Published in final edited form as:

Sci Total Environ. 2019 February 15; 651(Pt 1): 1182–1188. doi:10.1016/j.scitotenv.2018.09.148.

The Impact of surface properties and dominant ions on the effectiveness of G-nZVI heterogeneous catalyst for environmental remediation

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Abstract

The surface properties of nanocomposites are influenced by the existence of inorganic species that may affect its performance for specific catalytic applications. The impact of different ionic species on particular catalytic activity had not been investigated to date. In this study, the surface charge (zeta potential) of graphene-oxide-supported nano zero valent iron (G-nZVI) was tested in definitive cationic (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) and anionic (Br^- , Cl^- , NO_3^- , SO_4^{2-} , and HCO_3^-) environments. The efficiency of G-nZVI catalyst was inspected by measuring the generation of reactive oxygen species (ROS) for the degradation of 1,1,1-trichloroethane (TCA) in sodium percarbonate (SPC) system. Tests conducted using probe compounds confirmed the generation of $\text{OH}^\bullet$ and $\text{O}_2^{\bullet-}$ radicals in the system. In addition, the experiments performed using scavenging agents certified that $\text{O}_2^{\bullet-}$ were primary radicals responsible for TCA removal, along with prominent contribution from $\text{OH}^\bullet$ radicals. The study confirmed that G-nZVI catalytic capability for TCA degradation is notably affected by various cationic species. The presence of Ni^{2+} and Cu^{2+} significantly enhanced (94%), whereas Na^+ and K^+ had minor effects on TCA removal. Overall, the results indicated that groundwater ionic composition may have low impact on the effectiveness of G-nZVI-catalyzed peroxide TCA treatment.

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Conflicts of interest

The authors declare that they have no conflict of interest.

Keywords

Surface charge; ionic composition; G-nZVI nanocomposite; reactive oxygen species; advanced oxidation process

1. Introduction

Sodium percarbonate ($\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$, SPC) is a solid phase oxidant that has received tremendous attention owing to its potential as a substitute for hydrogen peroxide (H_2O_2) for in-situ chemical oxidation (ISCO) processes (Danish et al., 2017a; Danish et al., 2016c; Fu et al., 2017). SPC is a preferred chemical oxidant compared to H_2O_2 because it is easier and safer to be stored, handled, and transported, as well as effective over a wider range of pH. The SPC has been used successfully for the treatment of contaminants such as aliphatic and aromatic hydrocarbons in groundwater (Danish et al., 2017a; Fu et al., 2016).

SPC releases free H_2O_2 in solution that reacts with iron or other transition metals to produce oxidative and reductive radicals such as hydroxyl ($\text{OH}^\bullet$) and superoxide radicals ($\text{O}_2^{\bullet-}$) which are effective for degradation of a wide array of groundwater contaminants (Cui et al., 2017; Danish et al., 2017b; Yu et al., 2018; Zang et al., 2014). Ferrous iron (Fe^{2+}) is the standard catalyst used in Fenton and Fenton-like oxidation processes. The application of Fe^{2+} has some flaws, it requires high level of doses and cannot be regenerated efficiently from Fe^{3+} , which often limits the oxidation capacity of the system (Vicente et al., 2011). Furthermore, aqueous Fe^{2+} is relatively insoluble at pH 5 in many aquifer systems. Due to these limitations, a variety of chelating agents have been employed to enhance its solubility and availability, which leads to enrichment in degradation performance (Fu et al., 2017; Miao et al., 2015a; Miao et al., 2015b). However, the use of an additional reagent for in-situ applications increases costs and can initiate other issues, such as biodegradation of the reagent. So, it is necessary to find an alternative way to address these concerns using some modern technologies.

Recently, it has been recognized that above mentioned deficiencies can be overcome by application of nano zero valent iron (nZVI) as an alternative source of Fe^{2+} . The use of nZVI compared to Fe^{2+} chemical provides a long-term solution and a limitless source of Fe^{2+} for the generation of radicals which are necessary for degradation of organic contaminants (Ahmad et al., 2015a; Danish et al., 2016d). In addition, its tiny size provides large surface area (high reactivity), and makes it amenable for injection and migration as aqueous suspensions (Fu et al., 2014; Mueller et al., 2012; Stefaniuk et al., 2016; Tosco et al., 2014). However, there are some major limitations towards the use of nZVI, for example it is less stable and prone to aggregation, these imperfections reduced nZVI reactivity (Liu et al., 2005; Phenrat et al., 2007). The above mentioned reservations can be minimized through distribution of these prepared nanocomposite on a supported materials.

Graphene-based nanocomposites have been widely used as heterogeneous catalysts owing to their high surface area, electrical conductivity, and electron mobility. Graphene oxide (GO) has a single layer honeycomb structure comprising sp^2 hybridized carbon atoms. The π - π interaction between graphene atoms and contaminant molecules produces a unique and

profound mechanical and catalytic interactions. GO also contains several oxygen-containing functional groups which play an important role in conferring specific surface area and porosity. Additionally, it produce a strong interface with attached nanocomposite particles (Astruc et al., 2005; Luo and Zhang, 2018). The catalytic activity of nanoparticles supported on GO is enhanced because of a higher surface to volume ratio and densely packed composite, as well as effective electron transport amongst conduction and valence bands.

Several studies have demonstrated that solution properties and ionic composition can influence the effectiveness of oxidative treatment of chlorinated organic solvents. The salts present in groundwater interact with the metal activator can quench radicals, or produce complexes which reduce the degradation performance (Bennedsen et al., 2012; Liang et al., 2006). The pH, humic acid content, and inorganic anionic species (Cl^- , CO_3^{2-} , HCO_3^- , NO_3^- , and SO_4^{2-}) influence on degradation efficiency. However, these impacts are not uniformed, for example, some anionic species showed negligible effect while others significantly retard catalytic activity (Gu et al., 2013; Li et al., 2017). In addition, studies have confirmed that inorganic anions and cations considerably affected the surface charge and adsorption density of materials (Parsons and Salis, 2016). These results directed that it is important to understand the influence of groundwater composition on performance for any new catalyst-oxidant system.

Several previous researchers have studied nZVI based nanocomposites, employing GO and other supports, as a heterogeneous catalyst for degradation of chlorinated organic compounds under various oxic environments (Ahmad et al., 2015b; Danish et al., 2016a; Farooq et al., 2016; Fu et al., 2014; Gu et al., 2018). However, the influence of different cationic species on the surface and catalytic properties of G-nZVI has not been investigated. Thus, the objective of this study is to examine the impact of cationic species on surface charge (zeta potential) of G-nZVI nanocomposite and its effect on degradation of TCA for a SPC oxidant system. The generation of ROSs was identified and measured using probe and scavengers tests. It is anticipated that the results will improve our understanding of the mechanisms and performance of these systems for treating groundwater contamination.

2. Materials and methods

2.1. Materials/chemicals

Analytical grade of TCA (>99%) tertiary butyl alcohol (TBA, 99%), graphite powder, calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), nickel sulfate (NiSO_4), and chloroform (CF, 99%) were purchased from Aladdin Industrial Corporation, Shanghai, China. Potassium permanganate (KMnO_4), sulfuric acid (H_2SO_4 , 99%), hydrogen peroxide (H_2O_2 , 30% wt.), hydrochloric acid (HCl, 37%), iron sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), magnesium sulfate (MgSO_4), potassium sulfate (K_2SO_4), copper sulfate heptahydrate ($\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$), *n*-hexane, ethylene glycol, and carbon tetrachloride (CT, 99.5%) were purchased from Shanghai Lingfeng Reagent Co. Ltd., China. Sodium nitrate (NaNO_3 , 98%), ethanol, manganese sulfate (MnSO_4), sodium sulfate (Na_2SO_4), and sodium acetate (NaAc) anhydrous were obtained from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Nitrobenzene (NB, 99%) was obtained from Shanghai Jingchun Reagent Co. Ltd., China. Sodium percarbonate (SPC) was purchased from Acros Organics, Shanghai, China. The

stock solution of 0.15 mM 1,1,1-trichloroethane (TCA) was prepared by dissolving Milli-Q ultra-pure water. The pH of the solution was adjusted using 0.1 M NaOH or 0.1 M H₂SO₄. The deionized water used in all experiments originated from a Milli-Q ultra-pure water system (Classic DI, ELGA, 102 Marlow, UK).

2.2. Preparation of graphene oxide supported nano iron (G-nZVI)

Graphene oxide (GO) supported nano zero valent iron (nZVI) was synthesized using the solvothermal technique. GO was prepared using modified Hummers method used in our previous study (Farooq et al., 2016). G-nZVI was synthesized as follows: initially, 0.250 g of GO already produced was mixed with 100 mL of ethylene glycol and sonicated for 3 hrs. 3.5 g of iron sulfate hydrate and 3.5 g sodium acetate anhydrous were added in above solution and continued to mix for next 2 hrs using a magnetic stirrer to make sure the exchange of ferrous ions on GO support. Then the mixture was transferred to Teflon lined autoclave and heated for 6 hrs at 200°C in an oven. The blackish suspension was separated using centrifugation and washed several times using deionized water and ethanol simultaneously to ensure the removal of impurities. The sample was vacuum dried at 50°C overnight. The G-nZVI nanocomposite is ready for experimentation.

2.3. Characterization of graphene oxide supported nano zero valent iron (G-nZVI)

The characterization of synthesized G-nZVI nanocomposite was carried out by scanning electron microscope (SEM, JSM-630LV, Tokyo, Japan) and transmission electron microscope (TEM, JEM-1400 electron microscope, operated at an accelerating voltage at 80 kV), x-ray diffraction (XRD), Fourier transformation infrared (FTIR), x-ray photo spectroscopy (XPS), Specific surface area, pore size, and total pore volume were measured using the Brunauer-Emmett-Teller (BET) method (Quantasord Jr. Instrument Quantachrome Co; UK) shown in Table S1, and energy dispersive spectroscopy (EDS). The properties of the synthesized nanocomposites are reported in Fig S1-S3. The XRD characteristic peaks at 44.15° clearly represent the formation of zero valent iron (ZVI).

2.4. Surface charge (zeta potential) G-nZVI nanocomposite

The surface charge (zeta potential) of G-nZVI catalyst was measured by zeta analyzer (Nano ZS, Malvern, UK), and the electrophoretic mobility was calculated using the following equation

$$\zeta = \left(\frac{4\pi\eta}{D_t} \right) \mu \quad (1)$$

Where ζ and μ are zeta potential and electrophoretic mobility, respectively, D_t is dielectric constant, and η is viscosity of medium. The surface charge of various inorganic ions solutions (0.05 and 0.5 M) was calculated.

2.5. Experimental procedures

The standard TCA solution (0.15 mM) was prepared by adding solution to ultra-pure Milli-Q water and continuous stirred for 1 hr. The reactor used in batch tests have volume of 250

mL cylindrical shape made of glass (an inner diameter of 6.0 cm and a height of 9.0 cm), followed a decreasing diameter of arc shape (a height of 2.5 cm), which connected with two openings at the top, one for dosing (diameter of 2.0 cm and a height of 2.0 cm after covering) and the other for sampling (diameter of 1.5 cm and height of 1.5 cm after covering). The gage height of suspension could reach 10.5 cm and headspace volume around 8 cm³. The temperature was maintained in a jacketed reactor by continuously circulating water at constant temperature ($20 \pm 5^\circ\text{C}$) using a temperature bath (DC Ningbo, China). The predetermined amounts of TCA, SPC, G-nZVI and other reagents were added in the reactor and subsequently mixed using a magnetic stirrer. The pH of the solution was monitored using a pH meter. One milliliter samples were withdrawn from the headspace of the reactor and added to gas chromatography vials containing 1.0 mL of *n*-hexane. All experiments were performed in triplicate and the average values reported. Radical probe tests were conducted to confirm the presence of ROS in the system. The test procedure was the same as that used for TCA, with the exception that TCA is replaced by NB and CT, which are OH[•] and O₂^{•-} probes, respectively. Control tests were performed for each experimental condition. The standard deviation was in the range of 0.014~0.034 for all experiments.

2.6. Analytical methods

One milliliter of TCA, CT, and NB aqueous samples were mixed with 1.0 mL of *n*-hexane and placed in vortex stirrer for 3~5 min then allowed separation of layers for 5 min. The concentration of TCA was analyzed using gas chromatography ((Agilent 7890A, Palo Alto, CA, USA) equipped with DB-VRX column (length 60 m, I.D. 250 μm , and thickness 1.4 μm), an autosampler (Agilent 7693) and electron capture detector (ECD) with the split ratio of 20:1. The temperatures of detector and injector were fixed at 260°C and 240°C respectively, while, the oven temperature was kept at 75°C. In case of measurement of CT, the oven temperature was maintained at 110°C whereas, all other parameters remained the same as for TCA. The concentration of NB was analyzed using a flame ionization detector with an HP-5 column (length 30 m, I.D. 250 μm , thickness 0.25 μm). The injector, detector, and oven temperatures were 250, 300, and 170°C, correspondingly. Radical scavenger tests were performed using tertiary butyl alcohol (TBA) and chloroform (CF) as scavenging chemicals for OH[•] and O₂^{•-} radical, respectively. We have performed experiments for H₂O₂ release from SPC. The analysis were performed using spectrophotometer (Thermo, United States), at 400 nm after developing color solution using ammonium molybdate. The 0.22 μm filter was used for determination of H₂O₂ concentration in aqueous phase. First diluted standard solution of H₂O₂ (0.01 mM to 6.0 mM) were prepared and find its absorbance using the above mentioned instrument and a straight line equation was obtained. Then the release of H₂O₂ in SPC (4.0 mM) system were determined by comparing results with standard curve. Fig. 1 demonstrated the role of SPC releasing H₂O₂ in G-nZVI heterogeneous catalyst process. Control tests without the addition of catalyst or oxidant were conducted at the same time for all experiments.

3. Results and discussion

3.1. Determination of zeta potential of nanocomposites

The surface charge (zeta potential) of bare nZVI, GO, and of the synthesized nanocomposite (G-nZVI) was carried out at pH range (2~11) as shown in Fig. 2. The zeta potential of GO; a support material used in this study, was observed as negative over the above-mentioned pH range. Its lowest zeta potential value of ~ -39 mV was measured at pH domain of 4~11 and the highest value of ~ -20 mV occurred at pH = 2. The bare nZVI zeta potentials was also negative but comparatively higher than GO. The zeta potential was ~ 4.76 mV and -37 mV at the lowest (2) and highest (11) pH values, respectively. The surface charge of G-nZVI was found as positive for pH less than 6.5, and maximum zeta potential (8 mV) was found at pH = 2. There found a negative value of surface charge at increasing pH, a minimum value of ~ -33 mV was perceived pH = 11. The zero-point charge (ZPC) value of synthesized G-nZVI is at pH 6.5. The decrease in zeta potential of G-nZVI in alkaline media is due to the ionization of surface edge groups and OH^- ions present on the GO sheet of the supported nanocomposite, which resulted in a more negative surface charge. However, in acidic conditions, these moieties become protonated, resulting in net-positive surface charge.

Conclusively, the zeta potential of G-nZVI is higher (more positive) than the bare GO and nZVI at a given pH owing to the presence of reduced-oxygen functional groups in the GO supported nanocomposite.

3.2. Zeta potential of G-nZVI nanocomposite under the influence of different inorganic ions

The influence of several selected inorganic ions on the surface charge of the G-nZVI nanocomposite was explored using zeta potential. The surface charge of G-nZVI nanocomposite was determined at two molar concentrations of chloride ions (0.05 and 0.5 M) of several alkali metal cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) as well as sodium salts of various anions (Br^- , Cl^- , NO_3^- , SO_4^{2-} , and HCO_3^-) at pH 6. The effect of chloride and sodium ions was investigated on the degradation of TCA and it was found that at small concentration it has small effect on removal efficiency as in current system we are only using 0.05 and 0.5 mM solutions so these have minimum effect on TCA degradation. Fig. 3a illustrates that the surface charge of G-nZVI nanocomposite changes drastically as a function of the dominant anion present in solution. The zeta potential decreased in the order of $\text{HCO}_3^- > \text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{Br}^- > \text{G-nZVI}$. The positively charged sodium ions develop a double layer on the surface of the negatively charged catalyst surface, and the anions are dispersed throughout the double layer. The thickness of grown double layer mainly depends on the size and polarizability of the counter-anion. The anions with high polarizability are strongly absorbed on GO surface due to high surface active properties and zeta potential (Borthakur et al., 2016; Schwierz et al., 2013).

The effect of chloride salts of various alkali metals was also investigated and it was found that the presence of different cations can significantly affect the surface charge of G-nZVI nanocomposite (Fig. 3b). The zeta potential increase was found to be the following order:

$\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+ > \text{G-nZVI}$. This effect originated due to cation adsorption on the negatively charged surface of the catalyst.

The impact of these salts on surface charge was also investigated for a 0.5 M salt solution, for which the thickness of the double layer would be compressed. The zeta potential values of G-nZVI nanocomposite are shown in Fig. 4a and b. It is observed that zeta potentials are greater for the 0.5 M solution compared to the 0.05 M solution, indicating a measurable impact of double-layer thickness.

3.3. Effect of solution pH on TCA degradation

The degradation of TCA as a function of pH was investigated, and the results are presented in Fig. 5. The magnitude of TCA degradation ranges from approximately 55 to 90%, revealing a significant impact of pH. This pH effect was attributed in part to change in surface charge observed for the G-nZVI nanocomposite, as described above, also as a source that increase the interaction of TCA molecules with the nanocomposite surface. The generation of more $\text{OH}^\bullet$ radicals at higher pH values also contributes to the increase in degradation performance. The increase in TCA degradation may be due: 1) at higher pH the surface charge of G-nZVI become more negative so it has more interaction with TCA, 2) previous studies also confirmed the increase in pH more $\text{OH}^\bullet$ radicals produced (Chen et al., 2017; Lei et al., 2015) 3) we are using here SPC system which is more effective at neutral or alkaline pH compared to acidic pH.

3.4. Identification of ROS for TCA degradation

It has been believed that various kind of ROS generated in traditional Fenton system may be also developed in modified Fenton like (SPC) system. The $\text{OH}^\bullet$ is generally exist as predominant radical in Fenton system, studies have shown that other ROSs ($\text{HO}_2^\bullet$, HO_2 , and $\text{O}_2^{\bullet-}$) are present at higher concentrations and ratios of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ (Lipczynska-Kochany and Kochany, 2008). $\text{O}_2^{\bullet-}$ is considered as a reductant and can react with CT at a rate constant of $3800 \text{ M}^{-1} \text{ s}^{-1}$ in dimethyl sulfoxide and it is understood that $\text{O}_2^{\bullet-}$ can reduce CT in modified Fenton system (Teel and Watts, 2002). Thus, it is possible that oxidation and reduction reactions occur simultaneously in the G-nZVI activated SPC system. Therefore, experiments were conducted using chemical probe compounds to investigate the free radical species generated during TCA degradation. The probe compounds were selected on the basis of their susceptibility to capture specific radical species. The generation of $\text{OH}^\bullet$ was confirmed using NB as a probe compound as it has higher reactivity with $\text{OH}^\bullet$ ($k_{\text{OH}} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). CT was selected as the probe compound for $\text{O}_2^{\bullet-}$ due to its higher reaction rate ($k_{\text{O}_2^{\bullet-}} = 1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) with reductant compared to $\text{OH}^\bullet$ ($k_{\text{OH}} = 3.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$). The initial concentrations of CT, NB, and SPC were maintained at 0.05, 2.0, and 25 mM, respectively.

The degradation of CT and NB in the presence of G-nZVI activated SPC, as well as control tests, are presented in Fig. 6, where the C_i the concentration of NB and CT at any time "i". The results indicated that approximately 45% NB was degraded while CT degradation found to be about 56%. The significant degradation of NB and CT indicates the existence of $\text{OH}^\bullet$ and $\text{O}_2^{\bullet-}$ radicals in G-nZVI/SPC system. It can be also concluded that $\text{O}_2^{\bullet-}$ was the

dominant ROS in system under consideration (G-nZVI/SPC). Similar results were obtained at more than 0.1 M H₂O₂ concentration Fenton system and found the O₂^{•-} radicals were responsible for transformation of CT (Smith et al., 2004).

The presence of OH[•] and O₂^{•-} in the TCA degradation process was identified by the probe compounds. Scavenger-molecule tests were conducted to further investigate the effect of these radicals on degradation performance of TCA. Two scavenging compounds, TBA and CF, were selected to define the role of ROSs in the system. TBA has very high reactivity towards OH[•] radicals ($k_{OH} = 5.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$), while CF considered as a scavenger for O₂^{•-} owing to its excellent selectivity ($K_{O_2^{\bullet-}} = 3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$). Different concentrations (1.0, 10, and 30 mM) of scavenging compounds were applied to test the effect of scavenger concentration on TCA degradation.

The results (Fig. 7a) elucidated that TCA degradation was decreased from 90% to 63%, 58% and 52% at TBA dosages of 1.0, 10, and 30 mM, respectively. This confirmed that increase in OH[•] scavenging agent (TBA) retard OH[•] species to interact with targeted contaminant (TCA) which eventually decrease the degradation of TCA. This further validated the presence of OH[•] in G-nZVI activated SPC system. Moreover, in case of CF (scavenging agent for O₂^{•-}) TCA degradation was found to be 58%, 50%, and 46% at 1.0, 10, and 30 mM CF concentrations, respectively (Fig. 7b). The decrease in TCA is due to the presence of CF as scavenging agent which consumed O₂^{•-} radical generated in G-nZVI activated SPC system. These scavenger tests further confirmed the presence of OH[•] and O₂^{•-} radicals in system as well as their contribution towards TCA degradation.

3.5 Effect of cations on TCA degradation

The presence of various cations (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cu²⁺, Ni²⁺, and Mn²⁺) in groundwater can have a significant influence on TCA degradation. Previous studies have reported that sulfate and nitrate anionic species had a negligible effect on the removal of chlorinated organic solvents (Ahmad et al., 2015a; Danish et al., 2017c; Danish et al., 2016b), so in the present study we selected sulfate salts of various cations. The cations tested were divided into two categories; alkali and transition metals cations. Control experiments were also conducted in the absence of catalyst and SPC and the results indicated that there was less than 3% TCA removal (due to volatilization). We had also conducted the adsorption experiments of catalyst in our previous studies and found GO adsorption rate was 18% while G-nZVI have 23% adsorption capacity. We had performed experiments initially to find out the best SPC and G-nZVI concentration and evaluated that efficient degradation of TCA was found at 25 mM and 0.8 g/L. Fig. S4-S5 showed the effect of SPC dose on TCA degradation.

The effect of alkali metals (Na⁺, K⁺, Ca²⁺, and Mg²⁺) on TCA degradation efficiency was investigated (Fig. 8a). Previously, we have confirmed that surface charge of above mentioned alkali metals become more positive at higher concentration. So, for current experimentation 1.0, 10 and 30 mM concentration was selected as reference to evaluate cations effect. The results showed that Na⁺ have no effect on degradation even if applied at higher concentration while K⁺ can slightly enhance about 0.8~1.5% at 10 mM and 30 mM concentration respectively. Conversely, Mg²⁺ showed a retardation effect on TCA

remediation and degradation efficiency decreased to 86% and 80% at 10 mM and 30 mM respectively. Liu et al. reported a similar result for a heterogeneous photo-Fenton process (Liu et al., 2010). On the other hand, Ca^{2+} showed no significance effect on removal efficiency at 1.0 and 10 mM but the degradation enhanced to 93% when 30 mM concentration was applied. The effect of transition metal in solution (1.0 mM) on TCA degradation was also investigated and the results are shown in Fig 8b. The results confirmed that Ni^{2+} and Cu^{2+} noticeably increase the TCA degradation performance to 92% and 94% respectively this may be due to second transition metal interaction with nZVI while, Mn^{2+} retard the TCA removal to 81%. Experiments were also performed to check the effect of temperature (20~50°C) on TCA degradation as shown in Fig. 9. It was found that TCA removal increase with increase in temperature. It is observed that the presence of the metals had a minor impact on TCA degradation, changing the magnitude of degradation by ~10% or less.

4. Conclusions

nZVI is a widely used a heterogeneous catalyst that shows promising use in advanced reaction systems such as the G-nZVI material employed in this study. Optimal use of these systems for groundwater treatment requires an understanding of the influence of water ionic composition on their effectiveness. The impact of different cationic species had not been investigated to date. The results of this study suggest that the ionic composition of groundwater has a relatively minor effect on TCA degradation for the G-nZVI catalyzed system. This is in contrast to other Fentonlike systems, which have been shown to be more sensitive to ionic composition. For example, Yan et al. evaluated bicarbonate and calcium ions, which are often the most abundant ions in groundwater, and observed that they have a strong effect on dioxane degradation (Yan et al., 2016). These contrasting results indicate that the G-nZVI system is a robust medium for treatment of groundwater contaminated by TCA and similar compounds.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This study was financially supported by the grant from the Natural Science Foundation of Shanghai, China (16ZR1407200). The contributions of Mark Brusseau were supported by the NIEHS Superfund Research Program (PS 42 ES04940).

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Highlights

- Dominant groundwater cations effect the performance efficiency for degradation
- Surface charge and organic ions effect investigated for the degradation of TCA a persistent contaminant in hydrosphere.
- Generation of reactive oxygen species for remediation of TCA in percarbonate system.
- The ionic composition of groundwater has a relatively minor effect on TCA removal for the G-nZVI catalyzed system.

Fig. 1:
Release of H_2O_2 at $[\text{SPC}] = 4.0 \text{ mM}$, and $[\text{T}] = 25^\circ\text{C}$

Fig. 2.
Zeta potential of GO, nZVI, and G-nZVI at various pH.

Fig. 3. Zeta potential of solutions of G-nZVI nanocomposite in presence of 0.05 M a) sodium salts of different anions, b) chloride salts of various cations. The G-nZVI bars represent the standard conditions presented in Figure 1 (deionized water).

Fig. 4. Zeta potential of solutions of G-nZVI nanocomposite in presence of 0.5 M a) sodium salts of different anions, b) chloride salts of various cations. The G-nZVI bars represent the standard conditions presented in Figure 1 (deionized water).

Fig. 5. Degradation of TCA at various pH $[TCA]_0 = 0.15$ mM, $[G-nZVI] = 0.8$ g/L, and $[SPC] = 25$ mM.

Fig. 6.

Recognition of ROSs $[TCA]_0 = 0.15$ mM, $[G-nZVI] = 0.8$ g/L, $[SPC] = 25$ mM, $[CT]_0 = 0.05$ mM, and $[NB]_0 = 2.0$ mM.

Fig. 7. Scavenger test a) $[TBA]_0 = 1.0, 10, \text{ and } 30 \text{ mM}$, $[SPC] = 25 \text{ mM}$, $[G\text{-}nZVI] = 0.8 \text{ g/L}$, $[TCA]_0 = 0.15 \text{ mM}$, and b) $[CF]_0 = 1.0, 10, \text{ and } 30 \text{ mM}$, $[SPC] = 25 \text{ mM}$, $[G\text{-}nZVI] = 0.8 \text{ g/L}$, and $[TCA]_0 = 0.15 \text{ mM}$.

Fig. 8. Effect of various cations on TCA degradation a) Na⁺, K⁺, Ca²⁺, Mg²⁺, and b) Cu²⁺, Ni²⁺, and Mn²⁺ ([TCA]₀ = 0.15 mM, [G-nZVI] = 0.8 g/L, [SPC] = 25 mM)

Fig. 9:
Effect of temperature on TCA degradation at $[TCA]_0 = 0.15$ mM, $[G-nZVI] = 0.8$ g/L and $[SPC] = 25$ mM.