

Degradation of chlorinated organic solvents in aqueous percarbonate system using zeolite supported nano zero valent iron (Z-nZVI) composite

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Abstract Chlorinated organic solvents (COSs) are extensively detected in contaminated soil and groundwater that pose long-term threats to human life and environment. In order to degrade COSs effectively, a novel catalytic composite of natural zeolite-supported nano zero valent iron (Z-nZVI) was synthesized in this study. The performance of Z-nZVI-catalyzed sodium percarbonate (SPC) in a heterogeneous Fenton-like system was investigated for the degradation of COSs such as 1,1,1-trichloroethane (1,1,1-TCA) and trichloroethylene (TCE). The surface characteristics and morphology of the Z-nZVI composite were tested using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Total pore volume, specific surface area, and pore size of the natural zeolite and the Z-nZVI composite were measured using Brunauer-Emmett-Teller (BET) method. SEM and TEM analysis showed significant elimination of aggregation and well dispersion of iron nano particles on the framework of natural zeolite. The BET N₂ measurement analysis indicated that the surface area of the Z-nZVI composite was 72.3 m²/g, much larger than that of the natural zeolite

(0.61 m²/g). For the contaminant analysis, the samples were extracted with n-hexane and analyzed through gas chromatograph. The degradation of 1,1,1-TCA and TCE in the Z-nZVI-catalyzed percarbonate system were 48 and 39 % respectively, while strong augmentation was observed up to 83 and 99 %, respectively, by adding the reducing agent (RA), hydroxyl amine (NH₂OH·HCl). Probe tests validated the presence of OH[•] and O₂^{•-} which were responsible for 1,1,1-TCA and TCE degradation, whereas both free radicals were strengthened with the addition of RA. In conclusion, the Z-nZVI/SPC oxidation with reducing agent shows potential technique for degradation of groundwater contaminated by 1,1,1-TCA and TCE.

Keywords Nano scale zeolite composite · Zero valent iron · 1,1,1-TCA · TCE · Groundwater remediation

Introduction

1,1,1-trichloroethane (1,1,1-TCA) and trichloroethylene (TCE) are typical chlorinated organic solvents (COSs) that are extensively found in contaminated soil and groundwater, posing environmental problems globally (Gu et al. 2012; Zhang et al. 2015). The COSs are widely used in various industrial applications such as in detergents, pesticides, paint thinners, resins, and glues, but their non-eco-friendly disposal results in considerable contamination of soil and groundwater (McCarty and Perry 2010). The COS contaminants in soil and groundwater resources cause severe threats to human life and environment due to a number of harmful characteristics, e.g., carcinogenicity and cytotoxicity harmful for the central nervous system, the immune system, and the endocrine system (Bellona and Drewes 2007; Clewell et al. 1995; Wigle et al. 2007; Zhao et al. 2015). In recent years, scientists and

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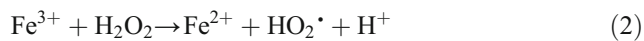
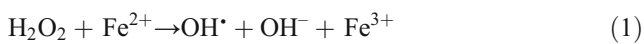
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researchers have focused to develop efficient and state-of-the-art technologies such as enhanced solubilization flushing (Watts and Teel 2005), permeable reactive barriers (Vogan et al. 1999), in situ air stripping (Adams et al. 2011), thermal treatment, and in situ bioremediation (Miao et al. 2015a, b, c) to remediate the chlorinated solvent-contaminated groundwater. Most of the biological technologies are cost-effective for remediation, but their prolonged treatment period makes them inefficient for practical and commercial applications (Oller et al. 2011). In contrast, in situ chemical oxidation (ISCO) is considered as an efficient method for effective degradation of COSs (Akyol and Yolcubal 2013; Wu et al. 1999).

Several studies utilized potassium permanganate, persulphate, ozone, and fenton reagent in chemical oxidation processes as chemical oxidants for remediation of contaminated groundwater and soil (Huang et al. 2001; Liang et al. 2004; Neyens and Baeyens 2003; Sunder and Hempel 1997). Fenton reagent represents an attractive option due to its high reactivity-degrading COSs with low environmental impacts (Burbano et al. 2005; Che and Lee 2011; Li et al. 2015). In Fenton process, hydrogen peroxide is decomposed by Fe²⁺ to generate very active species, mainly hydroxyl radicals (OH[•]), as shown in Eqs. 1 and 2 (Che and Lee 2011).



Hydroxyl radicals (OH[•]=2.76 V) generated during this process show higher oxidation potential than permanganate (1.68 V), persulfate (2.01 V), and ozone (2.01 V) (Liang et al. 2004) and can react with COSs at higher degradation rates. OH[•] reactions with organic compounds are diffusion-controlled with second-order rate constant $K > 10^9 \text{ M}^{-1}\text{s}^{-1}$ (Miao et al. 2015a, b, c). However, in Fenton process, H₂O₂ is unstable with a short life-time when injected into the groundwater. Moreover, Fenton process is strongly pH-dependent at an optimum value of 3–4 (Watts and Teel 2005). Precipitation of Fe²⁺ to (Fe(OH)₃) near neutral pH causes loss of catalyst and injection-well plugging problems (Klamerth et al. 2010; Watts and Teel 2006). Nano zero valent iron (nZVI) due to its high surface area and reactivity has been used as a reagent in many environmental remedies since ferric ions are converted into ferrous ions at an increased rate as shown in Eq. 3 (Crane and Scott 2012).

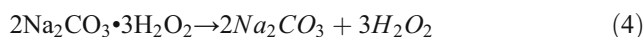


Fe⁰ is considered to be an efficient catalyst by generating more Fe²⁺ and ultimately increasing the production of OH[•] (Han et al. 2015; Ramirez et al. 2007). However, the main drawback is the significant leaching of cation of iron in the

acidic pH range using heterogeneous Fenton-like systems (Liou et al. 2004).

In order to address such issues, iron precursors supported on cation exchange resins (Fukushima et al. 2000; Shin et al. 2008) and minerals (Sun et al. 2012; Xu and Wang 2012) have been synthesized in heterogeneous Fenton-like systems. In this study, a novel catalyst is synthesized using the economically viable and abundantly available natural zeolite having an Al/Si ratio of 1.56 that provided a support to attach nano iron particles. So far, no data is available for the degradation of organic contaminants (1,1,1-TCA and TCE) using natural zeolite-supported iron nano (Z-nZVI) composite (Liou et al. 2005) in the presence of hydrogen peroxide. Natural zeolite has very short specific surface area (0.6018 m²/g) due to the presence of impurities like feldspar and quartz (Miura et al. 2009). The zeolites are cheap and extensively utilized for soil fertility improvement and as adsorbents (Nishimoto et al. 2015) but not utilized as catalyst for degradation of COSs (Devi et al. 2009; Fukuchi et al. 2010, 2013).

A number of studies have been conducted to find alternative oxidants having identical oxidation potential to Fenton reagent such as sodium persulfate (SPS), calcium peroxide (CaO₂), and sodium percarbonate salt (SPC, 2Na₂CO₃•3H₂O₂) (Anipsitakis and Dionysiou 2004; Bogan et al. 2003; Christina and Sedlak 2008; Liang et al. 2004; Miao et al. 2015a, b, c; Northup and Cassidy 2008). Recently, SPC has attracted much attention as an alternative to liquid H₂O₂ (Devi et al. 2009) due to its stability in handling, storage, and transportation together with low cost. Solid-powdered SPC ensures the safety in applications in order to reduce the chances of splashes and spilling during transportation as compared to the liquid H₂O₂. In recent ISCO practices, SPC is being used as an alternative oxidant (de la Calle et al. 2012) due to similar functional benefits as liquid H₂O₂. Equation 4 shows the reaction of SPC in Fenton-like process.



As compared to the Fenton reagent, the SPC is more advantageous; e.g., (i) the SPC is considered to be applicable in a wider pH range, (ii) the SPC decomposition products are non-toxic for microbes that make it compatible for further bioremediation, and (iii) the oxidation products of SPC are water, sodium carbonate, and carbon dioxide that are naturally occurring substances (Neamtu et al. 2004). Therefore, in this study we synthesized natural zeolite-supported Z-nZVI composite to investigate its activity as a catalyst to degrade 1,1,1-TCA and TCE with SPC as an oxidant. To the best of our knowledge, natural zeolite-supported Z-nZVI composite-catalyzed SPC system has not been well studied yet. Moreover, the addition of reducing agent (RA) such as hydroxylaminechloride (NH₂OH•HCl) seems to be very effective and potentially applicable in the degradation of organic

solvents by boosting the reduction of ferric into ferrous ions and further promoting the generation of free radicals (Miao et al. 2015a, b, c; Savant et al. 2009; Wei et al. 2015). To elucidate the 1,1,1-TCA and TCE degradation performance, free radical probe compounds were used to investigate the presence of dominant free radicals in Z-nZVI-catalyzed SPC system with and without the addition of the RA. The spectrophotometer was used to investigate the presence of the iron ions in the Z-nZVI-catalyzed SPC system. A novel Z-nZVI composite was synthesized in this research study, and the availability of the oxidative degradation of 1,1,1-TCA and TCE with SPC and Z-nZVI composite with and without addition of RA was evaluated.

Materials and methods

Materials and chemicals

1,1,1-TCA (99.0 %) and TCE (99.0 %) as organic solvents were obtained from Aladdin (Shanghai, China). Sodium borohydride (99.5 %), nitrobenzene (NB, 99.0 %), carbon tetrachloride (CT, 99.5 %), ethanol (99.8 %), ferrous sulfate heptahydrate (99.0 %), sodium nitrate (99.0 %), sodium chloride (99.5 %), sodium sulfate (99.0 %), sodium bicarbonate (99.5 %), SPC (98 %), and aluminosilicates (99.0 %) were acquired from Acros Organics (Shanghai, China). Hydroxylamine hydrochloride (99.0 %), 5,5-potassium biphthalate (99.0 %), and 1,10-phenanthroline monohydrate (98.0 %) were obtained from Shanghai Jingchun Reagent Ltd., Co. (Shanghai, China). The stock solution of 0.15 mM (1,1,1-TCA or TCE) was prepared separately by dissolving in ultra-pure Milli-Q water. To adjust the solution pH, 0.1 M NaOH and 0.1 M H₂SO₄ were used. All reagents were of analytical grade that were utilized without further purification. The deionized water prepared by Milli-Q ultra-pure water process (Classic DI, ELGA, 102 Marlow, UK) using distilled water was used in all experiments.

Preparation of the Z-nZVI composite

The Z-nZVI composite was synthesized using wet ion exchange method (Chen et al. 2011; Wang et al. 2010). To reproduce the results, a detailed description of the utilized method is presented. In this method, natural zeolite (0.5 g) and ferrous sulfate heptahydrate (1.0 g) were mixed in ultra-pure water (250 mL) in a three-neck flask. The initial solution pH was maintained at 4 to inhibit the oxidation of Fe²⁺ using nitric acid (1.0 M), and the mixture was treated with ultrasound for 10 min. The mixture was then stirred briskly at room temperature for another 30 min. A strong RA, i.e., NaBH₄ (1.0 M), was added for effective reduction of Fe²⁺. Black solid particles were separated from solution using vacuum filtration flask

with a 47-mm diameter membrane filter, and sulfate ions from black solid particles were removed through deionized water. Black particles were finally washed with ethanol eliminating traces of sulfate ions and water and further vacuum-dried. Nitrogen atmosphere was provided throughout the process of reduction of Fe²⁺.

Characterization of Z-nZVI composite

Surface characteristics and morphology of natural zeolite and Z-nZVI composite were tested using scanning electron microscopy (SEM, JSM-630LV, Tokyo, Japan) and transmission electron microscopy (TEM, JEM-1400 electron microscope operated at an accelerating voltage at 80 kV), respectively, before and after contaminant degradation. Energy-dispersive X-ray spectra (EDS) was acquired using SEM to estimate the iron content and other elements in the Z-nZVI composite. Total pore volume, specific surface area, and pore size of zeolite and Z-nZVI composite were measured using the Brunauer-Emmett-Teller (BET) method (Quantasorb Jr. Instrument Quantachrome Co., UK). In order to determine the nature and crystal structure of the Z-nZVI composite (before and after usage), X-ray diffractometer (XRD) along with Rigaku D/max diffractometer (2550VB/PC; CuK α ($\lambda=0.154$ nm radiation) were used respectively.

Experimental procedures

Stock solutions of 1,1,1-TCA (0.15 mM) and TCE (0.15 mM) were prepared separately by allowing the pure non-aqueous phase liquid 1,1,1-TCA or TCE to equilibrate with Milli-Q ultra-pure water under gentle stirring for 60 min in the absence of light. A cylindrical glass reactor (inner diameter of 6.0 cm and height of 9.0 cm) was utilized with two openings at the top of the reactor; one is for the dosing purpose and the other for sampling. A temperature bath (DC Ningbo, China) maintained the temperature of the reactor at 20 \pm 0.5 °C by circulating the water through the jacket of the reactor. A known quantity of SPC and Z-nZVI was added in the reactor containing 1,1,1-TCA or TCE solution, and the effective homogeneity of the solution was maintained through a magnetic stirrer. The initial and final pH of solution was recorded. All reagents were added into the reactor before SPC and Z-nZVI addition. Samples were taken at a specific interval of time from the reactor and immediately quenched with n-hexane before COS analyses. All experimental tests were performed twice, mean values were reported, and standard deviations were in the range of 0.015–0.041. Probe tests were performed to find the presence of the reactive oxygen species in the Z-nZVI/SPC system during the reaction period. Same procedure was adopted for probe tests as that of 1,1,1-TCA and TCE degradation except the replacement of 1,1,1-TCA and TCE with NB (OH \bullet probe) or carbon CT (O₂ \bullet^- probe). Control tests

were conducted simultaneously for each experiment without addition of Z-nZVI composite.

Analytical methods

Samples (1.0 mL) of 1,1,1-TCA, TCE, CT, and NB were withdrawn and extracted with n-hexane (1.0 mL) using a vortex stirrer and were analyzed using a gas chromatograph (Agilent GC 7890A, Palo Alto, CA, USA). For 1,1,1-TCA and TCE, oven and injector temperatures were constant at 75 and 240 °C, respectively, and the detector (ECD) was at the temperature of 260 °C. However, in the case of CT, the oven temperature was changed to 100 °C and the rest of the procedure was identical as that of 1,1,1-TCA and TCE. NB measurements were obtained from a flame ionization detector (FID) where the oven, injector, and the detector temperatures were at 175, 250, and 300 °C, respectively. N-hexane is commonly used as a non-polar solvent in chromatography technique for the extraction of COSs from the aqueous solution due to its exceptional advantage of having strong resistance against de-protonation. The average extraction recovery rates (a cleaner GC trace) of N-hexane to extract 1,1,1-TC was in the range of 85–95 %, whereas TCE, CT, and NB have 89.7, 87.5, and 93.1 %, respectively. Spectrophotometer (T-60 UV–VIS Spectrophotometer, Purkinje General Instrument Co., Ltd., Beijing, China) at an absorbance of 512 nm was used to determine Fe²⁺ and Fe³⁺ ions (Tamura et al. 1974). pH meter (Mettler Toledo Delta 320, Greifensee, Switzerland) was used to determine pH of the solution.

Results and discussions

Characterization of natural zeolite and Z-nZVI composite

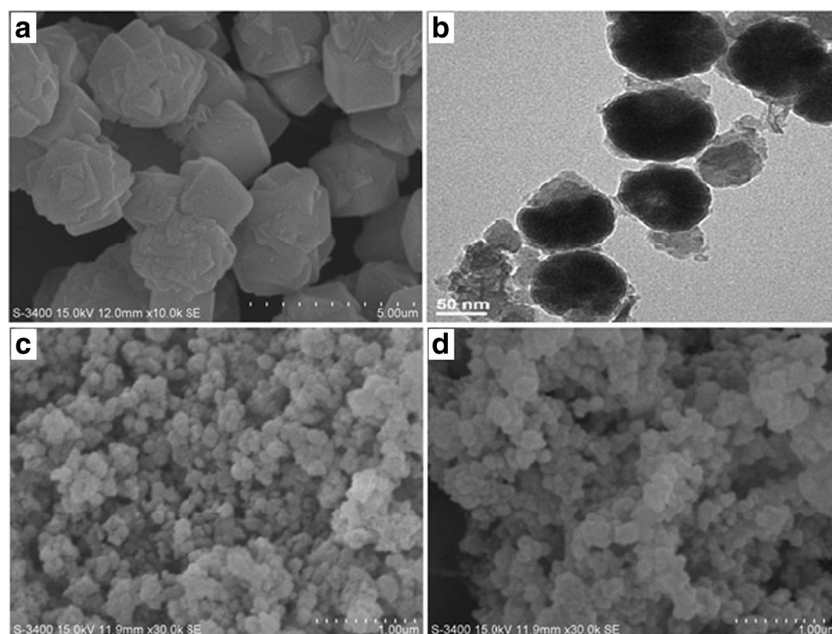
The summarized characterization results based on inorganic elemental contents, specific surface areas (SSAs), specific total pore volume, and average pore diameter of the natural zeolite and Z-nZVI composite are presented in Table 1. To demonstrate the adsorption-desorption, pore size, and pore volume distribution, N₂ isotherm of natural zeolite and Z-

nZVI composite is shown in Figs. S1 and S2 (Supplementary Material). Morphologies of natural zeolite and Z-nZVI are compared, and the TEM and SEM images before and after 1, 1,1-TCA and TCE degradation are shown in Fig. 1. Natural zeolite has a thin layer structure, whereas nZVI particles are distributed on the natural zeolite sheet. It has been previously reported that nZVI particles (spherical shape with an average diameter of 80 nm) tended to aggregate (Wang et al. 2010) and were arranged in net chain due to their intrinsic van der Waals, magnetic interactions, and higher surface energies (He et al. 2007). This aggregation reduced the mobility and reactivity of nZVI particles (Liu et al. 2007). Our results (see Fig. 1a) indicate that the zeolite has a smooth surface as compared to Z-nZVI (Fig. 1b) that has an abrasive surface. Fe⁰ particles are present in the form of light spots over the entire surface of the natural zeolite (Fig. 1c), and the average size of these particles is in the range of 50–100 nm by measuring the diameter of over 100 particles in the grid of different areas. These particles are quasi spherical in shape and distributed on the entire surface of natural zeolite without any noticeable aggregation. Literature also ensures that the support materials for iron particles limit the aggregation that is consistent with our results (Ahmad et al. 2015). Our observations are consistent with the explanation that exchanged Fe²⁺ ions act as seeds to grow Fe⁰ (Qu et al. 2013), and significant shares of Fe²⁺ ions are located in the sodalite cage and a portion in the hexagonal prism (Tong et al. 1996) on the external surface of the zeolite framework which ensured the production of dispersed nZVI particles on the natural zeolite surface (Wang et al. 2010). BET N₂ measurement analysis indicated that natural zeolite has a particle size of 9.97 μm and surface area of 0.60 m²/g, whereas in the case of Z-nZVI, particle size reached 81.0 nm (decreased) and surface area of 72.3 m²/g (increased). It has been reported in literature that increased surface area of the Z-nZVI composite is most likely due to the non-aggregation of the nZVI particles (Kim et al. 2013). After TCE degradation, the average particle size of Z-nZVI was increased from 81.0 to 278.9 nm and the surface area was decreased to 21.5 m²/g. Similar results were also observed in the case of 1,1,1-TCA degradation (see Table 1). The decrease in surface area of the spent Z-nZVI could be due to (i) sintering of the iron particles (Beydoun

Table 1 Summary of the elemental composition by weight % and characterization of natural zeolite and Z-nZVI

	Al %	Si %	Na %	Fe %	O %	SSA (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)	Average particle size (nm)
Natural zeolite	12.77	12.52	28.28	–	39.49	0.61	0.014	7.13	9969.0
Z-nZVI	9.73	9.91	6.60	53.13	20.64	72.3	0.226	13.84	80.9
Z-nZVI after TCE degradation	9.25	9.46	2.37	43.28	49.90	21.6	0.049	9.04	278.9
Z-nZVI after 1,1,1-TCA degradation	10.02	9.65	2.58	41.11	47.68	20.3	0.046	8.99	280.5

Fig. 1 Morphologies of natural zeolite and Z-nZVI. **a** SEM analysis of natural zeolite; **b** TEM analysis of Z-nZVI; **c** SEM analysis of Z-nZVI after 1,1,1-TCA degradation; **d** SEM analysis of Z-nZVI after TCE degradation



and Amal 2002), (ii) reactions occurring on nano particle surfaces (Wang et al. 2010), and (iii) the by-products, i.e., Fe (oxy) hydroxide formed during contaminant degradation process (Seol et al. 2013). Existence of iron in the Z-nZVI composite was verified through the EDS analysis (see Fig. S3) and the elemental composition (see Table 1). Total dissolved iron content was present in lower quantity, and Fe^{2+} ions were predominant in solution initially that made Z-nZVI more advantageous than other Fenton-like catalysts (Fig. S4). The XRD patterns of Z-nZVI before and after 1,1,1-TCA and TCE degradation have been recorded and shown in Fig. S5. The structure of the natural zeolite has noticeable peaks that indicate strong crystalline behavior, whereas the Z-nZVI composite structure shows resemblance with amorphous structure. The XRD results of Z-nZVI after 1,1,1-TCA degradation (Fig. S5b) show peaks 1, 2, 3, and 4 at 2 theta 23.86, 25.75, 26.21, and 27.80 that are likely due to the oxides of iron such as lepidocrocite and maghemite ($\gamma\text{-Fe}_2\text{O}_3$). The peaks 6 and 7 could be due to SiO_2 associated with the zeolite. In addition, peak 8 may be associated with FeO on the Fe^0 . The literature suggested that iron particles in XRD are composed of disordered aggregates (Lim et al. 2006; Zied et al. 2008). The XRD pattern of Z-nZVI after TCE (Fig. S5c) had similar structure to that after 1,1,1-TCA degradation.

Comparative degradation of 1,1,1-TCA and TCE in Z-nZVI-catalyzed SPC system

All experiments were performed with an initial concentration of 0.15 mM of both 1,1,1-TCA or TCE, 3.1 mM of SPC and 50 mg/L of Z-nZVI in aqueous solution. Control tests were performed without addition of SPC and Z-nZVI to find the

mass loss of 1,1,1-TCA and TCE. The results showed a minor loss (<1.5 %) of 1,1,1-TCA and TCE under all experimental conditions. The performance of 1,1,1-TCA and TCE degradation in SPC system catalyzed by Z-nZVI is shown in Fig. 2. About 49.6 % of 1,1,1-TCA and 39.7 % of TCE were degraded in a duration of 3 h. It is important to note that both 1,1,1-TCA and TCE removals followed the pseudo-first-order kinetic model.

It was observed that pH of the solution started to increase from an initial pH (4.0) as the reactions proceeded, and the final pH of the solution after termination of reactions was at 9.87–11.89. The results indicated that Z-nZVI has substantial potential to degrade both types of contaminants, i.e., 49.6 % of 1,1,1-TCA and 39.7 % of TCE, but could not degrade the contaminants completely. It is noteworthy that a larger amount of 1,1,1-TCA was degraded than TCE during the same interval of time under identical experimental conditions, indicating that Z-nZVI is more efficient to degrade 1,1,1-TCA as compared to TCE.

Role of reactive oxygen species by probe compound tests

Activation of different types of oxidants with transition metals to generate free radicals, such as OH^\bullet and superoxide anion radical ($\text{O}_2^{\bullet-}$), is a complex process (Anipsitakis and Dionysiou 2004). In Fenton and Fenton-like systems, many oxidation species like OH^\bullet and reduction species like $\text{O}_2^{\bullet-}$ have been observed, but OH^\bullet has been proved to be the most dominant and momentous to degrade chlorinated organic contaminants (Kim et al. 2001; Yang et al. 2010). Therefore, a sequential set of experiments was performed in this study to investigate the presence of reactive oxygen species in solution

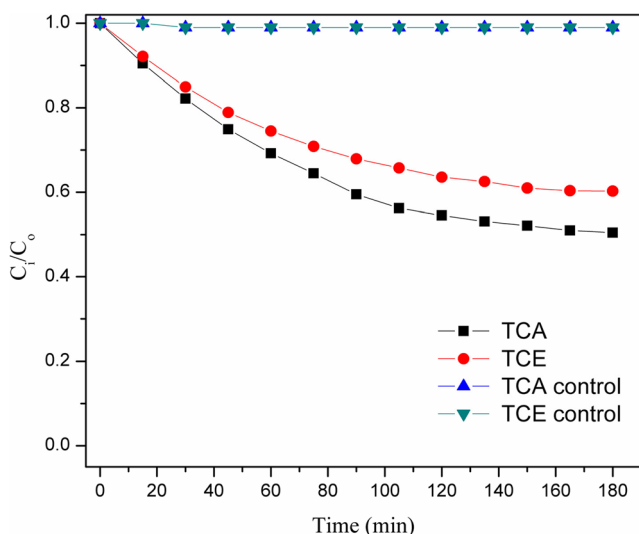


Fig. 2 1,1,1-TCA and TCE degradation performances in the Z-nZVI/SPC system. [T = 20 ± 0.5 °C]

by detecting free radicals using probe chemical compound tests. The data regarding material selection of probe compounds can be found in the Supplementary Material. The initial NB, CT, and SPC concentrations were set at 2.0, 0.05, and 3.1 mM, respectively. Approximately 59.33 % of NB was degraded indicating the presence of OH• in the system (see Fig. 3). Our findings are in line with the results published in the literature (Oturán 2000). Previous studies showed that 95.0 % of organic contaminants can react with OH• immediately at diffusion-control rates (Hoigne and Bader 1976). Moreover, about 43.19 % of CT was degraded in the Z-nZVI/SPC system which revealed the existence of O₂•⁻, and the results were consistent with the literatures (Liang and Su 2009; Navarro et al. 2009). Fenton process has been

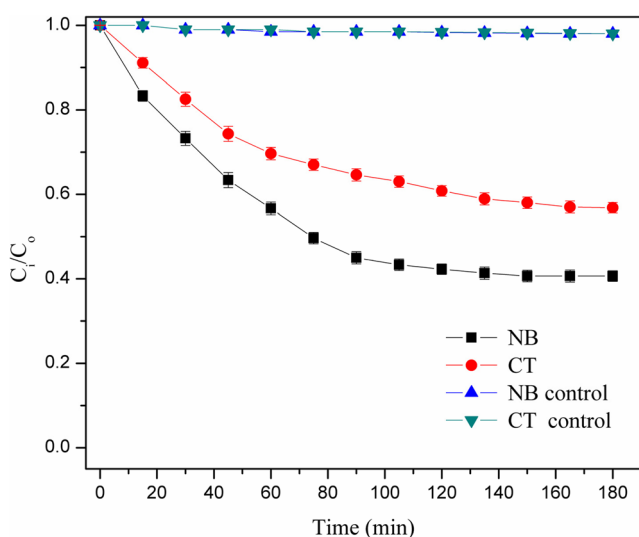


Fig. 3 Degradation of probe compounds in the Z-nZVI/SPC system. [NB]₀ = 1.0 mM, [CT]₀ = 0.05 mM, [Z-nZVI] = 50 mg/L, [T = 20 ± 0.5 °C]

considered not to react with strong oxidizing contaminants like hexachloroethane (Watts et al. 1999; Xu et al. 2015) due to low reactivity with OH•. However, the results obtained from this study demonstrated that the Z-nZVI-catalyzed SPC system has the ability to react with highly oxidizing and reducing contaminants for groundwater remediation.

Influence of reducing agent on degradation of 1,1,1-TCA and TCE

From the experiments, we observed that 1,1,1-TCA and TCE degradation was not very appreciable in the presence of Z-nZVI and SPC. An RA was employed in this study to examine its effect on transformation of iron ions and increase in 1,1,1-TCA and TCE degradation. Hydroxylamine (NH₂OH•HCl) was selected as an RA due to its strong capability to reduce Fe³⁺ to Fe²⁺. Degradation performances of 1,1,1-TCA and TCE with RA addition showed that 1,1,1-TCA was degraded more than 83.0 % and TCE more than 99.0 % (see Fig. 4). However, the degradation rates of both contaminants were lower in the absence of the RA, i.e., 48.0 % (1, 1,1-TCA) and 39.0 % (TCE). The calculated rate constants (K_{obs}) in the presence of RA of 1,1,1-TCA and TCE (based on the pseudo-first-order kinetic model) were 0.0096 and 0.0249 min⁻¹, respectively, which were 2.5- and 8.9-fold greater than the K_{obs} values obtained in the absence of RA. Similarly, the half-lives of 1,1,1-TCA and TCE degradation were 72 and 27 min⁻¹, respectively, showing a significant improvement with addition of RA as compared to the half-lives of 247 and 182 min⁻¹, respectively, in the absence of RA. The degradation of TCE followed the predominantly oxidative

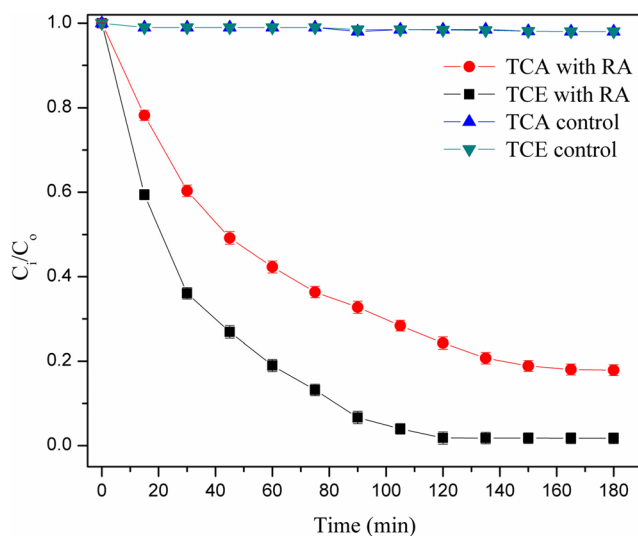
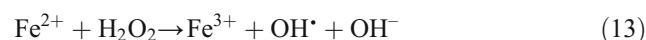
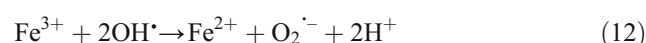
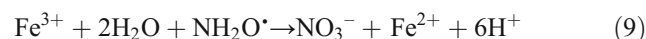
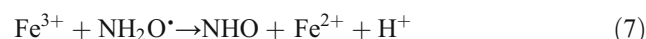


Fig. 4 Effect of reducing agent (NH₂OH•HCl) on the degradation of 1,1,1-TCA and TCE, [T = 20 ± 0.5 °C]

pathway with OH^\bullet transforming TCE into formic, dichloroacetic, oxalic, and glyoxylic acids and finally to carbon dioxide (Zhang et al. 2015). It has also been reported that addition of RA significantly enhanced the generation of OH^\bullet , leading toward the degradation of organic substrates (Fukuchi et al. 2013). On the contrary, $\text{O}_2^{\bullet-}$ contributes in the degradation of 1,1,1-TCA and TCE (Gu et al. 2012; Zhang et al. 2015). The significant increase in 1,1,1-TCA and TCE degradation with the addition of RA was therefore attributed to the generation of highly reactive species such as OH^\bullet and $\text{O}_2^{\bullet-}$. About 98.0 % of NB was degraded very efficiently with an addition of RA into the Z-nZVI/SPC system, and reduction of CT reached at a maximum value of 76.0 % (Fig. 5) in comparison with nearly 59.33 % of NB and 43.19 % of CT removals without RA addition. Furthermore, the calculated rate constants for NB and CT were increased from 0.0027 to 0.0052 and 0.0022 to 0.0045 min^{-1} , respectively, with the addition of RA. The results indicated that addition of RA nearly doubled the rate of reaction of NB and CT, thus confirming more OH^\bullet and $\text{O}_2^{\bullet-}$ species generated in the system.

The significant improvements in the generation of OH^\bullet and $\text{O}_2^{\bullet-}$ with the addition of RA in the Z-nZVI/SPC system was accredited due to the high concentration of Fe^{2+} and fast transformation of Fe^{3+} to Fe^{2+} . Therefore, the changes of Fe^{2+} and Fe^{3+} ions in the Z-nZVI/SPC system were determined (Fig. S4). A considerable increase in ferrous ions was observed with the addition of RA due to enhanced ferric reduction to ferrous and further promoting the OH^\bullet and $\text{O}_2^{\bullet-}$ radicals in the Z-nZVI/SPC system. Similar results were reported by Du when Fe^{2+} was present in large amount

in the homogeneous Fenton-like system (Du et al. 2006). The reactions accompanying catalytic decomposition of RA and H_2O_2 and reduction of Fe^{3+} to Fe^{2+} are shown in Eqs. 5, 6, 7, 8, 9, 10, 11, 12, and 13.



Addition of RA strongly encouraged the reduction of Fe^{3+} to Fe^{2+} and more generation of OH^\bullet and $\text{O}_2^{\bullet-}$ radicals in the Z-nZVI/SPC system. Moreover, by-products like NO_3^- , NO_2^- , NO^- , and N_2O were also produced with RA addition in the Z-nZVI/SPC system. It could be seen that the addition of RA produces part of N_2O as an end product that is highly soluble in water (Chen et al. 2011) and all other by-products are considered to have no toxic effects on the environment. The overall experimental results indicate that the Z-nZVI-catalyzed SPC system with the addition of RA is a promising technique for remediation of the groundwater contaminated with 1,1,1-TCA and TCE. Further expansion of the Z-nZVI-catalyzed SPC system applications in different directions will be emphasized in our future research study.

Conclusion

This study investigated the performance of our novel synthesized composite, i.e., Z-nZVI-catalyzed SPC, in a heterogeneous Fenton-like system for the degradation of 1,1,1-TCA and TCE as target COSSs. Several important conclusions can be withdrawn from this study.

- Reduced aggregation and increased surface area validated that the natural zeolite is an effective stabilizer and dispersant for zero valent iron. Z-nZVI-catalyzed SPC degraded 1,1,1-TCA and TCE to a certain extent; however, the addition of RA ($\text{NH}_2\text{OH}\cdot\text{HCl}$) substantially increased the

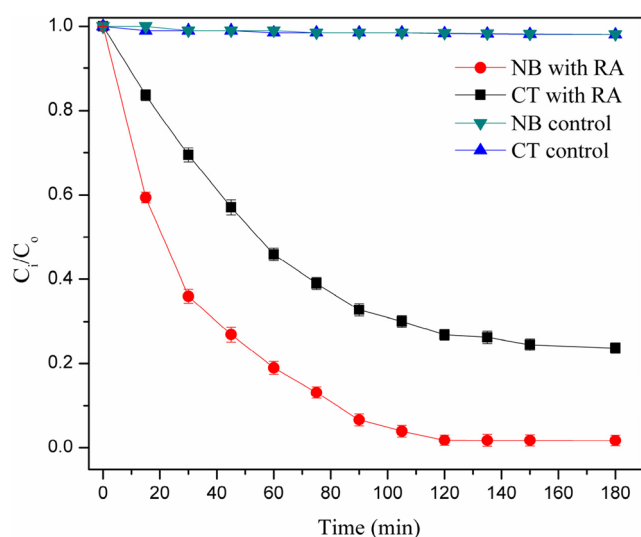


Fig. 5 Degradation of probe compounds in the Z-nZVI/SPC system with $\text{NH}_2\text{OH}\cdot\text{HCl}$ addition. $[\text{NB}]_0 = 1.0 \text{ mM}$, $[\text{CT}]_0 = 0.05 \text{ mM}$, $[\text{Z-nZVI}] = 50 \text{ mg/L}$, $[\text{T}] = 20 \pm 0.5 \text{ }^\circ\text{C}$

degradation of both contaminants by promoting the generation of reactive free radicals.

- The Z-nZVI composite increased the reduction of Fe^{3+} to Fe^{2+} on its surface that elevated generation of OH^\bullet . The presence of reactive oxygen species demonstrated that OH^\bullet and $O_2^{\bullet-}$ were exclusively responsible for 1,1,1-TCA and TCE degradation.
- EDS and BET analysis of the spent Z-nZVI indicated that it contained large amounts of iron that could persistently be utilized for contaminant degradation.
- The Z-nZVI/SPC has substantial potential to degrade both types of contaminants, i.e., 49.6 % of 1,1,1-TCA and 39.7 % of TCE, but could not degrade the contaminants completely. On the contrary, larger amount of 1,1,1-TCA was degraded than TCE during the same interval of time under identical experimental conditions, indicating that Z-nZVI is more efficient to degrade 1,1,1-TCA as compared to TCE.
- The Z-nZVI/SPC oxidation along with RA ($NH_2OH \cdot HCl$) can be used as a promising technique for remediation of groundwater contaminated with 1,1,1-TCA and TCE. However, further improvements in Z-nZVI/SPC degradation performance with a novel approach will be focused in our future research work.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

Adams JA, Reddy KR, Tekola L (2011) Remediation of chlorinated solvent plumes using in situ air sparging-A 2-D laboratory study. *Int J Environ Res Public Health* 8:2226–2239

Ahmad A, Gu X, Li L, Lv S, Xu Y, Guo X (2015) Efficient degradation of trichloroethylene in water using persulfate activated by reduced graphene oxide-iron nanocomposite. *Environ Sci Pollut Res* 22: 17876–17885

Akyol N, Yolcubal I (2013) Oxidation of nonaqueous phase trichloroethylene with permanganate in epikarst. *Water Air Soil Pollut* 224:1–19

Anipsitakis GP, Dionysiou DD (2004) Radical generation by the interaction of transition metals with common oxidants. *Environ Sci Technol* 38:3705–3712

Bellona C, Drewes JE (2007) Viability of a low-pressure nanofilter in treating recycled water for water reuse applications: a pilot-scale study. *Water Res* 17:3948–3958

Beydoun D, Amal R (2002) Implications of heat treatment on the properties of a magnetic iron oxide titanium dioxide photo catalyst. *Mater Sci Eng B* 94:71–81

Bogan BW, Trbovic V, Paterek JR (2003) Inclusion of vegetable oils in Fenton’s chemistry for remediation of PAH-contaminated soils. *Chemosphere* 50:15–21

Burbano AA, Dionysiou DD, Suidan MT, Richardson TL (2005) Oxidation kinetics and effect of pH on the degradation of MTBE with Fenton reagent. *Water Res* 39:107–118

Che H, Lee W (2011) Selective redox degradation of chlorinated aliphatic compounds by Fenton reaction in pyrite suspension. *Chemosphere* 82:1103–1108

Chen L, Ma J, Li X, Zhang J, Fang J, Guan Y, Xie P (2011) Strong enhancement on Fenton oxidation by addition of hydroxylamine to accelerate the ferric and ferrous iron cycles. *Environ Sci Technol* 45:3925–3930

Christina RK, Sedlak DL (2008) Factors affecting the yield of oxidants from the reaction of nanoparticulate zero-valent iron and oxygen. *Environ Sci Technol* 42:1262–1267

Clewell H, Gentry P, Gearhart J, Allen B, Andersen M (1995) Considering pharmacokinetic and mechanistic information in cancer risk assessments for environmental contaminants: examples with vinyl chloride and trichloroethylene. *Chemosphere* 31:2561–2578

Crane RA, Scott TB (2012) Nanoscale zero-valent iron: future prospects for an emerging water treatment technology. *J Hazard Mater* 211: 112–125

de la Calle RG, Gimeno O, Rivas J (2012) Percarbonate as a hydrogen peroxide carrier in soil remediation processes. *Environ Eng Sci* 29: 951–955

Devi LG, Kumar SG, Reddy KM, Munikrishnappa C (2009) Photo degradation of methyl orange an azodye by advanced Fenton process using zero valent metallic iron: influence of various reaction parameters and its degradation mechanism. *J Hazard Mater* 164:459–467

Du Y, Zhou M, Lei L (2006) Role of the intermediates in the degradation of phenolic compounds by Fenton-like process. *J Hazard Mater* 136: 859–865

Fukuchi S, Miura A, Okabe R, Fukushima M, Sasaki M, Tsutomu S (2010) Spectroscopic investigations of humic-like acids formed via poly condensation reactions between glycine, catechol and glucose in the presence of natural zeolites. *J Mol Struct* 982:181–186

Fukuchi S, Nishimoto R, Fukushima M, Zhu Q (2013) Effects of reducing agents on the degradation of 2, 4, 6-tribromophenol in a heterogeneous Fenton-like system with an iron-loaded natural zeolite. *Appl Catal B* 147:411–419

Fukushima M, Tatsumi K, Morimoto K (2000) Influence of iron (III) and humic acid on the photodegradation of pentachlorophenol. *Environ Toxicol Chem* 19:1711–1716

Gu X, Lu S, Qiu Z, Sui Q, Miao Z, Lin K, Liu Y, Luo Q (2012) Comparison of photodegradation performance of 1, 1, 1-trichloroethane in aqueous solution with the addition of H_2O_2 or $S_2O_8^{2-}$ oxidants. *Ind Eng Chem Res* 51:7196–7204

Han Y, Yang MD, Zhang W, Yan W (2015) Optimizing synthesis conditions of nanoscale zero-valent iron (nZVI) through aqueous reactivity assessment. *Front Environ Sci Eng* 9:813–822

He F, Zhao D, Liu J, Roberts CB (2007) Stabilization of Fe–Pd nanoparticles with sodium carboxymethyl cellulose for enhanced transport and dechlorination of trichloroethylene in soil and groundwater. *Ind Eng Chem Res* 46:29–34

Hoigne J, Bader H (1976) The role of hydroxyl radical reactions in ozonation processes in aqueous solutions. *Water Res* 10:377–386

Huang KC, Hoag GE, Chheda P, Woody BA, Dobbs GM (2001) Oxidation of chlorinated ethenes by potassium permanganate: a kinetics study. *J Hazard Mater* 87:155–169

Kim JS, Zhang L, Keane MA (2001) Removal of iron from aqueous solutions by ion exchange with Na-Y zeolite. *Sep Purif Technol* 36:1509–1525

- Kim SA, Kamala-Kannan S, Lee KJ, Park YJ, Shea PJ, Lee WH, Kim HM, Oh BT (2013) Removal of Pb (II) from aqueous solution by a zeolite–nanoscale zero-valent iron composite. *Chem Eng J* 217:54–60
- Klamerth N, Rizzo LL, Malato L, Maldonado MI, Agüera A, Fernández-Alba AR (2010) Degradation of fifteen emerging contaminants at μgL^{-1} initial concentrations by mild solar photo-Fenton in MWTP effluents. *Water Res* 44:545–554
- Li R, Jin X, Megharaj M, Naidu R, Chen Z (2015) Heterogeneous Fenton oxidation of 2, 4-dichlorophenol using iron-based nanoparticles and persulfate system. *Chem Eng J* 264:587–594
- Liang C, Su HW (2009) Identification of sulfate and hydroxyl radicals in thermally activated persulfate. *Ind Eng Chem Res* 48:5558–5562
- Liang CJ, Bruell CJ, Marley MC, Sperry KL (2004) Persulfate oxidation for in situ remediation of TCE. I. Activated by ferrous ion with and without a persulfate thiosulfate redox couple. *Chemosphere* 55:1213–1223
- Lim H, Lee J, Jin S, Kim J, Yoon J, Hyeon T (2006) Highly active heterogeneous Fenton catalyst using iron oxide nanoparticles immobilized in alumina coated mesoporous silica. *Chem Commun* 4:463–465
- Liou RM, Chen SH, Hung MY, Hsu CS (2004) Catalytic oxidation of pentachlorophenol in contaminated soil suspensions by Fe^{+3} resin/ H_2O_2 . *Chemosphere* 55:1271–1280
- Liou RM, Chen SH, Hung MY, Hsu CS, Lai JY (2005) Fe (III) supported on resin as effective catalyst for the heterogeneous oxidation of phenol in aqueous solution. *Chemosphere* 59:117–125
- Liu Y, Phenrat T, Lowry GV (2007) Effect of TCE concentration and dissolved groundwater solutes on NZVI-promoted TCE dechlorination and H_2 evolution. *Environ Sci Technol* 41:7881–7887
- McCarty, Perry L (2010) Groundwater contamination by chlorinated solvents: history, remediation technologies and strategies. In: Ward CH (ed) *In situ remediation of chlorinated solvent plumes*. Springer, New York, pp 1–28
- Miao Z, Gu X, Lu S, Dionysiou DD, Al-Abed SR, Zang X, Wu X, Qiu Z, Sui Q, Danish M (2015a) Mechanism of PCE oxidation by percarbonate in a chelated Fe (II)-based catalyzed system. *Chem Eng J* 275:53–62
- Miao Z, Gu X, Lu S, Zang X, Wu X, Xu M, Ndong LBB, Qiu Z, Sui Q, Fu YG (2015b) Perchloroethylene (PCE) oxidation by percarbonate in Fe^{2+} -catalyzed aqueous solution: PCE performance and its removal mechanism. *Chemosphere* 119:1120–1125
- Miao Z, Gu X, Lu S, Brusseau ML, Zhang X, Fu X, Danish M, Qiu Z, Sui Q (2015c) Enhancement effects of chelating agents on the degradation of tetrachloroethene in Fe (III) catalyzed percarbonate system. *Chem Eng J* 281:286–294
- Miura A, Okabe R, Izumo K, Fukushima M (2009) Influence of the physicochemical properties of clay minerals on the degree of darkening via polycondensation reactions between catechol and glycine. *Appl Clay Sci* 46:277–282
- Navarro S, Fenoll J, Vela N, Ruiz E, Navarro G (2009) Photocatalytic degradation of eight pesticides in leaching water by use of ZnO under natural sunlight. *J Hazard Mater* 172:1303–1310
- Neamtu M, Zaharia C, Catrinescu C, Yediler A, Macoveanu M, Kettrup (2004) A Fe-exchanged Y zeolite as catalyst for wet peroxide oxidation of reactive azo dye Procion Marine H-EXL. *Appl Catal B* 48:287–294
- Neyens E, Baeyens J (2003) A review of classic Fenton's peroxidation as an advanced oxidation technique. *J Hazard Mater* 98:33–50
- Nishimoto R, Zhu Q, Miyamoto T, Sato T, Tu X, Aneksampant A, Fukushima M (2015) Monopersulfate oxidation of Acid Orange 7 with an iron (III)-tetrakis (N-methylpyridinium-4yl) porphyrin intercalated into the layers of montmorillonite and pillared clay. *J Mol Catal A* 396:84–89
- Northup A, Cassidy D (2008) Calcium peroxide (CaO_2) for use in modified Fenton chemistry. *J Hazard Mater* 152:1164–1170
- Oller I, Malato S, Sánchez-Pérez JA (2011) Combination of advanced oxidation processes and biological treatments for wastewater decontamination a review. *Sci Tot Environ* 409:4141–4166
- Oturan MA (2000) An ecologically effective water treatment technique using electrochemically generated hydroxyl radicals for in situ destruction of organic pollutants: application to herbicide 2, 4-D. *J Appl Electrochem* 30:475–482
- Qu X, Alvarez PJJ, Li Q (2013) Applications of nanotechnology in water and wastewater treatment. *Water Res* 47:3931–3946
- Ramirez JH, Costa CA, Madeira LM, Mata G, Vicente MA, Rojas-Cervantes ML, López-Peinado AJ, Martín-Aranda RM (2007) Fenton-like oxidation of orange II solutions using heterogeneous catalysts based on saponite clay. *Appl Catal B* 71:44–56
- Savant MM, Pansuriya AM, Bhuvra CV, Kapuriya N, Patel AS, Audichya VB, Pipaliya PV, Naliapara YT (2009) Water mediated construction of trisubstituted pyrazoles/isoxazoles library using ketene dithioacetals. *J Comb Chem* 12:176–180
- Seol AK, Seralathan KK, Kui-Jae L, Yool-Jin P, Shea PJ, Lee WH, Kim HM, Oh BT (2013) Removal of Pb (II) from aqueous solution by a zeolite nanoscale zero-valent iron composite. *Chem Eng J* 217:54–60
- Shin S, Yoon H, Jang J (2008) Polymer-encapsulated iron oxide nanoparticles as highly efficient Fenton catalysts. *Catal Commun* 10:178–182
- Sun H, Zhou G, Liu S, Ha MA, Tade MO, Shaobin W (2012) Nano- Fe^0 encapsulated in micro carbon spheres: synthesis, characterization, and environmental applications. *ACS Appl Mater Inter* 4:6235–6241
- Sunder M, Hempel DC (1997) Oxidation of tri- and perchloroethene in aqueous solution with ozone and hydrogen peroxide in a tube reactor. *Water Res* 31:33–40
- Tamura H, Goto K, Yotsuyanagi T, Nagayama M (1974) Spectrophotometric determination of iron (II) with 1,10-phenanthroline in the presence of large amounts of iron (III). *Talanta* 21:314–318
- Tong L, Wu F, Yan S, Ji T, Lin B (1996) Paramagnetic behavior in NiNaY zeolites. *Solid State Commun* 97:1043–1046
- Vogan JL, Focht RM, Clark DK, Graham SL (1999) Performance evaluation of a permeable reactive barrier for remediation of dissolved chlorinated solvents in groundwater. *J Hazard Mater* 68:97–108
- Wang W, Zhou M, Mao Q, Yue J, Wang X (2010) Novel NaY zeolite-supported nano scale zero-valent iron as an efficient heterogeneous Fenton catalyst. *Catal Commun* 11:937–941
- Watts RJ, Teel AL (2005) Chemistry of modified Fenton's reagent (catalyzed H_2O_2 propagations-CHP) for in situ soil and groundwater remediation. *J Environ Eng* 131:612–622
- Watts RJ, Teel AL (2006) Treatment of contaminated soils and groundwater using ISCO. *Pract Period Hazard Toxic Radioact Waste Manage* 10:2–9
- Watts RJ, Foget MK, Kong SH, Teel AL (1999) Hydrogen peroxide decomposition in model subsurface systems. *J Hazard Mater* 69:229–243
- Wei X, Guo S, Wu B, Li F, Li G (2015) Effects of reducing agent and approaching anodes on chromium removal in electro kinetic soil remediation. *Front Environ Sci Eng* 10:253–261, 1–9
- Wigle DT, Arbuckle TE, Walker M, Wade MG, Liu S, Krewski D (2007) Environmental hazards: evidence for effects on child health. *J Toxicol Environ Health Part B* 10:3–39
- Wu C, Maurer C, Wang Y, Xue S, Davis DL (1999) Water pollution and human health in China. *Environ Health Perspect* 107:251–256

- Xu L, Wang J (2012) Magnetic nano scaled $\text{Fe}_3\text{O}_4/\text{CeO}_2$ composite as an efficient Fenton-like heterogeneous catalyst for degradation of 4-chlorophenol. *Environ Sci Technol* 46:10145–10153
- Xu M, Gu X, Lu S, Miao Z, Zang X, Wu X, Qiu Z, Sui Q (2015) Degradation of carbon tetrachloride in thermally activated persulfate system in the presence of formic acid. *Front Environ Sci Eng* 1–9
- Yang Y, Zhang G, Yu S, Shen X (2010) Efficient removal of organic contaminants by a visible light driven photo catalyst $\text{Sr}_6\text{Bi}_2\text{O}_9$. *Chem Eng J* 162:171–177
- Zhang X, Gu X, Lu S, Miao Z, Xu M, Fu X, Qiu Z, Sui Q (2015) Degradation of trichloroethylene in aqueous solution by calcium peroxide activated with ferrous ion. *J Hazard Mater* 284:253–260
- Zhao F, Yin J, Zhang XX, Chen Y, Zhang Y, Wu B, Li M (2015) Reduction in health risk induced by semi-volatile organic compounds and metals in a drinking water treatment plant. *Int J Environ Sci Technol* 12:527–536
- Zied A, Bahaa M, Schwieger W, Unger A (2008) Nitrous oxide decomposition over transition metal exchanged ZSM-5 zeolites prepared by the solid-state ion-exchange method. *Appl Catal B* 84:277–288