

Original paper

Benzene and MTBE removal by Fenton's process using stabilized Nano Zero-Valent Iron particles

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ABSTRACT

A bench-scale study was designed for removal of Methyl Tertio Butyl Ether (MTBE) and benzene from south of Tehran groundwater. The experiments were implemented on a one-dimensional soil column with similar chemical and physical conditions of the region. Fenton's chemical oxidation with stabilized nano zero-valent iron particles (S-NZVI) as catalyst was used. For treatment of groundwater polluted with 2 mg L⁻¹ MTBE and 1 mg L⁻¹ benzene, optimum concentrations of H₂O₂ and S-NZVI were 1500 and 300 mg L⁻¹, respectively. The optimum concentrations led to 78 % elimination of MTBE and 87 % of benzene. Hazardous by-products (acetone and tertio-butyl alcohol) concentrations were less than 0.1 mg L⁻¹, which were considered to be negligible. The soil permeability was reduced to 30 % after removal process. To increase the system efficiency and reduce the consumption of iron, the reaction environment was acidified down to pH = 3.2 led to removal efficiency of 90 % and 96 % for MTBE and benzene, respectively. The scavengers (ions) reduced the system efficiency up to 15 %. This study indicates that theoretically the MTBE and benzene could be removed from groundwater using Fenton's chemical oxidation with S-NZVI.

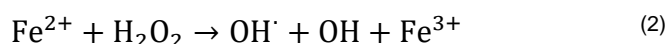
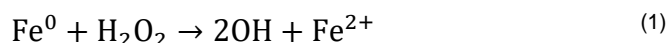
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1. Introduction

Polluted groundwater by gasoline spill is a worldwide environmental problem. Gasoline contains methyl tertio-butyl ether (MTBE) and benzene, which are the chemicals of concern (COCs) among the gasoline components. Accidental release of petroleum products (e.g., gasoline, diesel) from pipelines, aboveground storage tanks (ASTs), and underground storage tanks (USTs) are the most common causes of groundwater contamination in many countries. MTBE is highly water soluble, and has a low Henry's law constant and low soil adsorption coefficient. Therefore, the MTBE can easily move through the soil and then accumulate, distribute or migrate in groundwater. Due to taste and odor concerns, human health effects, and uncertainty about the carcinogenic effects of the MTBE in groundwater (class C in carcinogenic substances) (U.S. EPA, 1997), many governmental agencies have issued drinking water standards for the MTBE. The U.S. EPA has issued an interim measurement of 20–40 µg L⁻¹.

Benzene is ranked in 2003 CERCLA Priority List of Hazardous Substances based on frequency of its occurrence at EPA National Priorities List sites, toxicity, and potential for human exposure to these substances (Crimi and Taylor 2007). Long term effects of benzene toxicity have been proven. Benzene can cause adverse effects on central nervous system and eventually leukemia in humans. World Health Organization (WHO) has considered 10 µg L⁻¹ as a threshold for benzene in drinking water.

Fenton's reagent (H₂O₂/Fe²⁺) is one of the most effective methods for removal of refractory organics (Mohajeri et al. 2011). In Fenton's process, hydrogen peroxide can be activated chemically by catalysts such as transition metals (e.g., ferrous ion (Fe²⁺)) to produce hydroxyl free radicals (OH[•]) with high oxidation potential (OP):



Hydroxyl free radicals (OP=2.8 V) are capable of degrading organic compounds to simpler and usually less harmful organic components and eventually to carbon dioxide and water. In remediation process, reactions that would be considered thermodynamically favorable based on OP values may be impractical under area conditions. The rates of oxidation reactions are dependent on other groundwater physico-chemical parameters that must be considered simultaneously. These parameters are temperature, pH, concentration of the reactants and catalyst, level of metals (e.g., autochthonous iron), by-products reaction as well as system impurities (e.g., natural organic matter and oxidant scavengers) like ions.

In Fenton's process, iron as a catalyst can be provided from a variety of sources like autochthonous iron, ferrous salts (Fe²⁺) (e.g. FeSO₄), zero-valent iron powder (ZVI) and different forms of nano zero-valent iron particles (NZVI). Fe²⁺ ions are highly vulnerable in subsurface environment (Roden and Zachara 1996). In Fenton's process using ferrous salts, Fe²⁺ will generate immediately but it is hypothesized that in Fenton's oxidation with ZVI, Fe²⁺ is continuously formed and is available for reaction with H₂O₂ producing OH[•]. On the other hand, Fe²⁺ reacts with H₂O₂ before it is involved in precipitation reactions (Bergendahl and Thies 2004). This subject provides more opportunities for the spread of iron ions in the aquifer to access more radius of influence (ROI). The use of nanoscale zero-valent iron (NZVI) instead of micro/macro-scale zero-valent iron could potentially reduce the consumption of iron and be more effective in both cost feasibility and contaminant remediation because of its small size and large specific surface area. The NZVI is highly reactive with the contaminants and rapidly reacts with surrounding media in the subsurface, such as dissolved oxygen and water, and other non-target compounds. This means that there can be a significant loss of the NZVI reactivity that occurs before the particles reach the target components. Rapid aggregation, attachment to soil grains and limited mobility of bare

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nanoparticles in saturated porous media reduce their active surface and limit the particle stability and the ability to deliver the NZVI dispersions in the subsurface (Phenrat et al. 2008; Saleh et al. 2007). In addition, the agglomeration and particles attraction to soil grains lead to clogging of the soil pores. In order to overcome these problems, surface coatings can be added to the particles to provide electrostatic stabilization or steric repulsion. The stabilization increases the surface charge and reduces the interaction between the highly reactive surface of the bare NZVI particles and the geochemical conditions of the surrounding media (He et al. 2007). Based on laboratory column tests to assess the particles' ability to transport within the subsurface environment under different conditions, surface modifications have shown to decrease particle-grain attraction on average by two to four times, but depends on the coating as high as nine times (Saleh et al., 2007).

The main objectives of this study were 1) to assess the feasibility and effectiveness of applying the stabilized Nano Zero-Valent Iron (S-NZVI) as a catalyst in a simulated injection system; 2) to determine the effective components in the removal system including H_2O_2 , S-NZVI and in some cases required pH; 3) to determine the levels of some hazardous by-products including tertio-butyl alcohol (TBA) and acetone and 4) to assess the influences of physico-chemical conditions of groundwater on removal efficiency. Simulated soil column studies were conducted to fulfill the objectives. This study focuses on removal of contaminated groundwater by Fenton's oxidation using the stabilized-NZVI particles to gain more efficiency and ROI in special conditions of the case study aquifer described in the next section. The MTBE and benzene as the significant gasoline ingredients were investigated as the target contaminants.

2. Materials and methods

2.1. Study area

The considered aquifer is located in South of Tehran, Iran, between latitudes $35^{\circ} 33' N$ and $35^{\circ} 29' N$ and between longitudes $51^{\circ} 27' E$ and $51^{\circ} 23' E$. From the ground surface to approximately 30 m below, the soil consisted of hydraulic filling materials composed of fine clayey grain and sandy silt zones. The aquifer is mostly unconfined with approximately 20 m in depth and hydraulic conductivity (k) of 10^{-3} to $10^{-4} \text{ cm s}^{-1}$ (Idemitsu 2003; FTS, 2008). In towns and villages close to Tehran Oil Refinery Company (TORC), significant amount of water for daily life and agricultural use is taken from qanats and wells (Idemitsu 2003). According to technical reports provided by a committee for investigation of oil pollution in TORC, leakage from pipelines, USTs, ASTs and waste evaporation ponds are the main sources of the MTBE and benzene contaminants in the groundwater (Shirdam and Gandomkar 2005).

Based on natural conditions of the area including mostly fine grained aquifer, low permeability, low concentration of dissolved autochthonous iron and high levels of scavengers like ions, a sustainable process is needed to distribute the chemical agents in the subsurface area and to create an effective contact between the target contaminants and the reaction agents. In this study Fenton chemical oxidation (H_2O_2/Fe) with the stabilized nano zero-valent iron particles (S-NZVI) was used. Due to short life and low mobility of the bare NZVI, the ZVI and ferrous salts in groundwater environment, the S-NZVI was employed as the catalyst instead.

2.2. Materials

To simulate the qualitative conditions of contaminated groundwater, the MTBE and benzene were used as the COCs. To supply the water ions, magnesium sulfate hepta-hydrate, sodium bicarbonate, calcium chloride dehydrates and sodium sulfate, and to adjust the pH, sulfuric acid and sodium hydroxide were utilized. Hydrogen peroxide (35%) was used as the oxidant and hydroxyl radical generator. All chemicals and reagents were purchased from Merck (Darmstadt, Germany).

The S-NZVI or stabilized water dispersion of zero-valent iron nanoparticles (NANO FER 25S slurry 13 %; NANOIRON s.r.o Company, Rajhrad, Czech Republic) was used as the catalyst. NANO FER 25S has an average particle size of 50 nm and average surface area of $20\text{--}25 \text{ m}^2 \text{ g}^{-1}$ (Xue and Sethi 2012). The ingredients of this product (without aging effect) include 14-18 % NZVI, 2-6 % Fe_3O_4 , 0-1 % Carbon, 3 % surfactant and 77 % H_2O . This product with special surface modification is based on combination of a biodegradable organic and inorganic stabilizer. Due to the narrow size distribution of nanoparticles and sophisticated stabilization process, the product exhibits a high reactivity and very low degree of agglomeration, which

are excellent migration properties for the groundwater remediation technologies.

2.3. Preparation of soil column

Uncontaminated sand, silt and clay (50 % fine grained sand and 50 % low plasticity silt & clay) were mixed as simulated porous media to produce heterogenous soil column. According to Unified system, classification of the soil was "SM" with size distribution as follow: $D_{max} = 1.2 \text{ mm}$, $D_{80} = 0.6 \text{ mm}$, $D_{60} = 0.15 \text{ mm}$, $D_{50} = 0.074 \text{ mm}$ and $D_5 = 0.006 \text{ mm}$. The porous medium properties were simulated as bulk density, ρ_b , of 1.6 g cm^{-3} , particle density, ρ_s , of 2.7 g cm^{-3} , and average porosity of the packed system, n , of 0.38. The experiments were performed in a cylinder made from plexi-glass with length of 35 cm and internal diameter of 5 cm. To achieve an average of $k = 0.001 \text{ cm s}^{-1}$ using a falling head permeameter, a standard was defined for compacting of the soil mixture in the column. After adding 150 mL de-ionized water to 1000 g soil, each layer with a 10 cm height is compacted by a 650 g piston that is dropped five times from a height of 10 cm. A diffuser covers with the height of 3 cm made from permeable uncontaminated sand was placed on the top of the soil column to provide a uniform distribution of S-NZVI suspension and contaminated water into the column.

Before starting each experiment, soil column was flushed with a 1 mM HCl solution at approximately 10 pore volume (PV) (6 h flow at setup conditions) and then it was washed with de-ionized water at 4-5 PV (3 h flow at setup conditions). After this preparation process, the concentration of predominant dissolved anions and cations in effluent water were reduced to below 10 mg L^{-1} . The dissolved ions except bicarbonate and carbonate ions were measured by an ion chromatograph (761 compact IC- metrohm) (Anionic column: metrosep Dual 2/6.1006.100; Cationic column: metrosep cation 1-2/6.1010.000). Bicarbonate and carbonate ions were quantified by titration method. The cylinder was washed by de-ionized water and placed in oven for 24 h at 80°C .

2.4. Column experiments

Simulated removal system in this study can be seen in Fig. 1. For each experiment, a new soil column was prepared as explained in previous part. Natural qualitative conditions of the contaminated groundwater were used for simulation of the column. So, salts, the MTBE, benzene, sulfuric acid and caustic soda were added to de-ionized water to obtain the values of Table 1 for each reservoir. The concentrations after mixing the contents of three reservoirs at the top of the column can be seen in Table 1. Before starting each run, 1.5-2 PV (1.5-2 h flow) of contaminated water with approximately certain concentration of the MTBE and benzene was injected to pass through the column and create a medium with uniform concentrations. After assigning H_2O_2 and S-NZVI concentrations for each test, to find optimum values, the reservoirs were connected to the column. The run time was 1.5 h for all tests. Water head of all reservoirs was equal and varied between 140 and 135 cm during reaction time. Length of the soil column was 32 cm. To avoid agglomeration, deposition and oxidation of the 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 into the suspension for better mixing and removing DO. On the other hand, the S-NZVI suspension was produced by de-ionized and deoxygenated water. It is important to keep the NZVI surface fresh during synthesis and also before injection in each reactive zone (Chien et al. 2006). To reduce volatilization of the MTBE and benzene from the water, the reservoir was isolated against the air with a flexible cap (to avoid air pressure reduction above the water during the discharging) and was cooled. During the tests, to prevent light from entering into the column and H_2O_2 reservoir, aluminum foils were stretched around them. At the end of each test, a 4 mL sample was taken from the last sampling point on the column (P4) by a syringe and was stored in the sealed glass container with no headspace and then was kept in the refrigerator for maximum 3 days until analysis time. For investigation of degradation of the COCs and reaction by-products during run time, samples were taken from all sampling points on the column (P1, P2, P3, P4). The different pH and ion concentrations were adjusted to investigate the pH and ions influences on removal efficiency. Different concentrations of ions were added step by step from zero to natural levels found in the area.

2.5. Analytical methods

The concentrations of the MTBE, benzene, acetone and the TBA in liquid phase were measured using a purge and trap GC-MS (6890N Series GC; 5973N series MS; 3100 series TEKMAR purge & trap) with a 0.5 μm * 320 μm * 60 m capillary column (model TRB5). In accordance to EPA 524.2 method (U.S. EPA, 2008) Calibration curves

were prepared for the MTBE, benzene, the TBA and acetone. The method detection limits were 1 $\mu\text{g L}^{-1}$ for the MTBE and benzene and 10 $\mu\text{g L}^{-1}$ for acetone and the TBA.

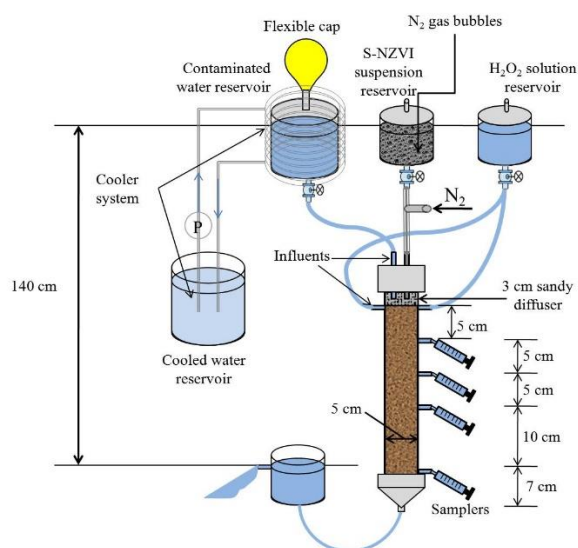


Fig 1. Laboratory soil column setup.

Table 1. Water chemistry of the reservoirs.

	Parameters	Cotaminated water reservoir	H ₂ O ₂ solution reservoir	S-NZVI suspension reservoir	Mixture of tree reservoirs
Cations	Na ⁺ (mg L ⁻¹)	240	480	<5	240
	Mg ²⁺ (mg L ⁻¹)	60	120	<5	60
	Ca ²⁺ (mg L ⁻¹)	165	330	<5	165
	CO ₃ ²⁻ (mg L ⁻¹)	ND	ND	<5	ND
Anions	HCO ₃ ⁻ (mg L ⁻¹)	345	690	<5	350
	Cl ⁻ (mg L ⁻¹)	255	510	<15	255
	SO ₄ ²⁻ (mg L ⁻¹)	480	960	<5	480
	TH (mgCaCO ₃ L ⁻¹)	460	920	-	460
Other parameters	pH	6.5-7	6.5-7	6.5-7	6.5-7
	TDS (mg L ⁻¹)	2100	4200	-	2100
	DO (mg L ⁻¹)	5	5	<1	4
	Temp. (average) (°C)	20	20	20	20
COCs	MTBE (average) (mg L ⁻¹)	6	ND	ND	2
	Benzene (average) (mg L ⁻¹)	3	ND	ND	1

3. Results and discussion

3.1. Degradation of COCs and optimum concentration of H₂O₂ and S-NZVI

In the first part of the study, all experiments were performed under neutral pH range. Ionic concentrations in the reservoirs were adjusted in accordance to Table 1 which corresponds to the natural concentrations found in the case study area. Although these experiments were performed at temperatures between 15 °C and 20 °C and under isolated conditions, some of the MTBE and benzene could have evaporated from the water in the reservoir.

The initial concentration of benzene in contaminated water reservoir was adjusted, so that it was approximately 1 mg L⁻¹ at the beginning of the column. The concentrations of the MTBE and benzene in the influent and effluent were measured to calculate removal efficiency. Blank experiments demonstrated that approximately 20 % of the MTBE and 30 % of benzene absorb to fine grained particles of the soil during the initial passage of contaminated water before the reaction start. Therefore, a preparation time of 1.5 h was considered to saturate the soil in order to eliminate the COCs absorbing capacity of the soil. To determine the optimum concentration of H₂O₂ and the S-NZVI, different concentrations were injected into the column.

After chain-initiating reactions (Eqs. (1) and (2)), a chain-propagating sequence usually takes place (ITRC, 2005), which can also generate superoxide ions (O₂⁻), hydroperoxide ions (HO₂⁻), and organic radicals (R[•]):

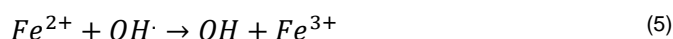
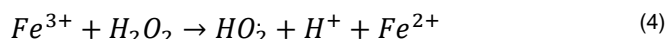
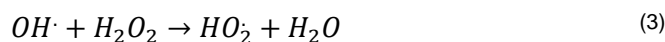
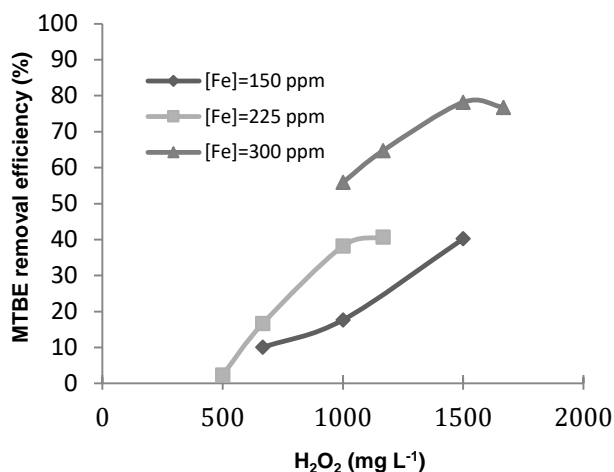


Fig. 2 shows that degradation of the MTBE and benzene is increased by increasing H₂O₂ and the S-NZVI concentrations but this procedure will continue till a certain level of each one. If H₂O₂ is added excessively, according to Eq. (3), generated hydroxyl radicals (OH[•]) react with remained H₂O₂ continuously and hydroperoxide radicals (HO₂[•]) are generated which have lower OP than hydroxyl radicals OP and may decrease the system efficiency. In addition, extra iron can

consume hydroxyl radicals as an important scavenger in accordance to Eq. (5). Therefore, an optimum ratio should be resulted for H₂O₂: Fe.

The optimum concentrations of 1500 and 300 mg L⁻¹ of H₂O₂ and the S-NZVI, lead to the removal of 78 % and 87 % for the MTBE and benzene, respectively. In this condition, the mili molar ratios are 44.12:0.032 for H₂O₂:(MTBE+benzene) and 44.12:5.33 for H₂O₂:Fe⁰. Bergendahl and Thies (2004) reported 95 % removal of 1 mg L⁻¹ the MTBE from de-ionized water at the pH = 7 in batch reactor by Fenton's oxidation using micro-ZVI, with optimum ratios of 6.5:0.011 of H₂O₂: MTBE and 6.5:4.5 of H₂O₂:Fe⁰. By using same technique, about 95 % removal of 1000 mg L⁻¹ the MTBE from de-ionized water at acidic pH is reported by Shahmansouri (2007) with the optimum ratios of 300:11.36 of H₂O₂: MTBE and 300:40 of H₂O₂:Fe⁰.



The increase in the ratios determined in this study is most likely due to some environmental reasons: 1) Soil column vs batch: in batch reactions, better mixing of agents and contaminants takes place whereas fine grained soil of porous media causes laminar flow. So, the reaction probability and H₂O₂:Contaminants ratio increase; 2) High concentration of ions in this study: ions as scavengers lead to higher consumption of oxidants and, so H₂O₂:Contaminants ratio increases; 3) Lower initial concentration of contaminants: which decreases reaction probability of oxidants with H₂O₂ vs scavengers and so more oxidants is required; 4) The type of iron: using nano-ZVI instead of micro-ZVI may reduce consumption of iron and increase the ratio of H₂O₂:Fe⁰; and furthermore 5) Non- acidic conditions: it can increase the consumption of oxidant as well.

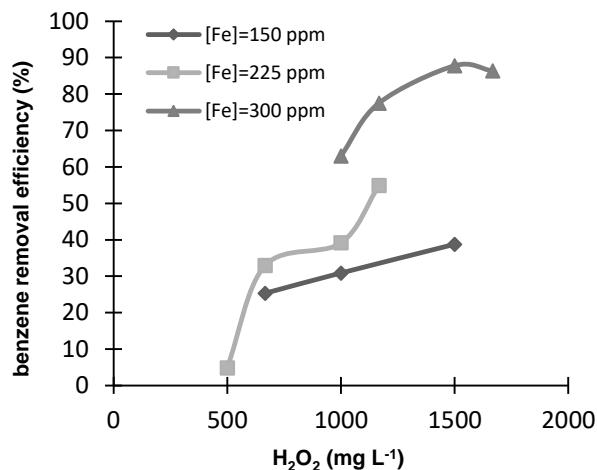


Fig 2. Optimum concentration of H₂O₂ and the S-NZVI at neutral pH range.

3.2. By-products concentrations

Samples taken from various points on the column (P1, P2, P3, P4) demonstrated the degradation of the COCs and selected hazardous by-products of the reaction (acetone and TBA) during the run time at optimum concentration of H₂O₂ and NZVI (Table 2). Fig. 4 illustrates the

generation of by-products followed by their degradation by OH[•] in the oxidation process. The amount of acetone is higher than the TBA because besides the MTBE, other degradation intermediates of the MTBE including TBA, methyl acetate and TBF (tertio-butyl formate) can be degraded to acetone (Burbano et al. 2002; Huang et al. 2002).

Table 2. Degradation of the COCs and concentration of selected hazardous by-products of the reaction (acetone and TBA) (H₂O₂=1500 mg L⁻¹ and S-NZVI=300 mg L⁻¹).

Sample point	Time (min)	[MTBE] (mg L ⁻¹)	[Benzene] (mg L ⁻¹)	[Acetone] (mg L ⁻¹)	[TBA] (mg L ⁻¹)
Influent	0	1.80	0.91	0	0
P1	15	1.01	0.5	0.74	0.22
P2	30	0.60	0.26	0.62	0.19
P3	45	0.51	0.18	0.36	0.04
P4	90	0.43	0.11	0.16	0.02

Fig. 3 illustrates the MTBE and benzene degradation curve kinetically. With assumption of pseudo first order kinetics for the reactions, degradation rate constants (k) of the MTBE and benzene were determined: K_{MTBE}=0.015 min⁻¹ (with R²=0.75) and K_{benzene}=0.02 min⁻¹ (with R²=0.89). Hong et al. (2007) have reported K_{MTBE}=0.77 min⁻¹ for Fenton treatment where reagents were added gradually to deionized water and the initial concentration of the MTBE was 2.8 mM). Burbano et al. (2002) have reported K_{MTBE}=1.75 min⁻¹ for classic Fenton treatment in deionized water, pH=3 and 0.023 mM MTBE as initial concentration. Alizadeh et al. (2013) have reported K_{benzene}=0.13 min⁻¹, for Fenton treatment using the NZVI as catalyst in deionized water, pH=7 and 1 mg L⁻¹ benzene as initial concentration. So, degradation rates of the MTBE and benzene reported in this study are less than values previously were reported by other researchers. This could be due to the differences between complete mixed conditions of batch reactors used in other researches and the conditions of this study (porous media, neutral pH, and natural level of ions) which reduce the availability of hydroxyl radicals to contaminants. The 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 in a slower process. This slow process will cause more

distribution of agents in subsurface media and therefore increase the ROI.

3.3. Effect of pH on removal efficiency

In some cases, the removal efficiency can be increased in a more acidic environment by injecting HCl, H₂SO₄ and C₂H₄O₂ before the remediation process initiation. Experiments were designed to investigate the effect of the pH on removal efficiency. In these tests, the optimum concentrations of H₂O₂ and the S-NZVI were used at 16-17 °C with simulated ion conditions. Fig. 4 (a) illustrates that the efficiency increases in lower pH, for instance, at pH = 3.2 the MTBE and benzene can be eliminated up to 90 % and 96 %, respectively. Acidic pH helps the iron to be solved in water. It seems that in alkaline conditions the OP of hydroxyl radicals reduces and the reactions go into production of Fe³⁺ instead of Fe²⁺ (Chen et al. 2001; Mascolo et al. 2008). Also at higher pH, Fe³⁺ ions react with hydroxide ions and produce non-reactive iron oxide deposits like Fe(OH)₂ and Fe(OH)₃ (Eq. (6)). Therefore, at higher pH some of the consumed irons wasted, while the iron intake increases.

3.4. Effect of ion concentrations on removal efficiency

Ions can act as scavengers in Fenton chemical oxidation. This means that ions can react with removal agents or can settle on the surface of the agents and hinder the reaction process. According to Table 3, five tests with five categories of TDS were designed to investigate effect of ion concentrations on removal efficiency. In these experiments, the optimum concentrations of H₂O₂ and the S-NZVI were used at 16-17 °C and pH = 6.5-7. Fig. 4(b) illustrates that at very low concentrations of ions, the removal efficiency will be approximately 92 % for the MTBE and 96 % for benzene. In natural ion concentrations in the groundwater, the removal efficiency is reduced by 15 % and 9 % for the MTBE and benzene, respectively. On the other hand, ion presence will increase consumption of the reaction agents. HCO₃⁻, CO₃²⁻, SO₄²⁻, Mg²⁺ and Ca²⁺ ions have more effect on efficiency reduction compared with Cl⁻, NO₂⁻, NO₃⁻, Na⁺ and K⁺ ions. Carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) react with OH⁻ and produce carbonate radicals with lower OP (Eq. (7)) (Kommineni et al. 1999). Sulfate ions (SO₄²⁻) consume hydroxyl radicals as well (Crittenden et al. 1996). Anions and cations probably have begun to compete for oxidizing radicals, which have caused the reduction of oxidation efficiencies (Mascolo et al. 2008). A similar study demonstrated that two-valance anions and cations (CO₃²⁻, SO₄²⁻, Mg²⁺ and Ca²⁺) have more effect on the inhibition of reaction. On the other hand, they have more deteriorating effect on the COCs removal efficiencies during Fenton process (Alizadeh Fard et al. 2013). The kinetics (k) of these reactions are less than target reaction kinetics but if the concentration of HCO₃⁻, CO₃²⁻ or SO₄²⁻ is high, the reaction rates (r) can compete with the rate of the target the COCs removal reactions.

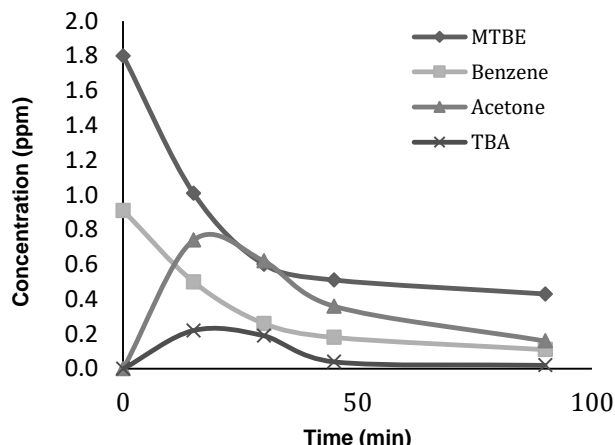
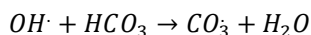


Fig 3. Concentration of the COCs and reaction by-products during run time (H₂O₂=1500 mg L⁻¹ and S-NZVI=300 mg L⁻¹).

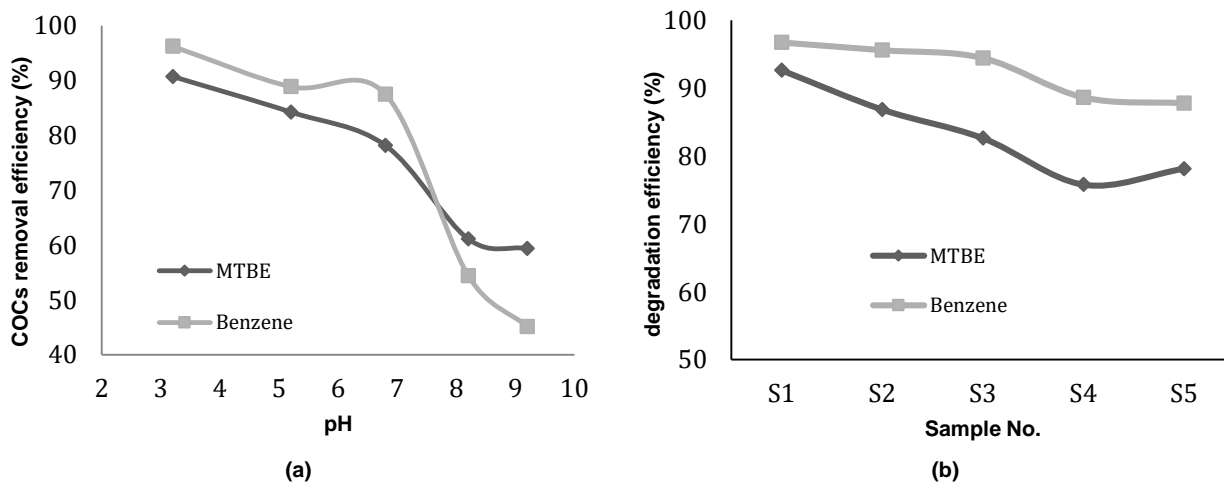


Fig 4. (a) Effect of pH on removal efficiency; (b) Effect of ion concentrations on removal efficiency (H₂O₂=1500 mg L⁻¹ and the S-NZVI=300 mg L⁻¹).

Table 3. Ion concentration (mg/L) to investigate the effect of ion concentrations on removal efficiency.

Sample No.	Na ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻
S1	3	16	2	ND	2	1
S2	63	52	17	85	66	121
S3	124	90	32	170	130	241
S4	185	127	47	256	193	361
S5 (natural conc.)	240	165	60	342	255	477

In addition, the NZVI is a powerful reductant and it can react with halogenated organic matters, carbonate, sulfate, nitrate ions and heavy metals and then transform to Fe²⁺, Fe³⁺ and iron oxides. These reactions consume iron particles or they cause the formation of an insoluble layer on the surface of iron particles. The use of the S-NZVI instead of the bare NZVI or ZVI, partially helps the particles to be more stable against the unwanted reactions during the infiltration of the media.

3.5. Effect of removal process on soil permeability

Reduction of permeability after reaction process is one of the shortcomings of the in-situ Fenton chemical oxidation. Agglomeration of iron particles and formation of ferric deposits during oxidation causes

soil pores obstruction. To investigate the effect of the removal process on soil permeability, five experiments were performed to eliminate the COCs using the optimum concentrations of H₂O₂ and the S-NZVI at simulated conditions mentioned in Table 1. Initial permeability (K) of the soil columns in all experiments was approximately 0.001 cm s⁻¹. At the end of each test, permeability was measured. Totally, the permeability of the soil was reduced by 30 % on average (with a standard deviation equals to 4.7 %) during the oxidation process (Table 4). In a similar study, 15 % reduction of permeability in a sandy soil has been reported (Shahmansouri 2007). It can be concluded that pores in fine grained soils are obstructed faster and easier by iron deposits than coarse grained soils. Therefore, in this study, removal process will have a greater impact on the soil permeability, because 50 % of the simulated soil column is composed of fine grained particles.

4. Conclusions

The use of the S-NZVI instead of the micro-ZVI powder can reduce consumption of iron as catalyst and increase the ratio of $H_2O_2:Fe^0$. The S-NZVI unlike the NZVI, ZVI and ferrous salts can supply Fe^{2+} ions continuously to react with H_2O_2 during the filtration in the column. Hydroxyl radicals are generated in a slower process. This factor helps the agents to distribute more in subsurface media and increases the ROI.

For remediation of simulated groundwater polluted with 2 mg L^{-1} the MTBE and 1 mg L^{-1} benzene, optimum concentrations of H_2O_2 and S-NZVI were 1500 and 300 mg L^{-1} , respectively; leading to the elimination of 78 % of the MTBE and 87 % of benzene in the column study. In cases of low buffering capacity of the reaction environment, acidification of groundwater before starting the removal process is an effective way to reduce drastic changes in the soil permeability and to increase the removal efficiency. Concentrations of generated by-products like

acetone and the TBA were approximately 0.1 mg L^{-1} on average at the end of the run time which seems to be relatively low.

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