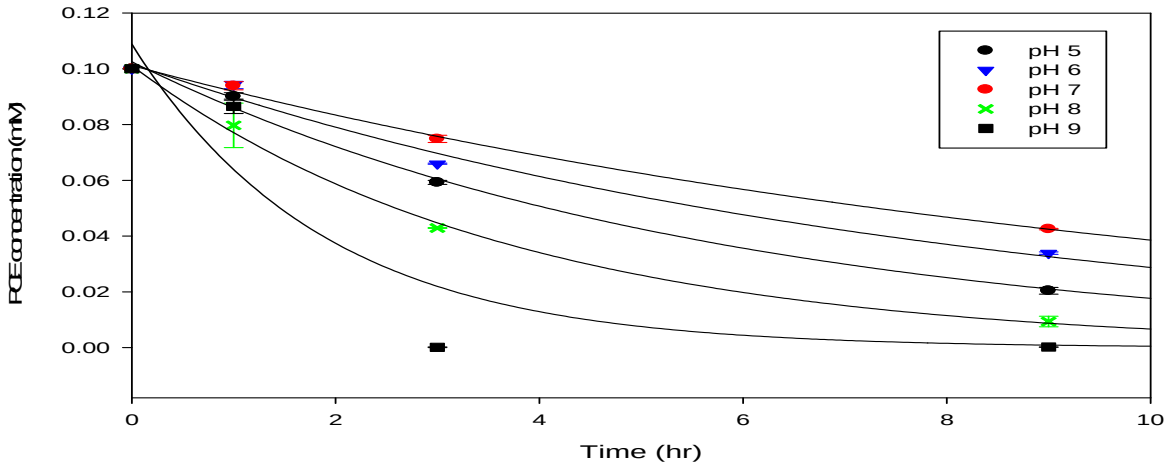

Figure 2. Effect of pH on the pseudo-first-order rate constant for PCE reduced by nZVI-vitamin B_{12}

Figure 3 illustrates the observed rate constants (K_{obs}) for PCE dechlorinations by nZVI and nZVI-vitamin B_{12}. Reductive dechlorination kinetics of PCE by nZVI-vitamin B_{12} was faster than that by nZVI over the pH range. The presence of vitamin B_{12r} significantly enhanced the dechlorination kinetics of PCE by 50 times at pH 8-9, when compared to that by nZVI. Vitamin B_{12r} has been known as a nucleophile [13] which plays an important role in reductive dechlorination by vitamin B_{12}. The nucleophilicity could be increased with the increase of suspension pH.

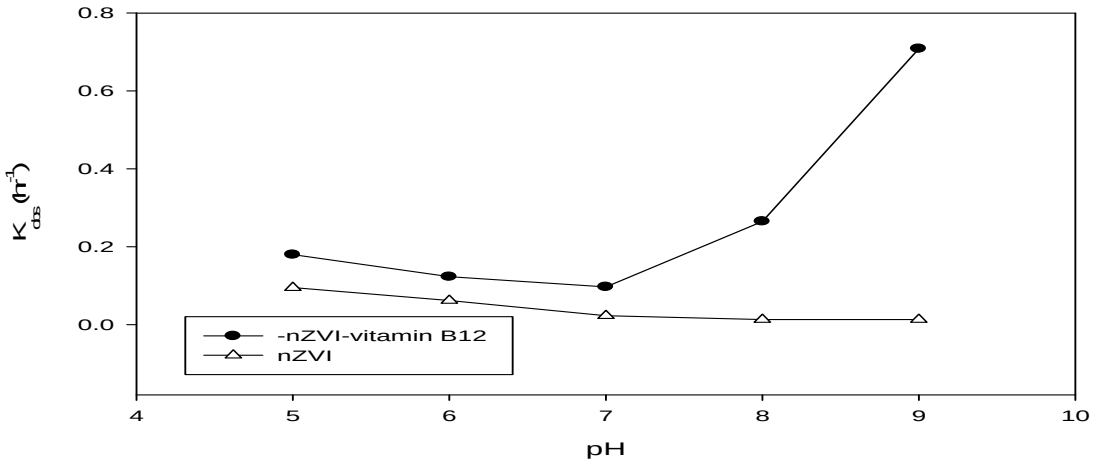

Figure 3. Comparison between observed rate constant (K_{obs}) of PCE reduction by nZVI alone and nZVI-vitamin B_{12}

3. Effect of vitamin B_{12} Concentration. Figure 4 illustrates the degradation pattern for the reductive dechlorination of PCE at different concentration of vitamin B_{12}. With increasing vitamin B_{12} concentration, the dechlorination kinetics of PCE increased significantly. The degradation kinetics of PCE at low concentrations of vitamin B_{12} (5nM and 5μM) showed a similar degradation kinetic pattern of PCE by nZVI (0.05g). By adding 0.5 mM of vitamin B_{12}, the dechlorination of PCE (K_{obs} = 0.73 hr^{-1}) was accelerated by 1000 times compared to reduction of PCE by nZVI alone. The predominant cobalt species present under the reaction condition was vitamin $B12_r$.

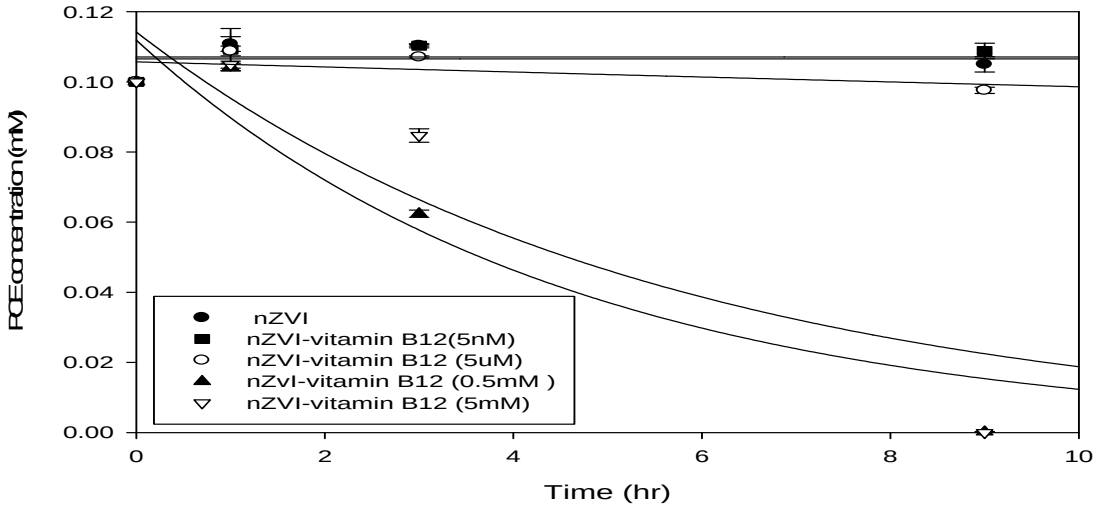

Figure 4: Effect of vitamin B_{12} concentration on the reduction of PCE by nZVI-vitamin B_{12}.

4. Effect of nZVI Concentration. nZVI plays an important role for reduction of vitamin B_{12}, therefore the concentration of nZVI strongly can affect the dechlorination rate of PCE. Figure 5 shows the effect of nZVI concentration on the dechlorination kinetics of PCE at different nZVI concentration. The dechlorination kinetics of PCE by nZVI-Vitamin B_{12} increased to the nZVI content of 0.5g, while the estimated K_{obs} by nZVI shows no significant dechlorination of PCE at pH 8.17. Interaction between 0.5g of nZVI and 0.5 mM vitamin B_{12} at this experiment condition accelerated the reductive dechlorination of PCE by 92 times, compared to the reductive dechlorination of PCE by nZVI.

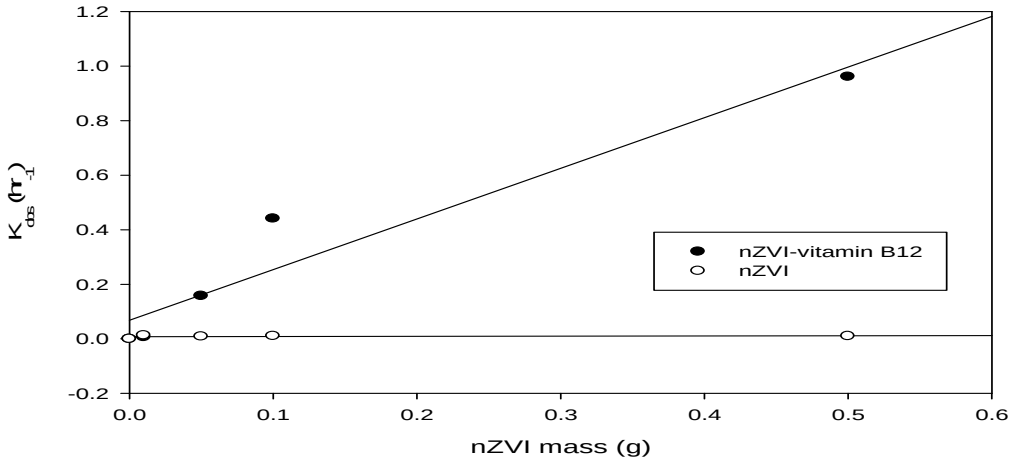

Figure 5. Effect of nZVI concentration on the reduction of PCE by nZVI-vitamin B_{12}.

The results obtained from this study showed that the reductive dechlorination of PCE was strongly affected by pH and concentrations of vitamin B_{12} and nZVI. Reductive dechlorination of PCE can be enhanced by the interaction between nZVI and vitamin B_{12} at high pH. Additionally, the dechlorination kinetic of PCE increased significantly with increasing pH and vitamin B_{12} and nZVI concentrations. The greatest dechlorination kinetic constant of PCE was $1.1hr^{-1}$ at pH 8.17, 5mM vitamin B_{12}, and 0.05g of nZVI.

Acknowledgements

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References

1. Vogel T. M., Criddle, C. S. and McCarty P. L. *Environ. Sci. Technol*. 1987; 21: 722.
2. Ukrainczyk L.,Chibwe M., Pinnavaia T.J. and Boyd S.A. *Environ. Sci. Technol*. 1995; 29: 439.
3. He J., Ritalahti K. M., Yang K. L., Koenigsberg S. S. and Loffler F. E. *Nature* 2003; 424: 62.
4. Pon G., Hyman M. R. and Semprini L. *Environ. Sci. Technol*. 2003; 37: 3181.
5. Mackay D.M. and Cherry J. A. *Environ. Sci. Technol*. 1989; 23: 630.
6. Burris D. R., Delcomyn C. A., Smith M. H. and Roberts A.L. *Environ. Sci. Technol*. 1996; 30: 3047.
7. Quinn J., Geiger C., Clausen C., Brooks K., Coon C., O'Hara S., Krug T., Major D., Yoon W.S., Gavaskar A. and Holdsworth T. *Environ. Sci. Technol*. 2005; 39: 1309.
8. Saleh N., Sirk K., Liu Y., Phenrat T., Dufour B., Matyjaszewski K., Tilton R.D., Lowry G.V. *Environ. Eng. Sci*. 2007; 24:45.
9. Philips D. H., Gu B., Watson D. B., Roh Y., Liang L., Lee S.Y. *Environ. Sci. Technol.* 2000; 34: 4169.
10. Chiu P.C. and. Reinhard M. *Environ. Sci. Technol*. 1995; 29: 595.
11. Chiu P.C. and. Reinhard M., *Environ. Sci. Technol*. 1996; 30: 1882.
12. Mathson L.J. and Tratnyek P.G. *Environ. Sci. Technol*. 1994; 28:2045-2053.
13. Assaf-Anid N., Hayes K.F and Vogel T.M. *Environ. Sci. Technol* 1994; 28:246.
14. Wang C. B. and Zhang W. X. *Environ. Sci. Technol* 1997; 31: 2154.