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Rapid and complete destruction of perchlorate in water and ion-exchange brine using stabilized zero-valent iron nanoparticles

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ABSTRACT

Perchlorate has emerged as a widespread contaminant in groundwater and surface water. Because of the unique chemistry of perchlorate, it has been challenging to destroy perchlorate. This study tested the feasibility of using a new class of stabilized zero-valent iron (ZVI) nanoparticles for complete transformation of perchlorate in water or ion-exchange brine. Batch kinetic tests showed that at an iron dosage of 1.8 g L^{-1} and at moderately elevated temperatures ($90\text{--}95^\circ\text{C}$), $\sim 90\%$ of perchlorate in both fresh water and a simulated ion-exchange brine ($\text{NaCl} = 6\% \text{ (w/w)}$) was destroyed within 7 h. An activation energy (E_a) of $52.59 \pm 8.41 \text{ kJ mol}^{-1}$ was determined for the reaction. Kinetic tests suggested that Cl(VII) in perchlorate was rapidly reduced to chloride without accumulation of any intermediate products. Based on the surface-area-normalized rate constant k_{SA} , starch- and CMC-stabilized ZVI nanoparticles degraded perchlorate 1.8 and 3.3 times, respectively, faster than non-stabilized ZVI particles. Addition of a metal catalyst (Al, Cu, Co, Ni, Pd, or Re) did not show any reaction improvement. This technology provides an effective method for complete destruction of perchlorate in both contaminated water and brine.

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1. Introduction

Perchlorate (ClO_4^-) has been primarily used in solid rocket fuels. It is also used in firework powder, roadside flares, airbag inflators, and fertilizers from Chile (Urbansky, 1998). Past massive applications of perchlorate have left a contamination legacy that perchlorate has been detected at about 400 sites in groundwater, surface water, soil, or public drinking water in more than 35 states across the United States, with concentrations ranging from $4 \mu\text{g L}^{-1}$ to more than 3.7 million $\mu\text{g L}^{-1}$ (US Government Accountability Office (USGAO), 2005). Recently, perchlorate was also detected in milk (Kirk et al., 2005) and bottled water (Snyder et al., 2005).

When ingested, perchlorate can impede the endocrine function by blocking iodide from entering the thyroid gland, thereby reducing the production of thyroid hormones. The adverse health effects were reportedly more profound for newborns, children, and pregnant women (Wolff, 1998). A study from the US Centers for Disease Control (CDC) found that almost any amount of perchlorate exposure was linked to a significant change in levels of thyroid hormones (Blount et al., 2006). To reduce human exposure, the USEPA adopted a drinking water equivalent level (DWEL) of $24.5 \mu\text{g L}^{-1}$. Meanwhile, California adopted a public health goal of $6 \mu\text{g L}^{-1}$ and Massachusetts set the nation's first drinking water standard of $2 \mu\text{g L}^{-1}$ for perchlorate.

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Perchlorate is highly water soluble, non-complexing, non-volatile, and chemically stable (Urbansky, 1998). For its unique chemistry, it has been highly challenging to remove perchlorate from water by traditional water treatment approaches (Hatzinger, 2005). In recent years, various treatment technologies have been developed and/or tested, including biological reduction (Logan and LaPoint, 2002; Min et al., 2004; Xu et al., 2003), ion exchange (IX) (Gu et al., 2001, 2003; Tripp and Clifford, 2004, 2006; Xiong et al., 2006), tailored activated carbon sorption (Chen et al., 2005; Parette et al., 2005), filtration (Yoon et al., 2003), and chemical reduction (Moore et al., 2003; Gu et al., 2006). However, these technologies are limited by some critical technical and/or economic drawbacks such as slow degradation kinetics and production of large volumes of concentrated process waste residuals. For instance, IX has been considered as one of the best available technologies for perchlorate removal (Gingras and Batista, 2002), and many commercial IX resins can offer high perchlorate sorption capacity. However, the regeneration efficiency of the IX resins has been found to be prohibitively poor. As a result, current IX processes are used on a disposable basis (i.e. the resin is disposed of after only one service run) or, when resin regeneration is practised, it will result in large volumes of spent regenerant brine. Spent IX brine is typically characterized with high salinity, concentrated perchlorate, and/or mixtures of concentrated acids and salts (1M FeCl_3 and 4M HCl) (Gu et al., 2001). Because of the highly stressful conditions, biological treatment of the spent brine is rather challenging. Consequently, cost-effective technologies that can destroy perchlorate in fresh water and regenerant brine are in dire need.

In recent years, zero-valent iron (ZVI) has attracted increasing interest for abiotic dechlorination of chlorinated organic compounds (Wang and Zhang, 1997), removal of nitrate (Huang and Zhang, 2004; Yang and Lee, 2005), reduction of chromate (Wilkin et al., 2005), and sorption of arsenic (Kanel et al., 2006). ZVI was also tested for reduction of perchlorate. For instance, Moore et al. (2003) and Moore and Young (2005) investigated perchlorate removal by commercial iron filings (size = 20–100 mesh, surface area = $0.08\text{--}5.65\text{ m}^2\text{ g}^{-1}$). Up to 66% of perchlorate (0.1 mM) was removed in 336 h at a high iron dosage of 1.25 g mL^{-1} . Gurol and Kim (2000) reported that UV light accelerated the perchlorate reduction rate with a dose of 20 g L^{-1} or higher metallic iron (size = 100 mesh, surface area = $0.74\text{ m}^2\text{ g}^{-1}$). Oh et al. (2006a) reported that 98% of perchlorate in water was reduced by cast iron (surface area = $1.29\text{ m}^2\text{ g}^{-1}$) in 1 h at 200°C via microwave heating and at pH 7.4. In another study, Oh et al. (2006b) reported that perchlorate in wastewater was completely removed by iron at an elevated temperature of 150°C in 6 h without pH control. Cao et al. (2005) observed that non-stabilized iron particles were able to degrade perchlorate at temperatures from 25 to 75°C .

Because ZVI-based reactions are surface-mediated processes, increasing surface area of ZVI was found to increase the reaction rates (Wang and Zhang, 1997). It has been reported that decreasing the size of ZVI particles to the nanoscale can greatly enhance the reaction rates for perchlorate reduction (Cao et al., 2005) and nitrate removal (Yang and Lee, 2005). However, because nanoscale ZVI particles tend

to agglomerate rapidly (in a few minutes) (He and Zhao, 2005; He et al., 2007), the “nanoparticles” without a stabilizer are actually agglomerates or flocs of ZVI particles in the micron scale.

To maximize the reactivity of ZVI nanoparticles, He and Zhao (2005) and He et al. (2007) modified the conventional water-based approach for preparing ZVI nanoparticles by applying a food-grade water-soluble starch or sodium carboxymethyl cellulose (CMC) as a stabilizer. Compared with conventional non-stabilized ZVI “nanoparticles”, the stabilized nanoparticles displayed much greater surface area, superior physical stability, and much faster TCE-dechlorination rates.

This present study aims to test the feasibility of using starch- or CMC-stabilized ZVI nanoparticles for perchlorate destruction in fresh water or in spent IX regenerant brine or contaminated saline water. The specific objectives are to (1) determine the rate and extent of perchlorate reduction by stabilized ZVI nanoparticles and (2) characterize the influences of temperature, salinity, and pH on the reactivity of the nanoparticles.

2. Materials and methods

2.1. Chemicals

The following chemicals were used as received: 4-(2-hydroxyethyl)-1-piperazineethane ethanesulfonic acid (HEPES, $\text{C}_8\text{H}_{18}\text{N}_2\text{O}_4\text{S}$) (Fisher, Fair Lawn, NJ, USA); aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) (Fisher); cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) (Fisher); cupric chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (Fisher); ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (Acros Organics, Morris Plains, NJ, USA); methyltrioxorhenium (VII) (MeReO_3 , 98%) (Strem Chemicals, Newburyport, MA, USA); nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) (Fisher); potassium hexachloropalladate (K_2PdCl_6 , 99%) (Acros Organics); sodium borohydride (NaBH_4) (MP Biomedicals, Aurora, OH, USA); sodium carboxymethyl cellulose (MW = 90,000, DS = 0.7) (Acros Organics); sodium chloride (NaCl) (Fisher); sodium chlorate (NaClO_3 , laboratory grade) (Fisher); sodium chlorite (NaClO_2 , 80%) (Fisher); sodium hypochlorite (NaClO) (Acros Organics); sodium perchlorate (NaClO_4 , >98%) (Aldrich, St. Louis, MO, USA); and a water-soluble starch (Alfa Aesar, Ward Hill, MA, USA).

2.2. Preparation of stabilized ZVI nanoparticles

Stabilized ZVI nanoparticles were prepared following a procedure reported previously (He and Zhao, 2005; He et al., 2007). In brief, the preparation was carried out in a 500 mL flask attached to a vacuum line. A solution containing 1.2% (w/w) starch or 1.2% CMC was prepared by dissolving a water-soluble starch or CMC with deionized (DI) water and then the solutions were purged with purified N_2 for half an hour to remove dissolved oxygen (DO). A stock solution of $0.2\text{ M FeSO}_4 \cdot 7\text{H}_2\text{O}$ was also prepared with DI water. The $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ stock solution was then added to the starch or CMC solution through a buret to yield a final concentration of 2 g L^{-1} of iron and 1% (w/w) of starch or CMC. The mixture was purged with N_2 for half an hour to remove DO and to mix

the solution. Fe(II) ions were then reduced to Fe(0) nanoparticles by adding a stoichiometric amount of sodium borohydride to the mixture. To ensure efficient use of the reducing agent, the reactor system was operated under inert conditions through continuous vacuuming. The flask was hand-shaken intermittently during the preparation. When gas (hydrogen) evolution ceased (after 15 min), the ZVI nanoparticles were ready for use. To test the effect of metal catalysts, a second metal (Al, Cu, Co, Ni, or Pd) solution was added at 0.3% (w/w) of Fe to the ZVI nanoparticles to yield a class of stabilized bimetallic nanoparticles. To test the catalytic effect of rhenium (Re), various masses of solid methyltrioxorhenium (MeReO_3) were dissolved to select Fe–Pd suspensions to achieve desired catalyst concentrations. For comparison, non-stabilized ZVI nanoparticles were also prepared following the same procedure but without the addition of a stabilizer.

2.3. TEM and DLS characterization

Transmission electron micrograph (TEM) images were obtained using a Zeiss EM10 transmission electron microscope (Zeiss, Thornwood, NJ) operated at 25 and 40 kV. The TEM image was analyzed using a specialty image-processing software ImageJ to obtain the particle size. Detailed procedures on the sample preparation and analyses were reported elsewhere (He and Zhao, 2005).

Dynamic light scattering (DLS) tests were performed with a Nicomp 380 Submicron Particle Sizer (PSS, Santa Barbara, CA) at a measurement angle of 90° (Internal He–Ne laser, wavelength 633 nm). DLS measures the dynamic particle size distribution of the nanoparticles in situ (aqueous solution). The particle size was measured based on number weighting, and the minimum particle diameter was set at 1 nm. The viscosity of various nanoparticle suspensions was measured with a Gilmont falling ball viscometer and then used to correct the influence of viscosity on particle mobility. Before the measurements, freshly prepared nanoparticle suspensions were first diluted to 0.1 g L^{-1} with nitrogen-purged 0.2% CMC or starch solutions. Samples were placed in the machine for 5 min prior to start of the measurements. Each sample was measured three times (10 min each). The DLS data were then processed with a software package (CW380) to yield the number-weighted size distributions.

2.4. Degradation of perchlorate

Batch kinetic tests for perchlorate degradation by the nanoparticles were carried out using 25 mL glass vials. The degradation was initiated by mixing 2.5 mL of a perchlorate stock solution ($1.0\text{--}10.0 \text{ mM}$) and 22.5 mL of a certain type of ZVI nanoparticle suspension (2 g L^{-1} Fe), which resulted in an initial ClO_4^- concentration of either 10 or 100 mg L^{-1} . These initial concentration values are within the range of reported perchlorate levels, especially in the source zones (USGAO, 2005) or in spent IX brine, and are comparable to those studied by other researchers (Cao et al., 2005; Hurley and Shapley, 2007; Moore et al., 2003; Oh et al., 2006a,b). In all cases, a ZVI dose of 1.8 g L^{-1} was tested, which required a stabilizer (CMC or starch) concentration of 0.9% (w/w) to

maintain effective particle stabilization. The iron dose amounts to the lower end of the range ($1.0\text{--}20.0 \text{ g L}^{-1}$ of non-stabilized ZVI) tested by Cao et al. (2005). Higher concentrations of ZVI were also prepared, but it would require the stabilizer concentration to be increased accordingly. Our tests indicated that when CMC exceeded 1.2% (w/w), it became gelatinized upon heating, and thus no longer suitable for the desired uses. The vials were then sealed with Teflon-lined caps, and placed in an oven (Thelco model 28, Gca/Precision Scientific), which was set at a desired temperature. We observed that stirring at 40 rpm on a rotator (Glas-Col, Terre Haute, IN, USA) at 80°C showed no significant effect on perchlorate reduction kinetics. Therefore, no stirring was provided in all tests. At predetermined times, duplicate sample vials were sacrificed for analyzing remaining perchlorate. Typically, $\sim 0.5 \text{ mL}$ of sample was diluted with acidified DI water ($\text{pH} = 3$) by 10–100 times to convert the remaining ZVI nanoparticles to soluble Fe(II), and then analyzed for perchlorate and reduction by-products such as chlorate, chlorite, hypochlorite, and chloride. Control experiments were carried out without the nanoparticles but under otherwise identical conditions.

To test pH effect, the degradation experiments were carried out at an initial pH ranging from 5.1 to 8.5 adjusted with 0.1 N NaOH and/or 0.1 N HCl, or at pH 7.0–7.4 by adding 5 mM HEPES buffer solution to the vials.

2.5. Chemical analyses

Anions (ClO_4^- , ClO_3^- , ClO_2^- , ClO^- , Cl^-) were analyzed using a Dionex ion chromatograph (DX-120) equipped with a suppressed conductivity detector. ClO_4^- was analyzed using an AS16 column, an AG16 guard column, and a $1000 \mu\text{L}$ sample loop. A degassed 50 mM sodium hydroxide solution was used as the eluent. The detection limit for perchlorate was $4 \mu\text{g L}^{-1}$. ClO_3^- , ClO_2^- , ClO^- , and Cl^- were analyzed using an AS14 column, an AG14 guard column, and a $100 \mu\text{L}$ sample loop. Detection limits for ClO_3^- , ClO_2^- , ClO^- , and Cl^- were 0.1, 0.1, 0.05, and 0.05 mg L^{-1} , respectively. A solution containing 3.5 mM sodium carbonate and 1.0 mM sodium bicarbonate was used as the eluent. The eluent flow rate was set at 1.0 mL min^{-1} .

3. Results and discussion

3.1. Characterization of nanoparticles

Fig. 1 shows the TEM image of ZVI nanoparticles prepared at 2 g L^{-1} Fe and stabilized with 1% CMC. The stabilized ZVI nanoparticles appeared as discrete nanoparticles and remained dispersed in water for more than 1 week. Five TEM images including 1711 particles were analyzed for estimating the particle size. The mean size of the freshly prepared CMC-stabilized nanoparticles was estimated to be $11.2 \pm 7.9 \text{ nm}$ (standard deviation). Meanwhile, DLS tests were also carried out to obtain the dynamic “wet” particle size distribution. The DLS results gave a particle diameter of $13.7 \pm 2.3 \text{ nm}$ (99.9% particles by number), which appears to agree with TEM-based “dry” particle size. Based on a mean diameter of 13.7 nm, the

Fig. 1 – TEM image of fresh ZVI nanoparticles stabilized with 1% (w/w) CMC. The scale bar represents 100 nm.

Fig. 2 – Perchlorate reduction by CMC-stabilized ZVI nanoparticles at various temperatures. Initial $[\text{ClO}_4^-] = 10 \text{ mg L}^{-1}$, ZVI = 1.8 g L^{-1} , CMC = 0.9% (w/w), initial pH (pH_0) = 6.5, and final pH (pH_f) = 7.5–7.8. Control tests were performed at 110°C with no ZVI. Data plotted as mean of duplicates, and errors refer to standard deviation.

surface area was calculated to be $55.6 \text{ m}^2 \text{ g}^{-1}$ following the method by He and Zhao (2005). DLS tests were also carried out for the starch-stabilized ZVI nanoparticles. A mean particle diameter of $22.6 \pm 2.8 \text{ nm}$ (99.9% by number) was obtained, which translates into a surface area of $33.7 \text{ m}^2 \text{ g}^{-1}$.

3.2. Kinetics and activation energy of perchlorate reduction

Fig. 2 shows the perchlorate reduction kinetics using 1.8 g L^{-1} ZVI nanoparticles stabilized with 0.9% CMC (w/w) at temperatures ranging from 25 to 110°C . The initial pH was ~ 6.5 and the final pH was 7.5–7.8 after 6 h. At 25°C , the degradation proceeded slowly with only 23% of perchlorate reduced in 6 h. When the temperature was raised to 50, 80, 95, and 110°C , the reaction was accelerated progressively. At 95°C , 97% perchlo-

rate was eliminated in 6 h, and at 110°C , complete perchlorate degradation was achieved within only 2 h. It is noteworthy that the perchlorate reduction (except at 110°C) displayed a rapid initial drop, and then bounced back up briefly before perchlorate was further degraded. A similar kinetic profile was also observed by Moore et al. (2003) and Moore and Young (2005), who tested the effectiveness of commercial iron filings for perchlorate degradation. In the perchlorate-laden solution, ZVI nanoparticles undergo the following competitive reactions (Gu et al., 2003; Cao et al., 2005):

As the reactions proceed, the surface of the ZVI nanoparticles is progressively oxidized to iron oxides. In the experimental pH range (6.5–7.8), the resultant iron oxides can rapidly adsorb ClO_4^- from water, resulting in the observed rapid drop in perchlorate concentration in the solution phase. However, the concurrent rapid adsorption and reduction of perchlorate rapidly depletes the perchlorate chemical potential in the solution phase such that the concentration gradient between the particle surface and the solution phase was reversed, and the sorbed perchlorate started releasing back into the solution. The perchlorate desorption was even further promoted as the concentration of chloride ions resulting from the reduction of perchlorate built up. At elevated temperatures (e.g. 110°C), the perchlorate sorption became thermodynamically less favored, whereas the perchlorate reduction was overwhelmingly enhanced. As a result, the “dipping” effect was less significant at higher temperatures. As will be discussed later in the chlorine mass balance study, the sorption/desorption process was a rather short-lived process and became negligible after 100 min of the reaction.

The degradation kinetic data can be interpreted using a pseudo-first-order rate model, Eq. (3), following the approach by Johnson et al. (1996):

$$\frac{d[\text{ClO}_4^-]}{dt} = -k_{\text{SA}} a_s \rho_m [\text{ClO}_4^-] = -k_{\text{obs}} [\text{ClO}_4^-], \quad (3)$$

where $[\text{ClO}_4^-]$ is the perchlorate concentration (mg L^{-1}) in water at time t (min), k_{SA} is the specific reaction rate constant based on surface area of the nanoparticles ($\text{L min}^{-1} \text{ m}^{-2}$), a_s is the specific surface area of the nanoparticles ($\text{m}^2 \text{ g}^{-1}$), ρ_m is the mass concentration of the nanoparticles (g L^{-1}), and k_{obs} is the observed pseudo-first-order rate constant (min^{-1}). Because the model describes only reactive degradation of perchlorate, it is only used for the degradation data after perchlorate concentration was recovered from the sorption/desorption perturbation step. A similar data-fitting approach was also used by Moore et al. (2003) to determine perchlorate reduction rates by ZVI filings.

Fig. 3 shows linearized plots ($\ln(C/C_0)$ vs. time) of the experimental and model-simulated kinetic data, where C_0 denotes the perchlorate concentration right after the perchlorate concentration profile was recovered from the initial sorption/desorption dip and where the perchlorate concentration began to drop again. Table 1 gives the fitted model parameters. Fairly good model fitting ($R^2 > 0.90$) was obtained.

Fig. 3 – Fitting a pseudo-first-order model to the experimental perchlorate reduction rate data of Fig. 2. Symbols: experimental data; lines: model fittings.

Table 1 – Observed pseudo-first-order rate constant of perchlorate reduction by CMC-stabilized iron nanoparticles at various temperatures

Temperature (°C)	k_{obs} (min ⁻¹)	R^2
25	0.0002	0.96
50	0.0003	0.94
80	0.0021	0.97
95	0.0096	0.97
110	0.0164	0.90

Evidently, the observed pseudo-first-order rate constant (k_{obs}) was improved by 82 times when the temperature was increased from 25 to 110 °C.

The degradation enhancement at elevated temperatures can be easily revealed when the experimental data are plotted in accord with the linearized Arrhenius equation

$$\ln k_{\text{obs}} = \ln A - \frac{E_a}{RT}, \quad (4)$$

where A is a constant, E_a the activation energy (kJ mol⁻¹), R the universal gas constant (8.314 J K⁻¹ mol⁻¹), and T the absolute temperature (K).

Fig. 4 also gives an activation energy (E_a) of 52.59 ± 8.41 kJ mol⁻¹ and an A value of 194,075 for the CMC-stabilized ZVI nanoparticles. This relatively high level of activation energy is associated with the unique chemistry of perchlorate. Although the chlorine in perchlorate is at its highest oxidation state (+7), and thus reduction of perchlorate is thermodynamically favorable, perchlorate is quite inert toward most of the common reducing agents due to the high kinetic barrier (Urbansky, 1998). However, the activation energy (E_a) determined in this study is much lower than those reported by others. For example, Gu et al. (2003) reported an activation energy of 120 ± 5 kJ mol⁻¹ when ferrous iron was used to reduce a perchlorate waste residual containing ferric chloride and hydrochloric acid at elevated temperatures (up to 200 °C) and/or pressure (~20 atm). Cao et al. (2005) reported an activation energy of 79.02 ± 7.75 kJ mol⁻¹ for

Fig. 4 – Linearized Arrhenius plot of the observed first-order rate constant (Table 1) as a function of $1/T$.

reduction of perchlorate (200 mg L⁻¹) by non-stabilized ZVI particles at various ZVI doses (1.0–20.0 g L⁻¹). The ZVI nanoparticles serve as both a reactant (electron donor) and a catalyst (Lowry and Liu, 2006). Accordingly, the much lower activation energy for the CMC-stabilized ZVI can be attributed to two factors. First, the presence of CMC greatly enhances the surface reactivity of the ZVI nanoparticles. As will be illustrated later on, the surface-normalized rate constant (K_{SA}) for CMC-stabilized ZVI is 3.3 times greater than that for non-stabilized ZVI. Second, the presence of CMC may also boost the catalytic activity of the ZVI nanoparticles. Both enhanced surface reactivity and elevated catalytic activity can result in a reaction pathway of much lower activation energy for perchlorate degradation.

3.3. Chlorine mass balance and reaction completeness

Perchlorate reduction follows the sequential reactions below (Rikken et al., 1996; Gu et al., 2003; Cao et al., 2005):

Thus, the completeness of perchlorate reduction can be revealed by following the production of chlorate, chlorite, hypochlorite, and/or chloride in the system. The concentration of chlorine-containing species (ClO_4^- , ClO_3^- , ClO_2^- , ClO^- , and Cl^-) was measured during a set of batch kinetic experiments. Fig. 5 shows the concentrations of ClO_4^- and Cl^- as well as the total chlorine-containing species against reaction time. Because ClO_3^- , ClO_2^- , and ClO^- were not detected during the tests, the total chlorine-containing species was actually the sum of ClO_4^- and Cl^- .

While chloride production increased steadily with time, perchlorate displayed an initial concentration dip due to the initial sorption/desorption effect. Because of the initial rapid adsorption, the measured total chlorine species at ~20 min accounted for only 72% of the total ClO_4^- initially added in the system, which suggests that a significant fraction of perchlorate added was initially adsorbed to the nanoparticles without being degraded. After ~60 min, when the effect of sorption/desorption became less significant, the sum of ClO_4^-

Fig. 5 – Chlorine mass balance during perchlorate reduction by CMC-stabilized ZVI nanoparticles. Initial $[\text{ClO}_4^-] = 10 \text{ mg L}^{-1}$, ZVI dose = 1.8 g L^{-1} , CMC = 0.9% (w/w), $\text{pH}_0 = 6.6\text{--}6.8$ and $\text{pH}_f = 7.7\text{--}7.8$. Data plotted as mean of duplicates, and errors refer to standard deviation.

and Cl^- accounted for 93–101% of total ClO_4^- initially added in the system. The nearly perfect mass balance indicates that (1) the initially strong sorption and desorption of perchlorate became negligible after ~ 60 min and (2) perchlorate was nearly completely reduced to chloride without production of significant amounts of intermediate products such as ClO_3^- , ClO_2^- , and ClO^- .

3.4. Perchlorate reduction by various iron nanoparticles

He and Zhao (2005) and He et al. (2007) reported that both water-soluble starch and CMC can stabilize ZVI nanoparticles. In addition, they reported that addition of a metal catalyst such as Pd on the ZVI nanoparticles can greatly catalyze degradation of chlorinated hydrocarbons. To test the effect of stabilizer type and metal catalysts on the perchlorate degradation, parallel kinetic tests were carried out using non-stabilized ZVI particles, starch- or CMC-stabilized ZVI nanoparticles, and stabilized nanoparticles with a metal catalyst (i.e. Al, Cu, Co, Ni, Pd, or Re).

Fig. 6 compares perchlorate degradation rates for various particles at 110°C under otherwise identical conditions. Again, Eq. (3) was used to interpret the experimental data, and Table 2 gives the fitted model parameters. Based on the k_{obs} values, starch- and CMC-stabilized ZVI nanoparticles degraded perchlorate 1.8 and 5.5 times, respectively, faster than non-stabilized ZVI particles. Based on the surface-area-normalized rate constant k_{SA} , starch- and CMC-stabilized ZVI nanoparticles degraded perchlorate 1.8 and 3.3 times, respectively, faster than non-stabilized ZVI particles. These improved k_{SA} values suggest that stabilizers not only increased the surface area of the nanoparticles (because of the much smaller particle size), but also resulted in a more reactive particle surface. On the other hand, the k_{SA} value for CMC-stabilized ZVI nanoparticles is more than two orders of magnitude greater than that for a cast iron (surface area- $1.29 \text{ m}^2 \text{ g}^{-1}$) reported by Oh et al. (2006a).

Fig. 6 – Perchlorate reduction by various ZVI-based particles. For all cases, ZVI dose = 1.8 g L^{-1} , initial $[\text{ClO}_4^-] = 10 \text{ mg L}^{-1}$, $\text{pH}_0 = 6.5\text{--}6.8$, $\text{pH}_f = 7.5\text{--}7.8$, and temperature = 110°C ; for stabilized ZVI nanoparticles, starch or CMC = 0.9% (w/w); for Fe–Pd bimetallic nanoparticles, Pd = 0.3% of Fe (w/w). Data plotted as mean of duplicates, and errors refer to standard deviation.

The k_{obs} and k_{SA} for CMC-stabilized nanoparticles are 3.0 and 1.8 times, respectively, greater than for starch-stabilized nanoparticles. This observation indicates that CMC is a more efficient stabilizer than starch, i.e. CMC gives not only smaller but also more reactive ZVI nanoparticles. The more effective particle stabilization of CMC is attributed to its carboxymethyl groups that interact with Fe(II) as well as the nanoparticles more strongly than the hydroxyl groups of starch do (He et al., 2007).

Interestingly, the presence of a second metal (e.g. Pd added at 0.3% of Fe) reduced k_{obs} and k_{SA} by 44.5%. Similar inhibitive effects were also observed when other metals such as Al, Co, Cu, and Ni were used (data not shown). When a second metal is added to the ZVI suspensions, the following redox reaction will take place:

However, this reaction should not consume the reducing power of the ZVI nanoparticles to any appreciable extent, given the minimal amount of the second metal added. The significant drop in perchlorate reduction rate with the catalysts is then primarily attributed to the fact that the metal catalysts can catalyze the corrosion reaction of the ZVI nanoparticles (Eq. (1)). This accelerated side reaction rendered more profound loss in the reducing power of the ZVI nanoparticles toward perchlorate. Cao et al. (2005) reported that addition of Pd or Ag to non-stabilized ZVI particles showed no performance enhancement for perchlorate degradation.

Rhenium has been well recognized to be able to catalyze perchlorate reduction through an oxygen transfer reaction (Cai and Espenson, 2005; Abu-Omar et al., 2000; Abu-Omar, 2006). A recent study reported that perchlorate was reduced completely to chloride within 24 h by hydrogen (40 psig) in the presence of methyltrioxorhenium (MeReO_3 , 0.5 mM) and

Table 2 – Physical parameters and perchlorate reduction rate constants for various iron nanoparticles at 110 °C

Type of nanoparticles	a_s (m ² g ⁻¹)	ρ_m (g L ⁻¹)	k_{obs} (min ⁻¹)	k_{SA} (10 ⁻⁵ L min ⁻¹ m ⁻²)
Non-stabilized Fe	33.5 ^a	1.8	0.0030	5.0
Starch-stabilized Fe	33.7	1.8	0.0055	9.1
CMC-stabilized Fe	55.6	1.8	0.0164	16.4
CMC-stabilized Fe/Pd	55.6	1.8	0.0091	9.1

^a From Wang and Zhang (1997).

Fig. 7 – Perchlorate reduction by CMC-stabilized ZVI nanoparticles in the presence of various background chloride concentrations at 95 °C. Initial $[\text{ClO}_4^-] = 100 \text{ mg L}^{-1}$, ZVI dose = 1.8 g L^{-1} , CMC = 0.9% (w/w), $\text{pH}_0 = 6.5\text{--}6.8$, and $\text{pH}_f = 7.5\text{--}7.8$. Data plotted as mean of duplicates, and errors refer to standard deviation.

palladium (0.5 mM) as catalysts (Hurley and Shapley, 2007). However, in our study, when MeReO_3 (0.5 mM) and Pd (0.5 mM) were also added to the CMC-stabilized ZVI nanoparticles, no improvement in perchlorate degradation was observed.

3.5. Effect of background chloride or salinity

As discussed earlier, chloride is one of the key products in perchlorate degradation, and will accumulate as the reaction proceeds. Moore et al. (2003) reported that the presence of 28.2 mM (or 1.0 g L^{-1}) of chloride nearly ceased perchlorate degradation by commercial iron filings (size = 20–100 mesh). On the other hand, it is practically very desirable to destroy perchlorate in saline water or spent IX brine, where high concentrations of perchlorate are co-present with high concentrations of chloride and/or other salts (Gingras and Batista, 2002; Xiong et al., 2006).

Fig. 7 shows the degradation kinetics of perchlorate in the presence of chloride (added as NaCl) from 0.1 to 36.4 g L^{-1} (0.02–6% w/w as NaCl). The degradation profile with 0.1 g L^{-1} of Cl^- nearly coincided with that when no chloride was added (with the same k_{obs} of 0.0018 min^{-1}). When chloride concentration was increased to higher levels (1.0 and 10 g L^{-1}), perchlorate reduction was actually enhanced. For example,

the k_{obs} value was 0.022 and 0.0027 min^{-1} at $\text{Cl}^- = 1.0$ and 10 g L^{-1} , respectively, a 22% and 50% increase compared with that when Cl^- was absent. On the other hand, Gotpagar et al. (1999) reported that pretreatment of the iron surface by chloride ions was able to enhance the initial degradation rate of trichloroethylene with ZVI. Johnson et al. (1998) observed that addition of chloride ions increased the rate of CCl_4 dechlorination with ZVI by as much as four times.

The reaction enhancement by chloride can be attributed to two factors. First, the addition of chloride ions can enforce the breakdown of the thin film of iron (hydr)oxides on ZVI surface. Hard Lewis base ions (such as Cl^- , Br^- , and I^-) were reported to be especially aggressive toward the passivating oxide layers to form strong complexes with iron centers (Gotpagar et al., 1999; Johnson et al., 1998). As the oxide layers are broken down by these diffusing anions, more ZVI surface becomes available for perchlorate reduction, resulting in improved perchlorate degradation. Second, chloride can promote localized corrosion on iron with irregular pit shapes, and pitting on the iron surface provides added reactive sites for perchlorate reduction (Gotpagar et al., 1999; Prinz and Strehblow, 1998).

However, when the chloride concentration was increased from 10 to 36.4 g L^{-1} , k_{obs} was decreased only by 23% (to 0.0023 min^{-1}), although this value is still 27% greater than that when no NaCl was added. This observation indicates that at the extremely high concentration of chloride, the competition of chloride ions with perchlorate for the sorption sites becomes prohibitively fierce as the beneficial effects of salinity are outweighed. Nonetheless, Fig. 7 shows that in the presence of 6% NaCl 87.4% of 100 mg L^{-1} ClO_4^- was destroyed by 1.8 g L^{-1} of CMC-stabilized ZVI nanoparticles at 95 °C in 450 min, indicating that the stabilized ZVI nanoparticles can effectively destroy perchlorate in typical IX brine.

As indicated by Eq. (2), as perchlorate is converted to chloride, Fe is oxidized to Fe^{2+} . The resultant ferrous ions are non-toxic and can be either reused or removed. For example, in case of IX brine treatment, the added chloride from perchlorate reduction actually enhances the regenerating power of the brine, and thus it is desirable to reuse the brine for regeneration. As perchlorate is re-concentrated in the reused brine, new ZVI nanoparticles can be produced in situ by reducing the existing Fe^{2+} ions in the brine with borohydride. Given the fairly low solubility of Fe^{2+} (e.g. 44 mg L^{-1} at pH 8.0), it can be removed, if desired, either by slightly raising the pH or by converting it to even less insoluble Fe^{3+} under ambient conditions.

Fig. 8 – Effect of pH on perchlorate reduction by CMC-stabilized ZVI nanoparticles in the presence of 6% NaCl (w/w) at 95 °C. Initial $[\text{ClO}_4^-] = 100 \text{ mg L}^{-1}$, ZVI dose = 1.8 g L^{-1} , CMC = 0.9% (w/w). The pH given refers to initial and final pH. Data plotted as mean of duplicates, and errors refer to standard deviation.

3.6. Effect of pH on perchlorate reduction.

As revealed by Eqs. (1) and (2), hydrogen activity (pH) can affect corrosion of iron as well as degradation of perchlorate. Fig. 8 shows perchlorate reduction using 1.8 g L^{-1} CMC-stabilized ZVI nanoparticles in the presence of 6% (w/w) NaCl at 95 °C and at various solution pH values. When the initial pH was 8.5, only 27.4% perchlorate was removed after 400 min with a k_{obs} of 0.0010 min^{-1} , which is 56.5% lower than at an initial pH of 6.8 ($k_{\text{obs}} = 0.0023 \text{ min}^{-1}$). The observed decrease in perchlorate degradation rate can be attributed to the formation of ferrous hydroxide and/or ferric hydroxide precipitates on the ZVI nanoparticle surface at elevated pH. The precipitates hinder the contact between ZVI nanoparticles surface and perchlorate, resulting in slower perchlorate reduction. Indeed, red precipitates were observed when the reacted ZVI solution at pH 8.5 was filtered through a $0.22 \mu\text{m}$ membrane filter. In contrast, faster perchlorate reduction kinetics ($k_{\text{obs}} = 0.0054 \text{ min}^{-1}$) was observed when the initial pH was lowered to 5.1. Because lower pH promotes both iron corrosion (Eq. (1)) and perchlorate degradation (Eq. (2)), this observation suggests that overall perchlorate reduction by ZVI nanoparticles is favored at lower pH. When a buffer (5 mM HEPES) was applied to hold solution pH in a range of 7.0–7.4, the degradation rate was greatly improved ($k_{\text{obs}} = 0.0092 \text{ min}^{-1}$).

4. Conclusions

Major findings and conclusions from this study are summarized as follows:

- (1) Perchlorate in both fresh water and brine can be rapidly and completely destroyed by low concentrations of stabilized ZVI nanoparticles at moderately elevated tem-

peratures. Based on the surface-area-normalized rate constant k_{SA} , starch- and CMC-stabilized ZVI nanoparticles degraded perchlorate 1.8 and 3.3 times, respectively, faster than non-stabilized ZVI particles. The activation energy (E_a) for the reaction was determined to be $52.59 \pm 8.41 \text{ kJ mol}^{-1}$. The nanoparticles were able to completely reduce perchlorate to chloride without accumulation of any intermediate products.

- (2) Temperature was found to be a critical factor for perchlorate reduction. The observed pseudo-first-order rate constant (k_{obs}) increased by 82 times (from 0.0002 to 0.0164 min^{-1}) when the temperature was increased from 25 to 110 °C.
- (3) Unlike degrading chlorinated organics, the presence of trace amounts (0.3% of Fe) of a metal catalyst (Al, Cu, Co, Ni, Pd, or Re) did not show any reaction improvement. On the contrary, the presence of Pd reduced the reaction rate by 44.5%. The inhibitive effect is attributed to accelerated corrosion reaction of the ZVI nanoparticles, which diminished the reducing power of the nanoparticles for perchlorate.
- (4) The stabilized ZVI nanoparticles can highly effectively destroy perchlorate in saline water or IX brine. The presence of high concentrations of NaCl (up to 6% w/w) increased perchlorate reduction rates by as high as 53%.
- (5) Solution pH can also affect the perchlorate reduction by ZVI nanoparticles. When the initial solution pH was lowered from 6.8 to 5.1, the perchlorate reduction rate was increased by 2.3 times. When a buffer solution (5 mM HEPES) was applied and pH was kept in the range of 7.0–7.4, the reaction rate was increased by ~4 times than without pH control.

The stabilized ZVI nanoparticles may offer an alternative means for completely destroying perchlorate in water that is small in volume and high in concentration such as perchlorate in source zones or IX brine.

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