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

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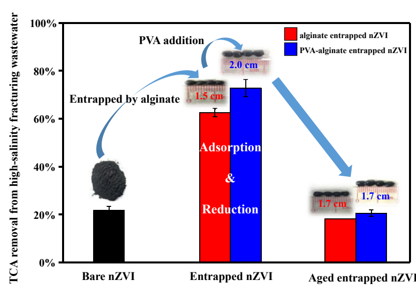
HIGHLIGHTS

- Increasing ionic strength decreased nZVI reactivity and increased Fe dissolution.
- Entrapping nZVI in polymer matrix improved reactivity and limited Fe dissolution.
- Entrapped nZVI removed model chlorinated organic via both adsorption and reduction.
- Aging process was mitigated by polymer matrix but still inhibited nZVI reactivity.

GRAPHICAL ABSTRACT



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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 ± 1.19% in Day-1 to 5.79 ± 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

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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.

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) (~5000 m^3 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, 2011, 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., 2008; 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 μg L^{-1} for drinking water, while their maximum concentrations reached 2000 μg 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, $BaCl_2 \cdot 2H_2O$, $CaCl_2 \cdot 2H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$,$SrCl_2 \cdot 6H_2O$,