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Nanoscale Zero-Valent Iron for Metal/Metalloid Removal from Model Hydraulic Fracturing Wastewater

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Abstract

Nanoscale zero-valent iron (nZVI) was tested for the removal of Cu(II), Zn(II), Cr(VI), and As(V) in model saline wastewaters from hydraulic fracturing. Increasing ionic strength (I) from 0.35 to 4.10 M (Day-1 to Day-90 wastewaters) increased Cu(II) removal (25.4-80.0%), inhibited Zn(II) removal (58.7-42.9%), slightly increased and then reduced Cr(VI) removal (65.7-44.1%), and almost unaffected As(V) removal (66.7-75.1%) by 8-h reaction with nZVI at 1-2 g L^{-1}. The removal kinetics conformed to pseudo-second-order model, and increasing I decreased the surface area-normalized rate coefficient (k_{sa}) of Cu(II) and Cr(VI), probably because agglomeration of nZVI in saline wastewaters restricted diffusion of metal(loid)s to active surface sites. Increasing I induced severe Fe dissolution from 0.37-0.77% in DIW to 4.87-13.0% in Day-90 wastewater; and Fe dissolution showed a significant positive correlation with Cu(II) removal. With surface stabilization by alginate and polyvinyl alcohol, the performance of entrapped nZVI in Day-90 wastewater was improved for Zn(II) and Cr(VI), and Fe dissolution was restrained (3.20-7.36%). The X-ray spectroscopic analysis and chemical speciation modelling demonstrated that the difference in removal trends from Day-1 to Day-90 wastewaters was attributed to: (i) distinctive removal mechanisms of Cu(II) and Cr(VI) (adsorption, (co-)precipitation, and reduction), compared to Zn(II) (adsorption) and As(V) (bidentate inner-sphere complexation); and (ii) changes in solution speciation (e.g., from Zn^{2+} to $ZnCl_3^-$ and $ZnCl_4^{2-}$; from CrO_4^{2-} to $CaCrO_4$ complex). Bare nZVI was susceptible to variations in wastewater chemistry while entrapped nZVI was more stable and environmentally benign, which could be used to remove metals/metalloids before subsequent treatment for reuse/disposal.

Keywords: nanoscale zero-valent iron; hydraulic fracturing; salinity; metals/metalloids; alginate entrapment; wastewater treatment.

1. Introduction

Increasing use of hydraulic fracturing for unconventional oil and gas exploration has resulted in substantial concerns about the associated environmental impacts. One of the major issues is the generation of large volumes of wastewater, and its potential adverse effects on the surrounding environment and human health (Vengosh et al., 2014; Chen et al., 2016; Chen et al., 2017). During hydraulic fracturing, up to 4 million gallons of water-based fluid is injected into a single drilled well to initiate and expand fractures, of which up to 70% is subsequently recovered as flowback and produced water (API, 2010). This wastewater stream contains high concentrations of salts (up to 350,000 mg L^{-1}), metals/metalloids (up to 116 mg L^{-1} Cu, 247 mg L^{-1} Zn, 2.2 mg L^{-1} Cr, 1.1 mg L^{-1} As), and organic compounds (such as hydrocarbons, benzenes, heterochorides, surfactants, oil and grease) (Abualfaraj et al., 2014; Shih et al., 2015). Fracturing wastewater requires proper treatment before possible reuse or final discharge into the environment (Lester et al., 2015).

Until recent years, the most popular management for fracturing wastewater was the disposal of the water into deep injection wells. However, this is becoming less viable due to limited access to disposal wells near drilling locations and increasing pressure from regulatory authorities and the public for a more sustainable solution (Lutz et al., 2013). Jiang et al. (2013) studied a process based on ceramic membrane filtration and ion-exchange for the treatment of fracturing wastewater from Marcellus formation with > 99% total dissolved solid (TDS) removal to meet the criteria for surface discharge, but the cost estimation was overwhelming (approximately 18.4 USD m^{-3}). Lester et al. (2013) demonstrated the potential of a conventional biological process to treat guar gum, a principal ingredient of fracturing fluids, under typical flowback conditions and found that 60% of chemical oxygen demand (COD) was removed within 31 h. Kekacs et al. (2015) investigated the application of aerobic biodegradation for organic compounds (served as corrosion inhibitor, surfactant, clay stabilizer, gelling agent, and biocide) in fracturing fluids, and suggested that 50-90% of them could be degraded aerobically via activated sludge. However, the effectiveness of biological treatment of fracturing wastewater is dependent on the microbial activity. Toxic and persistent metals/metalloids in fracturing wastewater, originating from shale formation or reagents in fracturing fluid, should be eliminated as much as possible before biological treatment. In particular, Cu(II), Zn(II), Cr(VI), and As(V) were predominant forms and susceptible to leaching under slightly acidic and oxidizing conditions (Johnson and Graney, 2015; Phan et al., 2015; Sun et al., 2017).

For metals/metalloids in industrial wastewater, current removal technologies such as coagulation and chemical precipitation result in significant production of metal-containing solid waste, which occurs less with the comparably effective nanoscale zero-valent iron (nZVI) treatment (Stefaniuk et al., 2016). The nZVI technology is becoming more economical and its costs are cheaper for Cu (0.0026 USD g^{-1} Cu) (Li et al., 2014b), Cr (0.00082-0.0012 USD g^{-1} Cr) (Li et al., 2007), and As (0.00078 USD g^{-1} As) (Tanboonchuy et al., 2011) than reverse osmosis (up to 0.57 USD g^{-1} As and 0.03 USD g^{-1} Cu), ion exchange (up to 0.07 USD g^{-1} As, 0.04 USD g^{-1} Cr, and 0.004 USD g^{-1} Cu) and activated carbon adsorption (up to 0.38 USD g^{-1} Cr and 0.04 USD g^{-1} Cu) (Adeleye et al., 2016). Li et al. (2014a) carried out a pilot-scale study in which they used a continuous stirring tank reactor with nZVI (2.14 g L^{-1}) to remove over 90% of metals in wastewater from non-ferrous metal smelting, which contained high salinity (8%, w/w) and high concentrations of As (520 mg L^{-1}), Cu (67 mg L^{-1}), Zn (10 mg L^{-1}), and Cr (< 10 mg L^{-1}). The nZVI reactor (0.22 g L^{-1}) was also able to remove greater than 96% of Cu (70 mg L^{-1}) from printed circuit board manufacturing wastewater (Li et al., 2014b). Moreover, an integration of the ZVI process with biological treatment was documented to enhance process stability and facilitate microbial growth for industrial wastewater treatment in over 50 small- to medium-sized full-scale treatment facilities (Ma and Zhang, 2008). Thus, nZVI technology is potentially effective for metals/metalloids removal from fracturing wastewater before subsequent biological wastewater treatment for reuse/disposal.

The basic removal mechanisms (adsorption, reduction, and co-precipitation) of metal/metalloid by nZVI have been extensively documented during the past decade. Neutral and acidic pH conditions (positively charged nZVI surface) facilitate metalloid removal (Fu et al., 2013), and alkaline pH conditions (negatively charged surface) contribute to metal removal by nZVI (Su et al., 2014). After adsorption, metals/metalloids with standard redox potential more positive than Fe were reduced (Li and Zhang, 2007). Multi-mechanisms for the removal of Cu(II) (reduction and precipitation), Zn(II) (adsorption and precipitation), Cr(VI) (adsorption, reduction, and co-precipitation), and As(V) (adsorption and reduction) by ZVI and nZVI have been reported (Li and Zhang, 2007; Liu et al., 2008; Yang et al., 2007; O'Carroll et. al., 2013). Nevertheless, high ionic strength in fracturing wastewater (I = 0.35-4.10 M) (Hayes, 2009) may lead to uncertainties in metal removal by nZVI with different mechanisms, and there are limited findings available in the existing literature. For example, Farrel et al. (2000) reported that high ionic strength accelerated Fe corrosion with diffusion/dispersion of iron oxides and continuous precipitation in the bulk water phase, which would interfere with metal (co)precipitation with nZVI. Our recent study revealed that an increase of ionic strength from 0.35 M to 4.10 M in fracturing wastewater significantly reduced Se(VI) removal by ZVI (Sun et al., 2017), possibly due to weak outer-sphere surface complexation, inhibition of Se(VI) reduction, and formation of stable and soluble Ca-Se complex.

Using nZVI in wastewater remediation also encounters limitations such as lack of stability, easy agglomeration, and difficult solid separation from the treated solution (Fu et al., 2014). To address these issues, a means of immobilizing nZVI particles by entrapment in a porous polymeric hydrogel, Ca-alginate, has been developed (Bezbaruah et al., 2009). Porosity in alginate allows metal ions to diffuse into the beads and come in contact with the entrapped nZVI particles while Fe^{2+} maintains its complex stability with inorganic and organic compounds (Garbayo et al., 2002; Babuponnusami and Muthukumar, 2013; Bezbaruah et al., 2014). Alginate is biodegradable, non-toxic and non-immunogenic, and produces thermally irreversible and water insoluble gels (Vold et al., 2006). However, the cross-linked alginate gels are relatively rigid and fragile for practical applications; hence, polyvinyl alcohol (PVA) can be incorporated as an alternative porous polymeric entrapment matrix to provide excellent physical properties for post-separation and reusability (Lv et. al., 2013). Thus, entrapment of nZVI in alginate and PVA-alginate, which are low-cost and commercially available materials used in industry, potentially presents a robust operation and better performance for metal removal from high-salinity fracturing wastewater.

In this study, both bare nZVI powder and alginate and PVA-alginate entrapped nZVI were tested for metal/metalloid removal in model fracturing wastewater. The target metals/metalloids were Cu(II) (116 mg L^{-1}), Zn(II) (247 mg L^{-1}), Cr(VI) (2.2 mg L^{-1}), and As(V) (1.1 mg L^{-1}), which were the maximum concentrations reported in Marcellus fracturing wastewater (Abualfaraj et al., 2014; Shih et al., 2015). The objectives of this research were to: (i) study the interactions between fracturing wastewater (ionic strength in particular) and metals/metalloids (Cu(II), Zn(II), Cr(VI), As(V)) removal by bare and entrapped nZVI; (ii) evaluate Fe dissolution from bare and entrapped nZVI and its correlation with metals/metalloid removal from fracturing wastewater; and (iii) investigate metal removal mechanisms by nZVI in fracturing wastewater using X-ray spectroscopic analyses and speciation modelling.

2. Methods and materials

2.1 nZVI and fracturing wastewater

The dry powder of nZVI (NANOFER STAR) used in this study was purchased from NANO IRON

(Czech Republic), which had average size of 50 nm, specific surface area of 19.4 m^2 g^{-1}, and Fe^0 content of 65-80%, respectively. The chemicals used in this research were reagent grade from Sigma Aldrich (viz. NaOH, HCl, KCl, NaBr, $BaCl_2·2H_2O$, $CaCl_2·2H_2O$, $Fe(NO_3)_3·9H_2O$, $SrCl_2·6H_2O$, $MgCl_2·6H_2O$, NaCl, H_3BO_3, $Cu(NO_3)_2·3H_2O$, $Zn(NO_3)_2·6H_2O$, CrO_3, $Na_2HAsO_3·7H_2O$, polyacrylamide, ethylene glycol, glutaraldehyde, Na-alginate, PVA, Na-citrate, citrate acid, Na_2HPO_4, NaH_2PO_4). Model fracturing wastewaters (representing the fluids returning to the ground surface in 1, 14, and 90 days after well creation, referred to as Day-1, Day-14, and Day-90 wastewaters, respectively, from here on) (Table 1) were synthesized according to a comprehensive report of "Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas" (Hayes, 2009), which represented significant temporal variation in ionic strength, iron content, and scaling (precipitation) in the field as elaborated in our previous studies (Chen et al., 2016; Chen et al., 2017; Sun et al., 2017). The speciation of Cu(II), Zn(II), Cr(VI), and As(V) in model fracturing wastewater was calculated using Visual MINTEQ ver. 3.0 (Table S1 in the Supporting information). However, it should be noted that dissolved organic matter in fracturing wastewater may form soluble complexes with metals and ferrous/ferric iron, thereby hindering the metal/metalloid removal (Liu et al., 2008; Tsang et al., 2009), which was not evaluated in this study.

2.2 Entrapment of nZVI in alginate and PVA-alginate

To immobilize nZVI without lowering its reactivity, entrapment was carried out according to the procedures (Fig. S1a in the Supporting information) demonstrated by previous research (Babuponnusami and Muthukumar, 2013; Bezbaruah et al., 2014). For alginate entrapped nZVI, 2% (w/v) Na-alginate solution (i.e., *solution 1*) was prepared by dissolving 2 g Na-alginate in 100 mL deionized water (DIW) at room temperature, and stirring with a magnetic stirrer for 3-5 h until the solution appeared uniform, followed by 30-min rest to allow air bubbles to escape and ensure no alginate floats in the solution. Then, 3.5% (v/v)

$CaCl_2$ solution (i.e., *solution 2*) was prepared by adding 23.2 g $CaCl_2$ into 500 mL DIW at room temperature. Next, 1 g nZVI powder was added into *solution 1* (i.e., *solution 3*). Using a peristaltic pump (BT100-2J Peristaltic Pump, Baoding Longer Precision Pump Co., Ltd.), *solution 3* was drop-wisely transferred into *solution 2* from 12 cm vertically above the water surface, with a 0.5 mm ID tubing at 2.5 mL min^{-1} of flow rate to form alginate-nZVI beads. *Solutions 2* and *3* were constantly stirred with glass rods while pumping to ensure almost all nZVI was transferred into the beads and no alginate-nZVI beads clustered together. Beads were hardened by immersion in *solution 2* for 6-9 h so that adequate hardness and porosity were obtained. Beads were rinsed and stored in DIW before being used in experiment.

For PVA-alginate entrapped beads, 7.5% (w/v) PVA solution (i.e., *solution a*) was prepared by dissolving 3 g PVA in 40 mL DIW at room temperature, and heating to 80°C for 1 h while stirring with a magnetic stirrer until complete dissolution. Then, 10% (w/v) Na-alginate solution (i.e., *solution b*) was prepared by dissolving 5 g Na-alginate in 50 mL DIW. Next, 10 mL *solution b* was added to *solution a*, and gently stirred for 45 min. After cooling down to 35°C, 1 g nZVI was added (i.e., *solution c*), and gently stirred for complete dispersion. The rest of the procedure to produce PVA-alginate entrapped nZVI beads was the same as the procedure for alginate entrapped nZVI beads as described above.

2.3 Metal/metalloid removal from fracturing wastewater by nZVI and entrapped nZVI

To investigate the kinetics of Cu(II), Zn(II), Cr(VI), and As(V) removal from fracturing wastewater, 2 g L^{-1} nZVI was reacted with 116 mg L^{-1} Cu(II) or 247 mg L^{-1} Zn(II), and 1 g L^{-1} nZVI was reacted with 2.2 mg L^{-1} Cr(VI) or 1.1 mg L^{-1} As(V) in 50-mL polypropylene copolymer centrifuge tubes containing 25-mL Day-1, Day-14, Day-90 wastewaters, respectively. Control tests were conducted with DIW containing the same metal concentrations and nZVI dosages. The nZVI dosages were selected to achieve the highest removal efficiency as well as removal rate according to preliminary tests (Cu(II) or Zn(II): 0.5-5 g L^{-1} nZVI, Cr(VI) or As(V): 0.1-2 g L^{-1} nZVI) in Day-14 wastewater (data not shown). To investigate the metal/metalloid removal by entrapped nZVI in Day-90 wastewater, 94 (nZVI: 2 g L^{-1}) or 47 (nZVI: 1 g L^{-1}) alginate entrapped nZVI beads, and 44 (nZVI: 2 g L^{-1}) or 22 (nZVI: 1 g L^{-1}) PVA-alginate entrapped nZVI beads were used, respectively, based on the mass balance calculation. Alginate and PVA-alginate beads without nZVI were also evaluated as control tests.

Stock solutions of Cu(II), Zn(II), Cr(VI), and As(V) were prepared by dissolving $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, CrO_3, and $Na_2HAsO_3 \cdot 7H_2O$ in DIW, respectively, which were added to model fracturing wastewater to provide target initial concentrations. The initial pH value of model fracturing wastewaters was adjusted to 5.9-7.2 using 0.1 M NaOH or HCl. The samples were shaken on a rotary shaker (30 rpm) at room temperature for 5-480 min, and then centrifuged at 4,000 rpm for 5 min. The supernatants were filtered through a 0.45-μm pore-size mixed cellulose esthers membrane filter (Millipore) and analyzed for As by atomic absorption spectrometry with vapour generation accessory (VGA-AAS, Agilent VGA77, limit of detection of 1 μg L^{-1}) and AAS for Cu, Zn, Cr, and Fe (limit of detection of 0.1 mg L^{-1}). The selective-reduction-VGA-AAS technique was employed for measuring the concentration of As(V) based on Shraim et al. (1999). All experiments were performed in duplicate.

The total organic carbon was measured by TOC analyzer (SSM-5000A). Gas chromatography/mass spectrometry (GC-MS) (Agilent 7890B GC analyzer, 5977 Mass Selective Detector) was used to identify dissolved organic content subsequent to a liquid-liquid extraction by hexane. A DB-5 MS column (30-m long and 0.25-μm thick film with 0.25 mm internal diameter, Agilent Technologies) was used, and helium was the carrier gas. Oven temperature were maintained at 35ºC for 4 min, increased at 10 ºC min^{-1} until reaching 100 ºC, then increased at 30 ºC min^{-1} until reaching 190 ºC. Samples were injected with a rate of 1 mL min^{-1} at 230 ºC and detected at 280 ºC. Selected ion monitoring was chosen for result acquisition.

2.4 Solid-phase characterization of Cu/Zn/Cr/As-loaded nZVI

To investigate metal/metalloid removal mechanisms by nZVI in fracturing wastewater, the PVA-alginate nZVI beads were selected for X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses, in consideration of its higher metal loading and lower salt interference than bare nZVI and alginate-nZVI. After reaction with Cu(II)/Zn(II)/Cr(VI)/As(V) in fracturing wastewater, PVA-alginate entrapped beads were separated by centrifugation and gently washed with DIW for three times to remove entrapped and loosely attached metals and salts. The crystalline structure of the Cu/Zn/Cr/As-loaded PVA-alginate entrapped nZVI was determined by using a high-resolution XRD (Rigaku SmartLab). The scanning degrees were from 5° to 70° 2θ with 5° min^{-1} speed duration at 45 kV and 200 mA. For XPS analysis, the entrapped nZVI was released by dissolving beads in 0.3 M sodium citrate solution and 20 mM phosphate buffer solution according to a previous study (Pramanik et al., 2011), as otherwise dense polymeric matrix outside nZVI interfered the surface analysis. The solid samples were freeze-dried and kept in a desiccator before analysis. The oxidation states of target metals/metalloids on the nZVI surface were determined using XPS (VG Multilab 2000) with Al K-alpha radiation. A broad scan was obtained using 100 eV pass energy, while narrow high resolution scans of Cu_{2p}, Zn_{2p}, Cr_{2p}, and As_{3d} were obtained using 25 eV pass energy with step size of 0.05 eV. The charge effect was corrected using the C 1s line at 284.6 eV. The obtained spectra were fitted using a curve-fitting program (Advantage) and a least-squares procedure with peaks of 30% of the Lorentzian-Gaussian peak shape after subtraction of a Shirley baseline. The component peaks were identified by comparison of their binding energies (BE_s) with the values reported in the literature.

3. Results and discussion

3.1 Metals/metalloids removal from fracturing wastewater by bare nZVI

The solution pH values in Day-1 wastewater increased from 7.20 to 7.96±0.23 in 2 h and then gradually to 8.49±0.03 in 8 h (Fig. S2), and they similarly increased from 6.50 to 7.87±0.09 in Day-14 wastewater and from 5.90 to 6.52±0.01 in Day-90 wastewater, respectively. The results in Fig. 1a and Fig. S3 show that maximum removals of 80.0±0.3% Cu(II) (from 116 mg L^{-1} in Day-90 solution), 52.7±2.7% Zn(II) (from 247 mg L^{-1} in Day-1 solution), 65.7±0.7% Cr(VI) (from 2.2 mg L^{-1} in Day-14 solution), and 73.6±5.1% As(V) (from 1.1 mg L^{-1} in Day-90 solution) were obtained after 8-h reaction with 2 g L^{-1} nZVI (for Cu(II) and Zn(II)) or 1 g L^{-1} nZVI (for Cr(VI) and As(V)), respectively. The results demonstrated the ability of nZVI to remove Cu(II), Zn(II), Cr(VI), and As(V) from high-salinity fracturing wastewater.

Due to the variation of ionic strength of the fracturing wastewater (Fig. 1a), the removal efficiency of Cu(II) after 8-h reaction with bare nZVI were 32.4±0.9% in Day-1 (I = 0.35 M), 35.7±2.6% in Day-14 (I = 2.49 M), and 80.0±0.3% in Day-90 (I = 4.10 M) wastewaters, respectively. Compared to 25.4±1.8% in DIW, Cu(II) removal by bare nZVI was significantly improved by increasing ionic strength in fracturing wastewater, especially for Day-90 wastewater. Meanwhile, Zn(II) removal gradually decreased from 52.7±2.7% (Day-1 wastewater) to 51.4±0.2% (Day-14 wastewater) and 44.1±3.0% (Day-90 wastewater), which were much lower than 58.7±0.4% removal in DIW and obviously inhibited by increasing ionic strength in contrast to Cu(II) removal. Compared to Cr(VI) removal in DIW (58.1±0.1%), there was slightly higher removal of 63.3±2.2% in Day-1 and 65.7±0.7% in Day-14 wastewater, followed by a pronounced decrease (44.1±3.0%) in Day-90 wastewater. However, the removal of As(V) from fracturing wastewater was comparable to in DIW, in a range of 66.7±4.3 to 75.1±4.0% in all conditions. The difference in performances of bare nZVI for Cu(II), Zn(II), Cr(VI), and As(V) removal from fracturing wastewater with increasing ionic strength probably suggests distinctive removal mechanisms, which will be discussed later in *Section 3.4*.

The time-dependent removal of Cu(II), Zn(II), Cr(VI) and As(V) by nZVI in fracturing wastewater (Fig. S3 and Table S2) conformed to pseudo-second-order kinetics model (details in Supplementary Information). As illustrated in Fig. 1b, increasing ionic strength significantly reduced the surface area normalized rate coefficient (k_{sa}, L m^{-2} h^{-1}) for Cu(II), from 2.57×10^{-1} L m^{-2} h^{-1} in DIW to 1.78×10^{-2} L m^{-2} h^{-1} in Day-90 wastewater. Similarly, for Cr(VI), an obvious trend of decreasing k_{sa} was obtained from 2.66×10^{-1} L m^{-2} h^{-1} in Day-1 to 1.81×10^{-1} L m^{-2} h^{-1} in Day-90 wastewater. Meanwhile, k_{sa} for As(V) removal by nZVI was not affected by elevating ionic strength in fracturing wastewater, which remained in a range of 6.06 - 9.56 $\times10^{-2}$ L m^{-2} h^{-1} and much lower than k_{sa} in DIW (1.69×10^{-1} L m^{-2} h^{-1}). Thus, increasing ionic strength in fracturing wastewater notably inhibited the reactivity of bare nZVI for metals/metalloids removal as reflected by decreased rate coefficients. Previous studies also observed that increasing ionic strength could enhance particle aggregation due to double layer compression and iron/iron-humate precipitation, which consequently reduce available surface sites and inhibit ZVI reactivity for contaminant removal (Sato et al., 2005; Tsang et al., 2009). Interestingly, the influence of fracturing wastewater on removal efficiency (Fig. 2) and kinetics (Fig. S4) could be mitigated by nZVI entrapment, which will be evaluated in *Section 3.3*.

3.2 Fe dissolution from bare nZVI in fracturing wastewater

Continuous Fe dissolution of bare nZVI was observed during metals/metalloids removal from fracturing wastewater (Fig. S5). After 8-h reaction in DIW (Fig. 3a), only 0.37±0.07% to 0.77±0.16% Fe was dissolved from bare nZVI. However, increasing ionic strength induced severe Fe dissolution in Day-1

(1.29±0.26 to 2.04±0.16%), Day-14 (4.15±0.42 to 6.79±0.46%), and Day-90 (4.87±0.32 to 13.0±1.0%) wastewater. In particular, the extent of Fe dissolution for Cr(VI) removal in Day-14 (6.79±0.46%) and Day-90 wastewater (13.0±1.0%) was much higher than those for Cu(II), Zn(II), and As(V). It is remarkable that a linear relationship between Fe dissolution and Cu(II) removal was observed in Day-14 (Fig. 4a) and Day-90 wastewater (Fig. 4b), by plotting the temporal change of Fe dissolution (Fig. S5) against the kinetic removal of metals/metalloids (Fig. S3) at the same reaction time.

Dissolved Fe mainly resulted from surface dissolution and reductive iron corrosion in high-salinity fracturing wastewater under acidic-aerobic conditions. It is likely that most dissolved Fe expeditiously formed precipitates with metal ions (Liu et al., 2008; Tsang et al., 2009) and in turn provided new adsorption sites for Cu(II) removal. Thus, the linear relationship for Cu(II) removal with Fe dissolution was consistent with co-precipitation and adsorption of Cu(II) by nZVI. For metals with standard redox potential more positive than Fe^0 (-0.44 V), such as Cu(II) (+0.34 V) and Cr(VI) (+1.51V), they could be further reduced to Cu(0) and Cr(III) after adsorption onto nZVI surface (Li and Zhang, 2007), which subsequently induced more Fe dissolution due to oxidation of Fe^0 ($Fe^0 + M^{n+} \rightarrow Fe^{m+} + M^{(n-m)}$, m = 1-3). Moreover, Cr(III) could precipitate as Cr(III) hydroxides and mixed Fe(III)/Cr(III) (oxy)hydroxides (Blowes et al., 1997), and remain stable at high pH conditions (Cornell and Schwertmann, 2003). Hence, subsequent Fe release into fracturing wastewater after nZVI treatment may be laden with metals/metalloids and arouse environmental impact, which requires toxicity assessment and appropriate nZVI surface stabilization in fracturing wastewater.

3.3 Metals/metalloids removal by entrapped nZVI in fracturing wastewater

Alginate and PVA-alginate entrapped nZVI was applied in Day-90 wastewater (Fig. 2 and Fig. S4), which represented the worst-case scenario for bare nZVI (i.e., lowest rate coefficient and highest Fe dissolution) for Cu(II), Zn(II), Cr(VI), and As(V) removal. After 8-h reaction with alginate entrapped nZVI in Day-90 wastewater, 51.6±0.1% Zn(II) was removed, in comparison to 42.9±4.6% removal by bare nZVI (Fig.2a). Even though PVA-alginate entrapped nZVI showed comparable removal of Zn(II) (41.7±2.9%) with bare nZVI, the rate coefficient k_{sa} (9.09×10^{-2} L m^{-2} h^{-1}) was higher than bare nZVI ($k_{sa} = 7.74\times10^{-2}$ L m^{-2} h^{-1}) (Fig. 2b and Table S3). The Cr(VI) removal was also promoted by alginate entrapped nZVI (52.6±2.9%) compared to bare nZVI (44.1±3.0%), while there was similar removal of PVA-alginate entrapped nZVI (43.4±2.9%). However, the removal rate of Cr(VI) by alginate ($k_{sa} = 1.18\times10^{-1}$ L m^{-2} h^{-1}) and PVA-alginate entrapped nZVI ($k_{sa} = 1.46\times10^{-1}$ L m^{-2} h^{-1}) was slower than bare nZVI ($k_{sa} = 1.81\times10^{-1}$ L m^{-2} h^{-1}). The smaller rate coefficient was probably a result of increased mass transfer resistance in a dense polymeric matrix outside nZVI surface (Lv et al., 2013).

For As(V), entrapped nZVI maintained similar removal efficiency after 8-h reaction, which was in the range of 71.5±4.0% to 73.8±1.4%, with a slightly higher k_{sa} of alginate-nZVI (9.56×10^{-2} L m^{-2} h^{-1}) than bare nZVI ($k_{sa} = 7.79\times10^{-2}$ L m^{-2} h^{-1}). However, entrapment significantly inhibited Cu(II) removal from 80.0±0.3% (bare nZVI) to 21.5±0.2% (alginate) and 21.0±0.6% (PVA-alginate) in Day-90 wastewater, despite obviously promoted k_{sa} (Fig. 2b and Table S3). In control tests with alginate and PVA-alginate beads only, there was negligible removal of Cu(II) (1.48±0.05% to 1.93±0.07%), Zn(II) (2.81±0.10% to 3.36±0.20%), Cr(VI) (1.92±0.27% to 2.88±0.41%), and As(V) (0.85±0.06% to 2.61±0.10%). Therefore, alginate and PVA-alginate entrapped nZVI beads proved to be more effective than bare nZVI particles for metals/metalloids removal (except Cu(II)) in high-salinity fracturing wastewater.

This was probably attributed to the reduced Fe dissolution from entrapped nZVI beads in fracturing wastewater (Fig. 3b and Fig. S6). After 8-h reaction in Day-90 wastewater, 6.93±0.50% (alginate) and 6.95±0.18% (PVA-alginate) Fe was released into solution during Cu(II) removal, which was significantly reduced from 9.43±0.40% Fe dissolution from bare nZVI (Fig. 3b). Similarly, much lower Fe dissolution during Zn(II) (3.20±0.38% to 3.36±0.02), Cr(VI) (7.25±0.73% to 7.36±0.56%), and As(V) (6.20±0.38% to 6.14±0.72) removal by entrapped nZVI was obtained than bare nZVI (4.87±0.32% for Zn(II), 13.0±1.0% for Cr(VI), and 9.40±0.63% for As(V), respectively). In view of the linear relation between Cu(II) removal by nZVI and Fe dissolution in Day-14 and Day-90 wastewaters (Fig. 4), nZVI entrapment significantly limited Fe dissolution and in turn inhibited Cu(II) removal.

The results of this study illustrate that immobilization of nZVI in alginate matrix can minimize high-salinity interference from fracturing wastewater, which is a culprit for nZVI agglomeration and its compromised reactivity, as well as high Fe dissolution. There is no obvious difference between alginate and PVA-alginate entrapped nZVI beads for the treatment of fracturing wastewater, in other words, the addition of PVA shows no superior performance to alginate beads. Nevertheless, dissolution of organic carbon is a by-product from PVA-alginate entrapped nZVI beads. After 8-h reaction in Day-90 wastewater, the TOC increased from 749.4±8.6 mg L^{-1} to 796.9±14.6 mg L^{-1}. In control tests with PVA-alginate beads (no nZVI), a similar TOC increase was also observed from 698.1±11.7 mg L^{-1} to 730.4±12.1 mg L^{-1} after 8-h reaction. The GC-MS analysis showed an emergence of substrate with C=O group, which was similar to alginate monomer. In view of prolific biodegradability of alginate, the residual organic carbon in the treated wastewater could be utilized as a readily available carbon source for the microorganisms in subsequent biological treatment and to some extent improve wastewater biodegradability.

3.4 Significance of fracturing wastewater chemistry on different removal mechanisms

The XRD spectra confirmed the zero-valent oxidation state and crystalline structure of bare nZVI and entrapped nZVI before the wastewater treatment (Fig. S1b). In comparison, the spectra of Cu/Zn/Cr/As-loaded PVA-alginate nZVI samples (Fig. 5) showed the peaks of magnetite/maghemite (Fe_3O_4/γ-Fe_2O_3) and lepidocrocite (γ-FeOOH), in addition to predominant Fe^0. The presence of ferric oxides indicated the oxidation of the Fe(II) and the corroding Fe^0 surface during the course of metals/metalloids removal, which was in agreement with the previous findings (Manning et al., 2002; Richmond et al., 2004).

The oxidation sates of metals/metalloids in the reacted PVA-alginate entrapped nZVI solids were determined using XPS analysis, after dissolution of the beads in 0.3 M sodium citrate and 20 mM phosphate buffer solutions. Distinctive peaks of Cu2p, Zn2p, Cr2p, and As3d photoelectrons (Fig. 6) were compared with characteristic BE_s values reported in the literature (Table S4). In general, both the reduced states and the initial ionic metals/metalloids were observed on the surface of entrapped nZVI.

The Cu2p spectra of the entrapped nZVI (Fig. 6a) exhibited two peaks at 932.0 eV (78.4%) and 933.8 eV (21.6%), respectively. The peak positions were in close agreements with the Cu(0) and Cu(II) 2p BE_s, respectively. It is evident that Cu(II) was removed by nZVI by co-precipitation and adsorption, and then reduced to Cu(0) on nZVI surface, corroborating previous findings for bare nZVI (Karabelli et al., 2008). Similarly, as shown in Fig. 6c, the Cr2p survey revealed two peaks at 586.3 eV (63.1%) and 578.9 eV (36.9%), suggesting that both Cr(III) as $Cr(OH)_3$ and Cr(VI) as CrO_4^{2-} were present on the nZVI surface. Thus, Cr(VI) was first adsorbed on nZVI surface and gradually reduced to Cr(III), which could precipitate as $Cr(OH)_3$ and co-precipitate with dissolved Fe as Fe/Cr (oxy)hydroxides (Yang et al., 2007; Liu et al., 2008).

In contrast, the valence state of Zn(II) and As(V) on the surface of entrapped nZVI remained the same as the dissolved ions initially added in the solution. The Zn2p survey (Fig. 6b) showed two peaks at 1021.4 eV (53.1%) and 1019.6 eV (46.9%), which corresponded to $ZnFe_2O_4$ and Zn(II) species. Similarly, the As3d survey (Fig. 6d) presented three photoelectron peaks at 44.9 eV (66.4%), 45.4 eV (26.0%), and 46.7 eV (7.6%), which represented As(V) in the form of AsO_4^{3-}, $HAsO_4^{2-}$, and $H_2AsO_4^-$, respectively. Thus, both Zn(II) and As(V) were attracted to the surface of entrapped nZVI, possibly by electrostatic interactions and specific bonding (Li and Zhang, 2007), and then adsorbed via surface complexation without reduction.

During the reaction with nZVI in DIW and fracturing wastewater, the solution pH values were in the range of 5.14±0.30 to 7.04±0.17 (DIW), 7.20 to 8.49±0.03 (Day-1), 6.50 to 7.87±0.09 (Day-14), and 5.90 to 6.52±0.01 (Day-90) (Fig. S2), which were higher than the zero point of charge (pH_{zpc}) for NANOFER nZVI (pH_{zpc} = 3.8 - 4.3) (Eglal and Ramamurthy, 2014). Thus, the nZVI surface was negatively charged in all circumstances. The contributions of various species of Cu(II), Zn(II), Cr(VI), and As(V) in Day-1, Day-14, and Day-90 wastewaters were listed in Table S1. In fracturing wastewater, Cu(II) species were positively charged (Cu^{2+}, $CuH_2BO_3^+$, $CuOH^+$, $CuCl^+$, $CuBr^+$) and thus negatively charged adsorbent would attract Cu(II) by electrostatic force. Meanwhile, increasing ionic strength in fracturing wastewater promoted Cu(II) removal (Fig. 1a) primarily because of enhanced iron dissolution for Cu(II) co-precipitation and adsorption on nZVI as discussed earlier (Fig. 4).

On the contrary, most of Zn(II) species were positively charged as Zn^{2+} (77.8%) and $ZnCl^+$ (17.8%) in Day-1 wastewater (Table S1), but increasing ionic strength and decreasing pH in Day-14 and Day-90 wastewater changed Zn(II) species to negatively charged as $ZnCl_3^-$ (Day-14: 26.3%, Day-90: 37.7%) and $ZnCl_4^{2-}$ (Day-14: 8.24%, Day-90: 8.83%). This consequently increased the electrostatic repulsion between negatively charged Zn(II) and nZVI surface even under the circumstances of compressed nZVI electrical double layer in saline wastewaters, thus accounting for the observed decrease in Zn(II) removal with the change of fracturing wastewater compositions (Fig. 1a).

In Day-1 and Day-14 wastewaters, the major components of Cr(VI) species were negatively charged as CrO_4^{2-} (Day-1: 63.0%, Day-14: 20.4%), $NaCrO_4^-$ (Day-1: 8.97%, Day-14: 53.4%), $HCrO_4^-$ (Day-1: 2.07%, Day-14: 0.598%), with a minor contribution from the soluble Ca-Cr complex ($CaCrO_{4\,(aq)}$) (Day-1: 25.9%, Day-14: 25.5%). The transformation from divalent (CrO_4^{2-}) to monovalent ($NaCrO_4^-$) chromate oxyanions in Day-14 wastewater could relieve electrostatic repulsion between negatively charged Cr(VI) and nZVI surface, and thus slightly promoted Cr(VI) removal compared to Day-1 wastewater and DIW (Fig. 1a). However, a significant proportion of stable $CaCrO_{4\,(aq)}$ (95.3%) was found in Day-90 wastewater, which could effectively inhibit Cr(VI) adsorption onto nZVI for subsequent reduction (Fig. 6c). This was in close resemblance with the observed decrease in removal efficiency in Day-90 wastewater (Fig. 1a).

In a neutral pH range (5.9-7.2) and aerobic condition, As(V) existed in the form of $H_2AsO_4^-$ and $HAsO_4^{2-}$ oxyanions (Table S1). Increasing ionic strength and decreasing pH from Day-1 to Day-90 wastewater significantly promoted the contribution of $H_2AsO_4^-$ (Day-1: 19.4%, Day-14: 83.3%, Day-90: 96.6%) to the total As(V) in fracturing wastewater. Yet, the significant increase of ionic strength in Day-1 to Day-90 wastewater had marginal influence on the As(V) removal by nZVI (Fig. 1a), which was consistent with recent findings on ZVI surface (Sun et al., 2017) and nZVI (Lata and Samadder, 2016), implying stable inner-sphere adsorption of As(V). Furthermore, in Day-90 wastewater, the predominant form of As(V) as $H_2AsO_4^-$ in solution (96.6%, Table S1) was transformed to AsO_4^{3-} (66.4%) and $HAsO_4^{2-}$ (26.0%) (Fig. 6d) upon adsorption on the nZVI surface. The observed transformation suggests that the majority of As(V) were coordinated as bidentate inner-sphere surface complex by edge- and double-corner sharing, and the remaining As(V) as monodentate inner-sphere surface complex on the Fe oxides (Antelo et al., 2005; Hiemstra and Van Riemsdijk, 2009). This accounts for the high stability of the adsorbed As(V) on the bare and entrapped nZVI. Moreover, distinctive removal mechanisms of metals/metalloids may lead to synergistic or competitive effects on nZVI performance in fracturing wastewater treatment, which needs to be further investigated.

4. Conclusions

This study has demonstrated that nZVI effectively removed metals/metalloids (Cu(II), Zn(II), Cr(VI), and As(V)) from high-salinity fracturing wastewater. However, bare nZVI particles were susceptible to decreasing metal removal rate and severe Fe dissolution in fracturing wastewater. Distinctive sequestration mechanisms by nZVI and change of solution speciation were the major driving factors accounting for different trends of metals/metalloids removal with increasing ionic strength in fracturing wastewater. Surface stabilized nZVI by entrapment in alginate polymeric matrix enhanced system resilience and restrained Fe dissolution, which was more environmentally benign than bare nZVI. Thus, the application of entrapped nZVI could be a potential candidate to remove metals/metalloids from fracturing wastewater before biological treatment and reuse/disposal. Future investigations for long-term chemical stability of entrapped nZVI and bio-toxicity assessment of the treated fracturing wastewater need to be performed to further validate the applicability and compatibility of entrapped nZVI treatment.

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