

## Application of nano-sized iron for POPs removal

Kim J-H<sup>1</sup>, Bokare V<sup>1</sup>, Cho S-H<sup>1</sup>, Lee J-W<sup>2</sup>, Chang Y-S<sup>1</sup>

<sup>1</sup>School of Environmental Science and Engineering Pohang University of Science and Technology(POSTECH), San 31, Hyojadong, Namgu, Pohang, Kyungbuk, 790-784, South Korea

<sup>2</sup>R&D Center, HYORIM Industries INC., 463-839, South Korea

### Abstract

In the present study, a novel synthesis of nano-sized iron (nZVI) was carried out. This novel nZVI was then used for TCE degradation from contaminated ground water. Pilot scale (2x1 x 0.75m soil box for simulation of the contaminated site) studies showed that nearly 99% of TCE was removed. Such nanoparticles are easily delivered to the contaminated site, as they are highly dispersed and mobile. This paper presents the progress and preliminary results of lab and pilot scale studies on the application of these novel nZVI particles for removal of persistent organic pollutants from the environment.

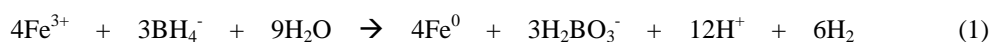
### Introduction

Nanotechnology is the science of manipulating materials at the nanoscale (1-100nm) either by scaling up from single groups of atoms or by reducing the bulk material. Such unique materials offer great catalytic potential for treatment of ground water, surface water and wastewater that are contaminated by various sources. Active research is taking place worldwide in this respect and the pursuit for the development of the ultimate decontaminant is still going on. Among the nano materials of choice, iron nanoparticles are highly desired for environmental cleanup.

Various reports have been published till date about the field scale applications of nano-sized iron for remediation. However, research on novel synthetic routes to produce iron nanoparticles and their application for degrading emerging contaminants continues. Our study presented here describes the application of zero-valent iron nanoparticles for degradation and removal of organic contaminants in the ground water.

### Materials and Methods

nZVI can be produced and synthesized by wet chemical procedure where in the iron is reduced with a strong reductant like sodium borohydride<sup>1,2</sup>. This is the most facile and popular procedure used for the synthesis of zero-valent iron nanoparticles. The synthesis is achieved by adding, sodium borohydride (NaBH<sub>4</sub>) to ferric chloride hexahydrate(FeCl<sub>3</sub>·6H<sub>2</sub>O) in aqueous solution as below.



We have used pickling water as source of ferric ions instead of ferric chloride hexahydrate. All other chemicals had >99% purity and were used without further purification. Distilled water (DW) used in these experiments was generated by a Barnstead Nanopure system and was degassed by passing argon gas in a sealed bottle for 2 hours prior to use. The pickling water was diluted in order to keep the Fe concentration fixed at 0.15 M. nZVI was also synthesized using the same Fe concentration [FeCl<sub>3</sub>·6H<sub>2</sub>O (Kanto Chemicals, Japan), 0.15M Fe concentration]. Borohydride (0.24M, prepared in DW) was added to the iron solution at a flow rate of 0.02 mL s<sup>-1</sup>. Excessive borohydride is the key factor for rapid and uniform synthesis of iron nanocrystals. The precipitate was centrifuged and washed with degasses distilled water several times to remove all the impurities and unreacted borohydride.

### Pilot Scale Test

The experiments were conducted in a 2m long by 1m high by 0.75m wide flow box filled with sand<sup>3</sup>. The total volume of sand was 1.35m<sup>3</sup>. Peristaltic pumps were employed at front and back of the box for achieving equilibrium, as shown in Figure 1.



Figure 1. Pilot test was conducted in a sandy media packed box (2m x 1m x 0.75m, L x H x W)

As part of the intermediate scale test design process, stabilization of influent TCE concentration is a key factor because of its strong volatility. from surface water. Although it is moderately soluble in water, wet-deposited TCE can revolatilize back to the atmosphere. Hence precautions were taken to prevent the volatilization of TCE. TCE solutions were stored in 20L capacity Tedlar bags. Using water tank for TCE storage leads to huge amounts of TCE loss due to evaporation, Tedlar bags on the other hand have no head space and hence minimal loss occurs. TCE recovery is more than 90% in two days. The surface of the sand was covered with cement which was in turn covered by polyvinyl sheets in order to prevent volatilization from the cemented surface.

380L of water containing 20ppm TCE was spiked in the sand box. 274mg TCE (99% pure, Aldrich) and 20L D.W. (Distilled Water) were used to make a 20ppm solution. 500g nZVI was synthesized using 2.5L pickling water and 31.25g/L sodium borohydride 8L.

Freshly formed nanoparticles were allowed to settle by using electronic magnet and washed with degassed distilled water for removing excess unreacted borohydride and other impurities. 1.25kg of nZVI was obtained by this synthesis procedure. By using direct-push approach, the slurry injection which has 20~30cm influence diameter could be reached targeting depth intervals within a treatment area as Mobile-PRB<sup>4</sup> (Permeable Reactive Barrier). Direct push technology refers to a growing family of tools used for performing subsurface investigations by driving, pushing, and vibrating small-diameter hollow steel rods in the ground. By holing to end of the probe it can be injected to targeting depths. Probe was made from stainless steel and was designed for top, middle and bottom points having length of 0.45m, 0.75m and 1.1m respectively. Four side holes were made at the end of the probe from where the slurry was injected. nZVI injector is a cylindrical device with 1L capacity and equipped with two solenoid valves to control injection. This device was operated by air pressure and was adjusted to the velocity of slurry injection. The concentration of the slurry injected was 13.8g/L and injection depths were 0.15m, 0.3m 0.45m 0.60m, 0.7m, 0.8m respectively.

Six monitoring wells located within 0.9m of depths in the box had multi level sampling points at 0.1m, 0.45m and 0.8m from bottom, respectively. These samplers were made from stainless steel tube and each sampler was attached to one supporter rod. The box was divided into 2 halves; two monitoring wells were located in the first quarter of the box to monitor the influent concentration. Injection site was in the adjacent quarter. The other half of the box had monitoring wells to determine the changes in TCE concentration at periodic intervals. The I.D (Inside Diameter) was 1/2in. Peristaltic pump was used for sampling. Since the sampling device was cylindrical in shape, there was a possibility that samples from previous cycles are still stored inside hence initial 15mL sample was discarded. 50mL of solution was sampled and stored in polypropylene conical tubes.

## RESULT AND DISCUSSION

In the box test, pre-injection and post-injection monitoring was carried out to obtain baseline data. Results are shown in Table 1.

**Table 1. Key parameters in sampling point in the box**

Parameter	Sampling point								
	MW 2			Injection Area			MW 6		
	Base line	Post-injection (1day)	Post-injection (3day)	Base line	Post-injection (1day)	Post-injection (3day)	Base line	Post-injection (1day)	Post-injection (3day)
Do(mg/L)	8.17	3.43	2.35	6.21	0.88	0.24	6.68	6.8	1.88
ORP(mV)	611.8	533	143.7	575.8	-509.6	-504.6	602.3	612.4	302.1
pH	7.22	9.43	8.87	7.48	9.34	9.48	7.14	8.24	8.27
TCE(mg/L)	2.00	1.31	0.87	3.61	0.85	0.45	4.56	1.01	0.88
Cis-DCE (mg/L)	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = not detected

6 monitoring wells located within 0.9m of depths in the box were used for multi level sampling at 0.1m, 0.45m and 0.8m. Water samples were collected by using a peristaltic pump. As TCE travels down its concentration increases as evident by the sampling data.

Residual TCE was analyzed with HSS (Head Space Sampler)/GC-ECD. 1ml gas phase of TCE was injected in GC-ECD after heating the samples for 10min at 80 °C. Concentration of TCE were measured using a HP6890 GC equipped with a DB-624 capillary column (30m, 250um) and electron capture detector (ECD)

The synthesized nZVI could rapidly degrade TCE according to equations (2) and (3). The mechanism by which TCE is degraded by nZVI is via electron transfer. Temporal and spatial variation in TCE concentration in the M-PRB system are presented in Figure 2. Before Injection, the highest pre-injection concentration of TCE was observed at 5.51ppm and after injection the value decreased to 0.37ppm in 9days, mean TCE concentration of 4.36mg/L was decreased by 13% after 2days, 71% after 6days and 86% after 9days, respectively.

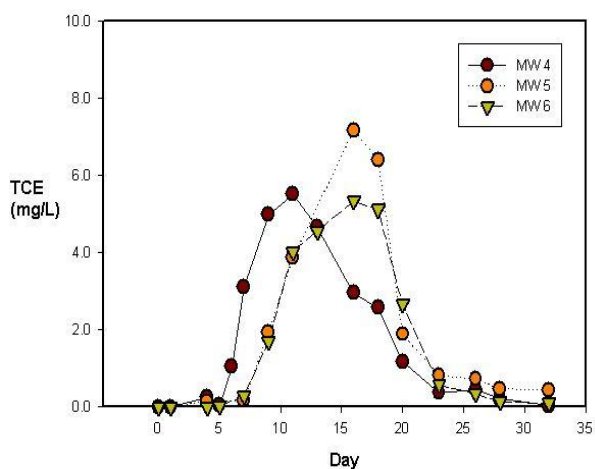


Figure 2. Variation of TCE concentration in the box test after nZVI injection

## Conclusion

Energy and environmental matters are a hot issue today, this study is significant to developing economical and effective treatment media in contaminated soil and groundwater by persistent organic pollutants. It is well known that nano-sized iron particles can degrade wide variety of pollutants both in soil as well as in ground water. Performing reserach has demonstrated that reactivity for the dechlorination of chlorinated organic compounds through a box test. The laboratory-synthesized particles have been shown to be quite stable under ambient conditions. It is expected that These nano-sized iron have huge potential in soil and groundwater treatment<sup>5</sup>. The pilot scale box test also have been shown that it is a good attempt to describe reaction of nFe and to concern with a matter what we would solve to apply further field scale.

## Acknowledgements

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