

Investigation of In-situ Remediation of Benzene and MTBE-contaminated Groundwater by Chemical Oxidation Using Stabilized Zero-Valent Iron Nanoparticles (Case Study: Southern Tehran Aquifer)

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Contaminated groundwater by gasoline spill is a worldwide environmental problem. Gasoline contains methyl tert-butyl ether (MTBE) and benzene, which are the chemicals of concerns (COCs) among the gasoline components. MTBE is highly water soluble and has a low Henry's law constant and low soil adsorption coefficient. Therefore, MTBE can easily move through the soil and then accumulate, distribute or migrate in groundwater. Accidental releases of petroleum products from pipelines and from aboveground and underground storage tanks are the most common causes of groundwater contamination in most countries. Due to issues of taste and odor, health concerns, carcinogenic effects of benzene and MTBE, many attempts have been made to remediate contaminated groundwater. Due to the limitations of conventional groundwater cleanup technologies (e.g., pump & treat, air stripping and permeable reactive barriers (PRB)), in-situ chemical oxidation (ISCO) has become one of the attractive remedial alternatives for petroleum-hydrocarbon contaminated groundwater in recent years.

In addition to oxidation-reduction potential (ORP) of oxidants, hydrogeological and geological characters and dispersion diagram of contaminants and other effective factors in aquifer must be identified and considered before designing ISCO system. Based on natural conditions of the case study area including approximately fine grained aquifer, low permeability, low concentration of dissolved autochthonous iron and high levels of scavengers like ions and other organic matters, we need a potent and stable process simultaneously to access an efficient distribution and link between chemical agents and target contaminants. Thus, in this study Fenton chemical oxidation ($\text{H}_2\text{O}_2/\text{Fe}$) using stabilized nano zero-valent iron particles (S-NZVI) was used. Among different sources of iron as catalyst in ISCO, S-NZVI was opted. This study focuses on in-situ remediation of contaminated groundwater by Fenton's oxidation using stabilized-NZVI particles to gain more efficiency and ROI in special conditions of southern Tehran Aquifer. The main objectives of this study were to 1. assess the feasibility and effectiveness of applying the S-NZVI in ISCO injection system as a catalyst on the control of petroleum-hydrocarbon plume; 2. determine the optimum components of the ISCO materials including H_2O_2 , S-NZVI, and in some cases required pH; 3. determine the level of some hazardous by-products including tert-butyl alcohol (TBA) and acetone in simulated conditions; 4. assess the influences of physicochemical conditions of groundwater on remediation efficiency. The tests were implemented on a bench-scale pilot with a one-dimensional soil column and similar chemical and physical conditions of the region.

Materials and methods: To simulate the qualitative conditions of the contaminated groundwater, MTBE, and BTEX were used as the chemical of concerns (COCs) but only MTBE and benzene were assessed as target contaminants. Uncontaminated and non-uniform sand, silt, and clay (50% fine grained sand and 50% low-Plasticity silt and clay) (Soil Unified Classification: "SM") were mixed as simulated porous media. To achieve the average porosity of $n=0.38$ and the average hydraulic conductivity (k) equal to 0.001cm/s , a standard was defined for compacting of the soil mixture in the column. Water head of all reservoirs was equal and varied between 140 and 135cm during reaction time and the length of the soil column was 32cm ($i=\Delta h/\Delta l \approx 4.3$).

Before starting each experiment, soil column was flushed with a 1mM HCl solution at approximately 10 Pore Volume (PV) and then was washed with de-ionized water at 4-5 PV. After this preparation process, predominant dissolved anions and cations in effluent water decreased to below 10 mg/L. Three clean reservoirs considered to inject polluted water, H_2O_2 solution and S-NZVI suspension into the column. Then salts, MTBE, BTEX, sulfuric acid and caustic soda were added to de-ionized water to obtain the required values for each reservoir. To avoid agglomeration, deposition and oxidation of S-NZVI particles by dissolved oxygen (DO) in its reservoir and to keep a homogenous suspension, before and during the injection, N_2 gas was sparged to the suspension for mixing and removing DO. To reduce volatilization of MTBE and BTEX from water, the reservoir was isolated against air with a flexible cap and was cooled too. At the end of each test, a 4mL sample was taken from the last sampling point on the column by a syringe and stored in a sealed glass container with no headspace. It was then kept in the refrigerator for

maximum 3 days until analysis time.

Discussion and results: At first, for investigation of system efficiency and finding optimum concentrations of the agents at simulated conditions including neutral pH range, temperatures between 15°C and 20°C and certain COCs and ion levels, different concentrations of agents were injected into the column. The concentrations of MTBE and benzene in the influent and effluent were measured to calculate remediation efficiency. Blank experiments illustrated that approximately 20% of MTBE and 30% of benzene can be absorbed in fine grained particles of soil during the initial passage of contaminated water before the reaction starts. Therefore, a preparation time of 1.5hr was considered to saturate the soil in order to eliminate COCs absorbing capacity of the soil. Degradation of MTBE and benzene can be increased with the increasing of H₂O₂ and S-NZVI concentrations. However, this procedure will continue till a certain level of each one (Fig. 1). It was concluded that for remediation of simulated groundwater polluted with approximately 2mg/L MTBE and 1mg/L BTEX, optimum concentrations of H₂O₂ and S-NZVI were 1500 mg/L and 300 mg/L, respectively. This leads to elimination of 78% of MTBE and 87% of benzene in the pilot with milli molar ratios.

and Then, to assess the degradation of COCs and hazardous by-products of the reaction (acetone and TBA) during run time, samples were taken from all sampling points on the length of the column. The by-products were generated first and then were degraded as an organic matter by hydroxide free radicals in oxidation process. At least, 90 minutes after the beginning of the reaction, by-product concentrations were obtained less than 0.1 ppm on average. Thus, it can be claimed that the remediation has no problem in this respect. The tests demonstrated that degradation rates of MTBE and benzene are less than values previously reported by other researchers. It is due to differences between complete mixed conditions of batches in other researches and conditions of this study including using porous media (laminar flow), the type of iron, and high levels of scavengers like ions which reduce the availability of radicals to contaminants. S-NZVI unlike NZVI, ZVI, and ferrous salts, supply Fe²⁺ ions continuously to react with H₂O₂ during passing through the column. Thus, hydroxyl radicals are generated continuously (not immediately) and degrade COCs. This process causes more distribution of agents in subsurface media and increases the ROI.

In the next part of the study, to investigate the effects of pH on remediation efficiency, the optimum concentrations (H₂O₂=1500mg/L and S-NZVI=300mg/L) were injected and all experiments performed at 16-17°C to simulate ion conditions. The tests demonstrated that the efficiency is more in lower pH so that 90% reduction in MTBE and 96% reduction in benzene occurred at pH=3.2. Thus, alkaline conditions result in drastic reduction of remediation efficiency or waste some of consumed iron. In the other hand, high pH conditions increase iron intake and low pH condition can help iron to be solved in water.

In the next part, to assess the effects of ion concentrations on remediation efficiency, the optimum concentrations were injected and all experiments were performed at 10-15°C, pH=6.5-7, and different ion conditions. Five categories of TDS were selected for injection. Results illustrated that at very low levels of ions, the removal efficiency will be approximately 92% for MTBE and 96% for benzene. Thus, existence of ions up to real concentrations of the area causes 15% and 9% reduction in removal efficiency of MTBE and benzene, respectively. On the other hand, they increase consumption of reaction agents. Ions including HCO₃⁻, CO₃²⁻, SO₄²⁻, Mg²⁺ and Ca²⁺ have more effect and ions including Cl⁻, NO₂⁻, NO₃⁻, Na⁺ and K⁺ have lower effect on efficiency reduction. Ions can consume iron particles and cause formation of an insoluble layer on the surface of particles. Using S-NZVI instead of bare NZVI or ZVI, partially, helps the particles to be more stable against the unwanted reactions during passing the media.

Conclusion: This study showed that using S-NZVI instead of micro-ZVI powder can reduce consumption of iron as catalyst and increase the ratio of H₂O₂/Fe₀. S-NZVI unlike NZVI, ZVI and ferrous salts, supply Fe²⁺ ions continuously to react with H₂O₂ during passing through the column. Thus, hydroxyl radicals are generated continuously (not immediately) and degrade COCs. This factor helps the agents to distribute more in the subsurface media and increases the ROI. Results illustrated that in theory MTBE and benzene could be removed in this system significantly. But in practice, full-scale pilot tests must be done after a design process to determine the method sufficiency.

Keywords: benzene, fenton chemical oxidation, groundwater, MTBE, Southern Tehran's aquifer, stabilized nano zero, valent Iron

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