**Removal of chlorinated organic solvents from hydraulic fracturing
wastewater by bare and entrapped nanoscale zero-valent iron**

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Abstract

With the increasing application of hydraulic fracturing, it is urgent to develop an effective and economically feasible method to treat the large volumes of fracturing wastewater. In this study, bare and entrapped nanoscale zero-valent iron (nZVI) were introduced for the removal of carbon tetrachloride (CT) and 1,1,2-trichloroethane (TCA) in model high-salinity fracturing wastewater. With increasing ionic strength (I) from Day-1 ($I = 0.35$ M) to Day-90 ($I = 4.10$ M) wastewaters, bare nZVI presented significantly lower removal efficiency of CT (from 53.5% to 38.7%) and 1,1,2-TCA (from 71.1% to 21.7%) and underwent more serious Fe dissolution from $1.31 \pm 1.19\%$ in Day-1 to $5.79 \pm 0.32\%$ in Day-90 wastewater. Particle aggregation induced by high ionic strength was primarily responsible for the lowered performance of nZVI due to less available reactive sites on nZVI surface. The immobilization of nZVI in alginate with/without polyvinyl alcohol provided resistance to particle aggregation and contributed to the superior performance of entrapped nZVI in Day-90 wastewater for 1,1,2-TCA removal (62.6-72.3%), which also mitigated Fe dissolution (4.00-4.69%). Both adsorption (by polymer matrix) and reduction (by immobilized nZVI) were involved in the 1,1,2-TCA removal by entrapped nZVI. However, after 1-month immersion in synthetic fracturing wastewater, a marked drop in the reactivity of entrapped nZVI for 1,1,2-TCA removal from Day-90 wastewater was observed with significant release of Na and total organic carbon. In summary, bare nZVI was sensitive to the nature of the fracturing wastewater, while the use of environmentally benign entrapped nZVI was more promising for wastewater treatment.

Keywords: nZVI; alginate entrapment; 1,1,2-trichloroethane; carbon tetrachloride; iron dissolution; fracturing wastewater treatment.

1. Introduction

Hydraulic fracturing is a method to enhance unconventional oil and gas production, which is being increasingly used, especially in the United States (Stringfellow et al., 2014). However, considerable concerns on the potential environmental and health impacts of the process have been raised (Chen et al., 2016; Yost et al., 2016). The production of large volumes of fracturing wastewater (FWW) (~5,000 m³ each well) is one of the principal aspects of concern, as FWW contains extremely high concentrations of salts (up to 350,000 mg L⁻¹), toxic metals/metalloids, radionuclides, and various organic constituents (Abualfaraj et al., 2014). A recent toxicity study based on real FWW indicated that rainbow trout (*Oncorhynchus mykiss*) could suffer from oxidative stress and endocrine disruption with the exposure to FWW (He et al., 2017), and chronic exposure to FWW could result in reproduction toxicity on *Daphnia magna* (Blewett et al., 2017). Hence, FWW should be properly treated prior to its reuse or final release into the environment.

Deep-well injection for FWW disposal has become less feasible due to the limited available injection sites and the pressure from the public for a more sustainable solution (Lutz et al., 2013). In recent years, conventional and advanced technologies have been put forward to treat the wastewater to a higher quality, especially membrane-based processes (Estrada and Bhamidimarri, 2016; Silva et al., 2017). However, severe membrane fouling induced by FWW, technical limitations (e.g., total dissolved solids (TDS) should be lower than 40 g L⁻¹ for reverse osmosis, and membrane distillation could not remove volatile organic compounds), and high capital and operating costs have limited their widespread application (Gregory et al., 2011; Silva et al., 2017).

Membrane bioreactor (MBR) technology, a combination of membrane separation and microbial transformation, is considered as a promising alternative and has been applied widely for municipal and industrial wastewater treatment (Sharghi and Bonakdarpour, 2013). The process with a halophilic bacterial consortium was able to remove 83-93% COD of hypersaline synthetic FWW (Sharghi and Bonakdarpour, 2013). However, high organic loads, a common characteristic of FWW, can induce membrane fouling and reduce sludge settling in the MBR process (Silva et al., 2017). The presence of excessive amounts of toxic contaminants could also suppress microbial activity. To overcome these limitations, a pre-treatment method could be introduced to partially remove the organics and metal/metalloid contaminants and thereby provide a better environment for microbial growth.

Due to the large surface area and unique catalytic activity, nanoscale zero-valent iron (nZVI) has been widely used for in situ soil and groundwater remediation (Yan et al., 2013; Stefaniuk et al., 2016). In addition to high removal capacity for metals/metalloids (e.g., Cu, Zn, Cr, and As), nZVI degrades a variety of organic compounds by chemical reduction, such as chlorinated organic compounds (Yan et al., 2013; Adeleye et al., 2016), which has been observed in FWW. Previous study demonstrated that nZVI could reduce 67% COD at circumneutral pH (7.5) and 85% toxicity in recalcitrant waste metalworking fluids, making the effluent more amenable for subsequent biological treatment (Jagadevan et al., 2012). Ma and Zhang (2008) integrated nZVI process with biological treatment at a full-scale application, which presented an efficient COD removal from industrial wastewater and contributed to process stability and microbial growth. Thus, nZVI could be a potential candidate for FWW pretreatment followed by biological treatment, such as by an

MBR process.

However, the application of bare nZVI powder may not be suitable for FWW treatment, owing to the possibility of particle aggregation in high ionic strength (Yan et al., 2013). Several strategies have been developed to stabilize nZVI, such as surface modification by polyelectrolytes, dispensing in an emulsified oil-water suspension, and immobilizing on a solid support (Crane and Scott, 2012; Lei et al., 2018). In order to minimize any potential toxicity effects, the immobilization of nZVI into a bio-based material could be a promising method to improve the application of nZVI in high-salinity FWW. Alginate, a natural biopolymer from marine brown algae, is nontoxic, biodegradable, non-immunogenic, and relatively insoluble in water, making it an ideal candidate for nZVI entrapment (Bezbaruah et al., 2014). Beads prepared from calcium alginate are sufficiently porous in nature to allow the contaminants to diffuse and make contact with entrapped nZVI. The immobilization of nZVI into calcium alginate beads has been successfully developed without reactivity sacrifice, as reflected by comparable performance with bare nZVI in nitrate, trichloroethene (TCE) and arsenic removal (Bezbaruah et al., 2009; Bezbaruah et al., 2011; Bezbaruah et al., 2014). Due to the rigid and fragile nature of crosslinked alginate, a flexible co-polymer, polyvinyl alcohol (PVA), was introduced to improve the durability and chemical stability (Lv et al., 2013). Previous studies investigated the reactivity of entrapped nZVI beads in background solution with low ionic strength, and/or evaluated the influence of single parameter (e.g., pH, nZVI dosage, and coexisting ions) (Bezbaruah et al., 2014; Liu et al., 2014; Chang et al., 2015), but not for wastewater with high ionic strength and various coexisting influencing factors. Our previous work has successfully applied entrapped nZVI for metal/metalloid removal from

FWW, which promoted Zn(II) and Cr(VI) removal and mitigated Fe dissolution (Sun et al., 2017), while the performance of entrapped nZVI for organic removal from FWW remains uncertain.

In this study, we evaluated the FWW treatment performance using both bare and entrapped nZVI with model FWW containing two chlorinated organic solvents, carbon tetrachloride (CT) and 1,1,2-trichloroethane (TCA), as representative organic contaminants. The two organics are carcinogenic and their mean concentrations detected in Marcellus Shale FWW were 9.5 times of their maximum contamination level of $5 \mu\text{g L}^{-1}$ for drinking water, while their maximum concentrations reached $2,000 \mu\text{g L}^{-1}$ (Abualfaraj et al., 2014). The objectives of the study were to: (i) investigate the relationship between FWW chemistry and organic degradation by bare nZVI; (ii) examine the effectiveness of entrapped nZVI for organic removal; (iii) evaluate the aging effects on the structure and reactivity of entrapped nZVI.

2. Materials and methods

2.1 Chemicals

The chemicals used for preparing model FWW (viz. NaOH, HCl, KCl, NaBr, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NaCl, and H_3BO_3) were reagent grade and obtained from Sigma Aldrich (USA). The initial pH of the model FWW was adjusted by using 0.1 M HCl or NaOH. The CT and 1,1,2-TCA compounds were purchased from Accuchem (USA) and Sigma Aldrich (USA). Methanol (99%, Tedia Company, Inc., USA) for CT and 1,1,2-TCA stock solution preparations and hexane (99%, Sigma Aldrich, USA) for CT and 1,1,2-TCA extractions were HPLC grade. Sodium alginate and PVA for nZVI entrapment were purchased from

Sigma Aldrich (USA). Deionized water (DIW) from a Milli-Q water process was used in the experiments.

2.2 Synthesis of fracturing wastewater

Model FWW in this study was synthesized based on Hayes (2009). Day-1, Day-14 and Day-90 FWW represented the wastewaters returning to the ground surface in 1, 14, and 90 days after well creation, respectively. The median concentrations of major inorganic compounds were chosen as the background levels as shown in our previous papers (Chen et al., 2017; Sun et al., 2017) and Table S1. A desired amount of the CT and 1,1,2-TCA stock solutions (prepared in methanol at 2,000 mg L⁻¹) were spiked into the model FWW by a glass syringe to yield a final concentration of each compound of 2 mg L⁻¹, corresponding to the maximum concentration detected in Marcellus Shale flowback water (Abualfaraj et al., 2014). The low concentration of methanol (0.1% v/v) in the prepared FWW would not induce cosolvent effects or affect the experimental results.

2.3 Bare nZVI and entrapment of nZVI

Commercially available nZVI Nanofer STAR (Nanoiron, Ltd., Rajhrad, Czech Republic) was air stable dry powder without surface modification, and had been used in our previous study (Sun et al., 2017). According to the manufacturer, Fe⁰ content, average particle size and surface area were 65~80%, 50 nm, and 25~30 m² g⁻¹, respectively. Entrapped nZVI beads were prepared according to the methods described in detail elsewhere (Babuponnusami and Muthukumar, 2013; Bezbaruah et al., 2014; Sun et al., 2017). Briefly, as shown in Fig. S1, 2.0 g of Na-alginate were dissolved in 100 mL DIW completely, and then were left to allow air bubbles to outflow (Solution 1). After that, 1.0

g nZVI was gently added to Solution 1 and continuously stirred with a glass rod (Solution 2). Then, the mixture was rapidly added drop-wise into 4.64% w/v CaCl_2 (Solution 3) by means of a peristaltic pump (Baoding Longer Precision Pump Co., Ltd. 0.5 mm ID tubing, 2.5 mL min^{-1} flow rate) from a height of 12 cm above the water surface to form alginate entrapped nZVI. The beads were retained in Solution 3 for 6-9 h to achieve adequate hardness and porosity, and then washed and stored in DIW.

For PVA-alginate entrapped nZVI, a 10% w/v Na-alginate solution was prepared by dissolving 5 g Na-alginate in 50 mL DIW. Then, 3 g PVA was added to 40 mL DIW and stirred at 80°C until complete dissolution. Then, 10 mL of 10% w/v Na-alginate solution was added into PVA solution and stirred for 45 min. One gram nZVI was added to the mixture after the temperature decreased to 35°C . The remaining steps to obtain PVA-alginate entrapped nZVI were the same as those for alginate entrapped nZVI. Blank alginate and PVA-alginate beads without nZVI were also prepared for comparison using the same procedures for the entrapped nZVI beads except the addition of nZVI.

Characteristics of the synthesized entrapped nZVI have been measured and presented in our previous study (Sun et al., 2017). In summary, the entrapped nZVI beads had a spherical shape and the average diameter of PVA-alginate entrapped nZVI (4 beads $\approx 2 \text{ cm}$) was slightly larger than alginate entrapped nZVI (4 beads $\approx 1.5 \text{ cm}$) (Fig. S2). In terms of comparative Fe content, the Fe amount in each PVA-alginate entrapped nZVI ($1.14 \mu\text{g bead}^{-1}$) was about two times that in alginate entrapped nZVI ($0.53 \mu\text{g bead}^{-1}$).

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176 2.4 CT and 1,1,2-TCA removal by bare and entrapped nZVI in fracturing wastewater

177 In order to investigate the degradation kinetics of CT and 1,1,2-TCA by bare nZVI, 1.0 g L⁻¹ nZVI
178 was used to treat 2 mg L⁻¹ CT or 1,1,2-TCA in 60-mL glass vials with triple sealed closures
179 containing 50-mL of Day-1, Day-14, or Day-90 FWW. The reaction was initiated by mixing nZVI
180 and FWW in the glass vials. Then, the vials were rapidly capped and placed in an end-over-end
181 rotary shaker (30 rpm) at room temperature for 5, 10, 15, 30, 60, 90, 120, and 240 min. All the
182 samples were tested in duplicate and control tests without nZVI were also included to evaluate the
183 loss of target compounds due to sorption and volatilization. In addition, a batch experiment
184 involving the replacement of FWW by DIW (i.e., CT/1,1,2-TCA, nZVI and DIW only) was also
185 carried out to investigate the effects of the fracturing wastewater chemistry. At a specified reaction
186 time, the samples were centrifuged at 4,000 rpm for 5 min and 1 mL of supernatant was mixed with
187 2 mL hexane thoroughly by vortexing for 3 min to extract the target compound (Danish et al., 2016;
188 Wu et al., 2014). After 5-min standing, the organic phase (target compound in hexane) was
189 transferred to a 2 mL gas chromatograph (GC) vial with a glass syringe. The GC vials were sealed
190 with parafilm and stored at 4°C before analysis. The recovery of the organics via the extraction
191 procedure was in the range of 85-95%.

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193 To investigate organic removal by entrapped nZVI in Day-90 wastewater, 1.0 g L⁻¹ nZVI was
194 replaced by 47 alginate entrapped beads or 22 PVA-alginate entrapped beads with 25 mL Day-90
195 FWW in 60-mL glass vials, based on a mass balance calculation. Control studies with FWW only
196 were conducted to evaluate the loss of organics during experiments. The removal of organics by

alginate and PVA-alginate beads without nZVI were also performed in parallel to investigate the effect of the polymer matrix on organic removal, in which the amount of alginate and PVA-alginate were the same as that used in organic removal by entrapped nZVI. All the experiments were carried out in duplicate.

2.5 Chemical stability of entrapped nZVI

Freshly made alginate or PVA-alginate entrapped nZVI beads containing 5 g nZVI were added in a bottle containing 300 mL of DIW, Day-1 or Day-90 model FWW. The bottles were placed at room temperature and shaken by hand for 5 min everyday. After aging for one month, the solid beads were collected after separation from the wastewaters, washed with DIW, and used for 1,1,2-TCA removal from Day-90 FWW as described above. In addition, the entrapped nZVI beads before and after aging were freeze-dried for characterization. The crystal phases were analyzed by high-resolution powder X-ray diffraction (XRD, Rigaku SmartLab, Japan). For the aqueous phase, the total organic carbon (TOC) content, Na and Fe content were measured before and after the 1-month aging process by TOC analyzer (SSM-5000A, Shimadzu, Japan, limit of detection of 0.1 mg L⁻¹) and atomic adsorption spectrometer (AAS, Agilent VGA77, USA, limit of detection of 0.1 mg L⁻¹), respectively. To illustrate the extent of dissolution, TOC, Na and Fe content in freshly made entrapped nZVI were calculated based on their compositions and mass balance (details in Supplementary Information). Gas chromatography/mass spectrometry (GC-MS) was also used to identify the dissolved organic contents following extraction with 2 mL of hexane as described in *Section 2.6*.

2.6 Analytical methods

GC-MS (Agilent 7890B GC analyzer, 5977 Mass Selective Detector, USA) was used to measure concentrations of CT and 1,1,2-TCA subsequent to the hexane extraction procedure. A DB-5 MS column (30 m long, and 0.25 μm thick film with 0.25 mm internal diameter) from Agilent Technologies was used, with helium as the carrier gas. The oven temperature was maintained at 35°C for 4 min, then increased at 10°C per min until 100°C was reached, and further increased at 30°C per min to 190°C. Samples were injected with a rate of 1 mL min⁻¹ at 230°C and detected at 280°C. Selected ion monitoring was used to acquire results. Calibration of standard organic concentrations including intermediates was carried out before the analysis of samples. Organic standards of 0.5 mg L⁻¹ were analyzed every 10 samples for quality assurance and quality control. The concentrations of Fe dissolved from bare and entrapped nZVI during the batch experiments were measured by the AAS (limit of detection of 0.1 mg L⁻¹) after further digestion by 5% HNO₃.

2.7 Statistical analysis

All experiments were performed in duplicate and the results were presented as mean $\pm$ standard deviations. One-way ANOVA followed by the Duncan test was applied to analyze the significance of the difference between two sets of data (SPSS version 22.0).

3. Results and discussion

3.1 Degradation of CT and 1,1,2-TCA by bare nZVI in fracturing wastewater

The degradation kinetics of CT and 1,1,2-TCA by bare nZVI in DIW and three aged FWWs are shown in Fig. 1. The removal of CT and 1,1,2-TCA was negligible in control tests (no nZVI) during

the whole experimental period and under all the conditions (data not shown). In contrast, rapid CT degradation was observed in the initial 60 min (Fig. 1a), and the degradation after 4-h reaction was 62.7±2.9% in DIW, 53.5±6.3% in Day-1 FWW, 50.4±4.6% in Day-14 FWW, and 38.7±1.4% in Day-90 FWW, respectively. Similarly, marginal 1,1,2-TCA degradation was observed after 60-min reaction (Fig. 1b), and the 4-h removal efficiency reached 94.1±2.8% in DIW, 71.1±1.1% in Day-1 FWW, 37.4±0.6% in Day-14 FWW, and 21.7±1.7% in Day-90 FWW, respectively.

The removal kinetics for both CT and 1,1,2-TCA by bare nZVI agreed with the pseudo-second-order kinetic model (Supplementary Information) and the resulting kinetic parameters are shown in Table 1. Interestingly, for both CT and 1,1,2-TCA, bare nZVI presented the greatest reactivity in DIW, while the highest calculated surface-area normalized rate constants (k_{SA} , L m⁻² h⁻¹) (i.e., 1.39×10⁻¹ L m⁻² h⁻¹ for CT and 2.61×10⁻¹ L m⁻² h⁻¹ for 1,1,2-TCA) were both observed in Day-1 FWW. This might be ascribed to the presence of moderate amount of Cl⁻ in Day-1 FWW (Table S1) that could enforce the breakdown of protective oxide film on nZVI surface and render more Fe⁰ available for target contaminants (Sun et al., 2016). However, the effect was relatively short-lived and nZVI was probably re-oxidized leading to the formation of a new passive oxide film (Liu et al., 2007; Reinsch et al., 2009; Xie and Cwiertny, 2012), thereby inhibiting the reactivity with subsequent exposure or at higher concentration of Cl⁻.

The results indicate that the performance of bare nZVI on CT and 1,1,2-TCA reduction was significantly affected by ionic strength (*I*), as indicated by the order of decreasing 4-h degradation efficiency: DIW (*I* = 0 M) > Day-1 (*I* = 0.35 M) > Day-14 (*I* = 2.49 M) > Day-90 (*I* = 4.10 M) (Figs.

1A&B). It is well recognized that increasing ionic strength compresses the electrical double layer on nZVI surfaces and alleviates the repulsive forces, thus enhancing particle aggregation that results in fewer accessible reactive sites and limited nZVI reactivity for organic degradation (Garner and Keller, 2014). The presence of NO_3^- (1.04 mM in Day-1, 4.01 mM in Day-14, and 6.27 mM in Day-90) in FWW could be partially responsible for the lower reactivity of bare nZVI in FWW compared to that in DIW. In addition to surface passivation, NO_3^- , as an iron reducible anion, can compete with target contaminants for the reactive sites on nZVI surface (Sun et al., 2016), and the extent of the inhibition would increase with increasing NO_3^- concentration (> 1 mM) (Liu et al., 2007). Hence, the reactivity of bare nZVI towards CT and 1,1,2-TCA degradation in FWW was clearly lower as a result of the nature of FWW water chemistry.

Due to aqueous corrosion of nZVI, continuous Fe dissolution was observed during CT and 1,1,2-TCA removal by bare nZVI in DIW and FWWs (Fig. 1c). The extent of Fe dissolution was independent of the organic species but largely dependent on the ionic strength. After 4-h reaction, only $0.57 \pm 0.08\%$ Fe was dissolved into DIW while much greater Fe dissolution corresponded to increasing I in Day-1 ($I = 0.35$ M, $1.31 \pm 0.09\%$), Day-14 ($I = 2.49$ M, $3.82 \pm 0.13\%$), and Day-90 FWW ($I = 4.10$ M, $5.79 \pm 0.32\%$). The increase in I could provide stronger separation between anodic and cathodic regions and allow the corrosion products (e.g., Fe^{2+}) to diffuse from the nZVI surface and enter the solution, which may even reverse surface passivation and lead to surface dissolution (Farrell et al., 2000). However, considering potential toxicity of iron in the environment (Lei et al., 2016; Lei et al., 2018), a high Fe concentration in FWW after nZVI treatment may require toxicity assessment and proper nZVI modification to suppress Fe dissolution in FWW.

3.2 CT and 1,1,2-TCA removal by entrapped nZVI in fracturing wastewater

Alginate entrapped nZVI was firstly introduced to Day-90 FWW, in which bare nZVI exhibited the poorest performance in CT and 1,1,2-TCA degradation. After 4-h reaction, alginate entrapped nZVI presented a comparable CT removal efficiency with bare nZVI ($p = 0.214$) (Fig. S3). Similar results were reported for TCE, nitrate, and arsenic removal (Bezbaruah et al., 2009; Bezbaruah et al., 2011; Bezbaruah et al., 2014). However, the rate constant k_{SA} ($2.36 \times 10^{-1} \text{ L m}^{-2} \text{ h}^{-1}$) for alginate entrapped nZVI was one order-of-magnitude greater than for bare nZVI ($3.71 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$) (Table 1). This could be attributed to the affinity of organics to alginate, which in turn enhanced the contact between CT and nZVI (Kuang et al., 2015). No significant increase in the reactivity of nZVI toward CT removal was observed after the entrapment, thus further addition of PVA in the polymer matrix was not conducted.

For 1,1,2-TCA removal, alginate entrapped nZVI not only produced a higher rate constant k_{SA} ($2.40 \times 10^{-1} \text{ L m}^{-2} \text{ h}^{-1}$) (Table 1), but also showed a superior performance in 1,1,2-TCA removal (Fig. 2a) compared with the bare nZVI. A pronounced decrease in 1,1,2-TCA concentration was observed in the first 60 min and the removal efficiency reached $62.6 \pm 1.7\%$ after 4-h reaction with alginate entrapped nZVI. It was evident that pure alginate beads (no nZVI) could absorb 1,1,2-TCA to some extent and contributed to the removal of $18.2 \pm 6.0\%$ 1,1,2-TCA within 4 h (Fig. 2a). Previous studies ascribed similar observation to physical sorption onto alginate beads, while the reduction was limited (Bezbaruah et al., 2011; Bezbaruah et al., 2014). In this study, the extremely high salt concentration ($I = 4.10 \text{ M}$) in Day-90 FWW may impose a “salting-out effect” on 1,1,2-TCA, which

exclude 1,1,2-TCA from the wastewater and thereby enhance the partitioning/penetration of the compound into the beads (Wang et al., 2010).

There appeared to be a synergistic effect between the alginate polymer matrix and the immobilized nZVI leading to the much greater 1,1,2-TCA removal (Fig. 2a). On one hand, the porous nature of the alginate allows the diffusion of the compound within the beads and thus contact with immobilized nZVI (Bezbaruah et al., 2014). As the immobilized nZVI particles are restrained within the confined space of the beads without significant modification of the surface, there is little compromise of their reactivity for contaminant reduction, as reported in DIW or background solutions with low *I* (Bezbaruah et al., 2009; Bezbaruah et al., 2011). On the other hand, due to the increased affinity of 1,1,2-TCA to the alginate polymer matrix, the adsorbed molecules are more available for the reduction by the immobilized nZVI (Kuang et al., 2015). The alginate polymer matrix could also serve as a physical barrier to the aggregation of entrapped nZVI, thereby providing more accessible reactive sites for reaction (Cho et al., 2015; Lee et al., 2016). These reasons possibly account for the superior performance of alginate entrapped nZVI in 1,1,2-TCA removal from Day-90 FWW compared to bare nZVI.

Introduction of PVA as a co-polymer for the entrapment further improved 1,1,2-TCA removal efficiency ($72.8 \pm 3.6\%$) after 4-h reaction compared to alginate entrapped nZVI (Fig. 2a). However, a smaller rate constant k_{SA} ($9.37 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$) was recorded (Table 1), which probably reflected the increased mass transfer limitation in the denser polymeric matrix enclosing nZVI after PVA addition (Lv et al., 2013). It was also found that 1,1,2-TCA was significantly removed by

adsorption onto PVA-alginate beads (without nZVI) after 30-min ($45.3 \pm 4.6\%$) and 4-h reaction ($60.2 \pm 1.8\%$) (Fig. 2a). The outstanding adsorption capacity of PVA-alginate beads was not anticipated, which might be due to specific bonding between PVA and 1,1,2-TCA that requires further investigation.

These results indicated that 1,1,2-TCA adsorption by the PVA-alginate polymer matrix was the primary removal mechanism for PVA-alginate entrapped nZVI beads. The difference between the total removal and the adsorption removal by the PVA-alginate entrapped nZVI suggested that at least 12.6% of 1,1,2-TCA was removed by the nZVI reduction. However, the contribution of chemical reduction was rather limited, possibly because substantial adsorption onto the matrix reduced the accessibility and subsequent reduction on the nZVI surface, which was similarly observed with polyelectrolyte coating (Phenrat et al., 2009) and powdered activated carbon-alginate matrix (Kim et al., 2010).

Therefore, in this study, the proposed mechanisms for 1,1,2-TCA removal by entrapped nZVI consisted of adsorption by the polymer matrix and chemical reduction by the immobilized nZVI. Kuang et al. (2015) suggested that the simultaneous removal of Cu and monochlorobenzene by alginate entrapped Ni-doped nZVI beads was a two-step process involving competitive adsorption and catalytic reduction. Similarly, oleic acid-coated alginate entrapped Pd-doped nZVI beads were reported to remove trichlorophenol in water via fast sorption by the polymer layer followed by subsequent dechlorination (Chang et al., 2015). Our results suggested that the adsorption capacity of polymer matrix (i.e., low in alginate but high in PVA-alginate) played a crucial role in

determining the relative significance of chemical reduction by the immobilized nZVI (i.e., high in alginate but low in PVA-alginate).

Besides, owing to the protective effect of the polymer matrix, much less Fe was released into the solution during 1,1,2-TCA removal by alginate entrapped nZVI ($4.69 \pm 0.30\%$) and PVA-alginate entrapped nZVI ($4.00 \pm 0.19\%$) (Fig. 2b) than with bare nZVI ($5.79 \pm 0.32\%$) (Fig. 1c). The polymer matrix was reported to adsorb metal ions via the carboxyl groups in alginate and hydroxyl groups in PVA (Lim et al., 2008; Bai et al., 2009; Wang and Wang, 2016), which was possibly responsible for the reduced release of aqueous Fe. Our previous work also demonstrated that nZVI entrapment could improve metal/metalloid (i.e., Zn, Cr, and As) removal from FWW and alleviate Fe dissolution (Sun et al., 2017). Hence, the high reactivity, easy recovery, and low Fe dissolution of entrapped nZVI make it a good candidate for high-salinity FWW treatment. The durability and long-term effectiveness of entrapped nZVI were investigated in the following section.

3.3 Long-term durability and stability of entrapped nZVI

Dissolution levels of different components of entrapped nZVI after 1-month aging in DIW, Day-1 and Day-90 FWW are presented in Table 2. TOC dissolution was only detected for the PVA-alginate entrapped nZVI, and a higher *I* in FWW caused greater TOC dissolution. After 1-month aging, 2.09% of the initial TOC content in PVA-alginate entrapped nZVI was dissolved into DIW while the TOC dissolution dramatically increased to 10.1% and 17.5% for PVA-alginate entrapped nZVI aged in Day-1 and Day-90 FWW, respectively. Lv et al. (2013) also reported a high TOC release from PVA-alginate entrapped nZVI applied in low *I* solution for Cr(VI) removal in the

first run, although the TOC release decreased sharply in the second and third runs.

The TOC release was associated with the decrease in the diameter of the PVA-alginate beads from initially 2.0 cm to 1.7 cm of 4 beads after 1-month aging in Day-1/Day-90 FWW (Fig. S2). GC-MS analysis revealed the existence of compounds with C=O group in the solution samples after aging of PVA-alginate entrapped nZVI. This functional group was only found in alginate, implying the dissolution of alginate during the aging process. Both alginate and PVA could form hydrogen bonds with the immobilized nZVI, and strong hydrogen bonding also existed between alginate and PVA (Zain et al., 2011; Lv et al., 2013; Huang et al., 2016). The addition of PVA seemed to outcompete and destabilize the hydrogen bonding between alginate and nZVI, thereby resulting in the release of alginate. The dissolution of water-soluble PVA could not be ruled out during the aging process. Hence, physical (e.g., freeze-thawing) or chemical (e.g., boric acid or sodium sulphate) cross-linking should be conducted on PVA to make it insoluble (Nunes et al., 2010; Zain et al., 2011; Wang and Wang, 2016) before application in future studies. Besides, leakage of Na from entrapped nZVI after 1-month aging increased with increasing *I* from Day-1 to Day-90 FWW (Table 2), which was primarily attributed to the ion-exchange reaction with residual Na on alginate (Lim et al., 2008; Huang et al., 2016), despite calcium chloride hardening before usage in this study.

Owing to the effective protection from the polymer matrix, there was negligible Fe dissolution after 1-month aging, where only at most 0.026% of the Fe content in the beads leached in Day-90 FWW (Table 2), which could be related to the presence of a few injured/broken beads (Fig. S2). Similar XRD patterns were obtained for both alginate and PVA-alginate entrapped nZVI before and after

the aging process (Fig. 3). In all the samples, only the typical peaks for Fe^0 at 2θ of about 45° and 65° were detected, indicating no formation of any new crystalline phase during the 1-month aging. In contrast, Reinsch et al. (2010) demonstrated that aging of nZVI in anaerobic DIW alone or in the presence of common groundwater anions (Cl^- , NO_3^- , SO_4^{2-} , HPO_4^{2-} , and HCO_3^-) for 1 month resulted in the oxidation of Fe^0 to Fe_3O_4 . Liu et al. (2015) even reported the formation of $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ and $\gamma\text{-FeOOH}$ after 5-day exposure of nZVI to static water.

In this study, Fig. 3 revealed that the immobilized nZVI remained Fe^0 state and/or amorphous iron oxides (i.e., precursor of crystalline iron oxides), validating the effective protection of entrapped nZVI from the polymer matrix against oxidation. Luo et al. (2014) also reported that the immobilization of nZVI in alginate microcapsules alleviated the susceptibility of nZVI to oxidation in the environment. Hence, the entrapment of nZVI in a polymer matrix could not only restrain Fe dissolution but also mitigate nZVI aging process in the aqueous environment.

Fig. 4 presents the reactivity of entrapped nZVI in terms of 1,1,2-TCA removal in Day-90 FWW before and after 1-month aging. The aging of entrapped nZVI substantially decreased its capacity for 1,1,2-TCA removal, except for alginate entrapped nZVI aged in DIW. A few studies documented that nZVI would gradually lose their reactivity with the progress of aging, especially for organics removal, as a result of the reduced Fe^0 content and/or a thickening surface iron oxide layer (Xie and Cwiertny, 2012; Pullin et al., 2017). In this study, on one hand, the oxidation of the immobilized nZVI into amorphous iron oxides was possible during the 1-month aging process, which would decrease Fe^0 content and suppress the performance of aged entrapped nZVI. On the other hand,

FWW contained a high concentration of salts, which might be adsorbed by the polymer matrix and thereby blocking the pores for contaminant diffusion. Certain amount of salts may even be able to pass through the polymer matrix and attach to the surface of the immobilized nZVI, resulting in less accessible reactive sites for organic reduction (Hwang et al., 2015).

With respect to PVA-alginate entrapped nZVI, the primary cause might be the dissolution of the polymer matrix, considering its pronounced contribution of adsorption to the overall 1,1,2-TCA removal. The released polymer debris might in turn result in pore clogging and mass transfer limitation. Although the 1-month aging notably inhibited their reactivity, entrapped nZVI particles still showed comparable efficiency for 1,1,2-TCA removal by bare nZVI in Day-90 FWW. These results reinforced the application potential of entrapped nZVI, yet more research is still needed to improve the long-term chemical stability of the polymer matrix for nZVI immobilization.

3.4 Economic viability

As shown in this study, entrapped nZVI is a promising material for high-salinity FWW wastewater treatment, while it can also be applied in permeable reactive barriers for simultaneous removal of metals and organics from groundwater wastewater (Kuang et al., 2015) and deployed as packing materials in a fixed-bed process with continuous-flow wastewater treatment (Chang et al., 2015). To illustrate the economic feasibility of entrapped nZVI for wastewater treatment, a preliminary cost analysis was performed in the present study.

The immobilization of nZVI in polymer matrix is a simple technique that only requires mechanical

stirring and dripping systems in the industrial scale. According to the online quotations from the largest regional supplier (Alibaba.com China, <https://www.1688.com>), the prices of sodium alginate, PVA, and CaCl_2 are approximately \$5 kg^{-1} , \$1.5 kg^{-1} , and \$0.1 kg^{-1} , respectively. The price for nZVI varied between £50 and £150 per kg (Crane and Scott, 2012), and a median price £100 kg^{-1} was chosen for cost analysis in this study. To simplify the scenario, fixed and variable costs for equipment, labour, maintenance etc., are supposed to be available on site. The total costs of entrapped nZVI were \$154.8 per kg nZVI for alginate entrapped nZVI and \$158.7 per kg nZVI for PVA-alginate entrapped nZVI, respectively (calculation details are available in Supplementary Information). Thus, the treatment costs are estimated to about \$154.8 m^{-3} and \$158.7 m^{-3} for FWW pretreatment with 1 g L^{-1} nZVI. Adeleye et al. (2016) reported that the costs of current technologies for wastewater treatment ranges from \$90 m^{-3} per day to \$2800 m^{-3} per day. Hence, the application of entrapped nZVI is financially viable for FWW treatment, and it will be even more competitive if the price of nZVI can be reduced by future technological advances.

4. Conclusions

This study investigated the potential application of nZVI for the removal of chlorinated organic solvents from high-salinity FWW. Bare nZVI was sensitive to FWW composition and suffered from substantial Fe dissolution and reduction in CT and 1,1,2-TCA degradation efficiency with increasing ionic strength in FWW. The decreased reactivity of nZVI was due to the combined effect of the complex water chemistry of FWW, and primarily attributed to its high ionic strength which induced particle aggregation. The effective immobilization of nZVI in alginate or PVA-alginate polymer matrix prevented particle aggregation and achieved superior performance for 1,1,2-TCA

removal, associated with less Fe dissolution. Entrapped nZVI could remove 1,1,2-TCA via both adsorption (by the polymer matrix) and chemical reduction (by the immobilized nZVI). Chemical reduction was the dominant removal mechanism observed in alginate entrapped nZVI while adsorption was the primary mechanism in PVA-alginate entrapped nZVI. With the protection of the polymer matrix, the oxidation of the immobilized nZVI was moderate without forming new crystalline phase during 1-month aging in fracturing wastewater. The aging process significantly inhibited the reactivity of entrapped nZVI for 1,1,2-TCA removal, but was however still comparable to the performance of bare nZVI in Day-90 FWW. Hence, entrapped nZVI overcame potential interference from the constituents of FWW and demonstrated practical advantages of high reactivity, economical production, easy storage, and environmental benignity for the treatment of high-salinity fracturing wastewaters.

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Table 1. Pseudo-second-order kinetics of CT and 1,1,2-TCA degradation in DIW, Day-1, Day-14, Day-90 **fracturing wastewater (FWW)** by nZVI and entrapped nZVI

Organic	nZVI type	Solution	q_{e2} (g kg ⁻¹)	k_2 (min ⁻¹ kg g ⁻¹)	k_2q_{e2} (min ⁻¹)	k_{sa} (L m ⁻² h ⁻¹)	R ₂ ²
CT	Bare nZVI	DIW	1.48	1.76×10 ⁻²	2.60×10 ⁻²	8.04×10 ⁻²	0.993
		Day-1 FWW	1.16	3.88×10 ⁻²	4.40×10 ⁻²	1.39×10 ⁻¹	0.997
		Day-14 FWW	1.29	1.45×10 ⁻²	1.86×10 ⁻²	5.75×10 ⁻²	0.970
		Day-90 FWW	1.05	1.14×10 ⁻²	1.20×10 ⁻²	3.71×10 ⁻²	0.980
	Alginate entrapped nZVI	Day-90 FWW	0.90	8.46×10 ⁻²	7.64×10 ⁻²	2.36×10 ⁻¹	0.980
1,1,2-TCA	Bare nZVI	DIW	2.23	1.35×10 ⁻²	3.00×10 ⁻²	9.28×10 ⁻²	0.970
		Day-1 FWW	1.53	5.51×10 ⁻²	8.44×10 ⁻²	2.61×10 ⁻¹	0.996
		Day-14 FWW	0.80	6.21×10 ⁻²	4.99×10 ⁻²	1.54×10 ⁻¹	0.999
		Day-90 FWW	0.46	1.24×10 ⁻¹	5.73×10 ⁻²	1.77×10 ⁻¹	0.999
	Alginate entrapped nZVI	Day-90 FWW	1.34	5.78×10 ⁻²	7.75×10 ⁻²	2.40×10 ⁻¹	0.996
	PVA-alginate entrapped nZVI	Day-90 FWW	1.71	1.77×10 ⁻²	3.03×10 ⁻²	9.37×10 ⁻²	0.990

Table 2. Dissolution from entrapped nZVI during 1-month aging.

nZVI type	Aging solution	Na dissolution (%)	Fe dissolution (%)	TOC dissolution (%)
Alginate entrapped nZVI	DIW	0.09	ND	ND
	Day 1 FWW	0.75	0.004	ND
	Day 90 FWW	3.18	0.025	ND
PVA-alginate entrapped nZVI	DIW	0.84	ND	2.09
	Day 1 FWW	2.89	0.002	10.1
	Day 90 FWW	7.07	0.026	17.5

Note: ND stands for non-detectable

Figure 1. CT (A) and 1,1,2-TCA (B) degradation by bare nZVI in DIW, Day-1, Day-14 and Day-90 fracturing wastewater. Average Fe dissolution from nZVI during the 4-h reaction for CT and 1,1,2-TCA removal from DIW, Day-1, Day-14 and Day-90 fracturing wastewater (C).

Figure 2. 1,1,2-TCA removal by bare and entrapped nZVI in Day-90 fracturing wastewater (A) and Fe dissolution from entrapped nZVI during the 4-h reaction (B).

Figure 3. XRD spectra of alginate entrapped nZVI (A) and PVA-alginate entrapped nZVI (B) after 1-month aging in DIW, Day-1 and Day-90 fracturing wastewater

Figure 4. 1,1,2-TCA removal efficiency of aged entrapped nZVI in Day-90 fracturing wastewater after 4-h reaction (different letters indicate significant difference).