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Aging effects on chemical transformation and metal(loid) removal by entrapped nanoscale zero-valent iron for hydraulic fracturing wastewater treatment

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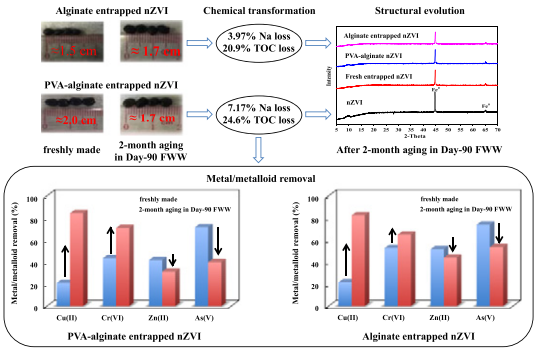
HIGHLIGHTS

- nZVI entrapment successfully prevented Fe^0 corrosion in fracturing wastewaters.
- Entrapped nZVI was chemically fragile due to dissolution of Na and TOC.
- nZVI passivation promoted Cu(II) and Cr(VI) but inhibited Zn(II) and As(V) removal.
- Effects of nZVI aging on removal efficiency depended on interaction mechanisms.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, alginate and polyvinyl alcohol (PVA)-alginate entrapped nanoscale zero-valent iron (nZVI) was tested for structural evolution, chemical transformation, and metals/metalloids removal (Cu(II), Cr(VI), Zn(II), and As(V)) after 1–2 month passivation in model saline wastewaters from hydraulic fracturing. X-ray diffraction analysis confirmed successful prevention of Fe^0 corrosion by polymeric entrapment. Increasing ionic strength (I) from 0 to 4.10 M (deionized water to Day-90 fracturing wastewater (FWW)) with prolonged aging time induced chemical instability of alginate due to dissociation of carboxyl groups and competition for hydrogen bonding with nZVI, which caused high Na (7.17%) and total organic carbon (24.6%) dissolution from PVA-alginate entrapped nZVI after 2-month immersion in Day-90 FWW. Compared to freshly-made beads, 2-month aging of PVA-alginate entrapped nZVI in Day-90 FWW promoted Cu(II) and Cr(VI) uptake in terms of the highest removal efficiency (84.2% and 70.8%), pseudo-second-order surface area-normalized rate coefficient k_{sa} (2.09×10^{-1} L m^{-2} h^{-1} and 1.84×10^{-1} L m^{-2} h^{-1}), and Fe dissolution after 8-h reaction (13.9% and 8.45%). However, the same conditions inhibited Zn(II) and As(V) sequestration in terms of the lowest removal efficiency (31.2% and 39.8%) by PVA-alginate nZVI and k_{sa} (4.74×10^{-2} L m^{-2} h^{-1} and 6.15×10^{-2} L m^{-2} h^{-1}) by alginate nZVI. The X-ray spectroscopic analysis and chemical speciation modelling demonstrated that the difference in metals/metalloids removal by entrapped nZVI after

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aging was attributed to distinctive removal mechanisms: (i) enhanced Cu(II) and Cr(VI) removal by nZVI reduction with accelerated electron transfer after pronounced dissolution of non-conductive polymeric immobilization matrix; (ii) suppressed Zn(II) and As(V) removal by nZVI adsorption due to restrained mass transfer after blockage of surface-active micropores. Entrapped nZVI was chemically fragile and should be properly stored and regularly replaced for good performance.

1. Introduction

Hydraulic fracturing, a common process for shale gas extraction, injects substantial amounts of "fracking fluid" at high flow rate and pressure into the well (Clark et al., 2013), with commensurate generation of over 1.4 billion gallons of highly-contaminated wastewater (combination of flowback and produced waters) in Marcellus Shale, the largest shale region in USA, each year (Goss et al., 2015). 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, hetero-chlorides, surfactants, oil and grease) (Abualfaraj et al., 2014; Shih et al., 2015; Oetjen et al., 2017).

Fracturing wastewater (FWW) treatment has become an emerging issue (Camarillo et al., 2016; Sun et al., 2017a; Sun et al., 2017b). Deep-ground injection and in-situ reuse become less viable due to high environmental risks (Lutz et al., 2013) and reduced gas production after long-term barite scaling (Paukert Vankeuren et al., 2017). Membrane filtration (He et al., 2014; Jiang et al., 2013), electrocoagulation (Kausley et al., 2017; Lobo et al., 2016), and advanced oxidation (Abass et al., 2017; Turan et al., 2017) are efficient treatment technologies of FWW, but continue to be impeded by high operational costs and energy consumption. Our previous research demonstrated that granular/nanoscale zero-valent iron (ZVI) could remove metals/metalloids from FWW (Sun et al., 2017a; Sun et al., 2017b). Alginate and polyvinyl alcohol (PVA) entrapped nZVI was more stable, environmentally benign, and cost-effective than bare nZVI, which could be used to remove metals/metalloids from FWW above ground under aerobic conditions before subsequent biological treatment for reuse/disposal (Butkovskyi et al., 2017; Camarillo et al., 2016; Kekacs et al., 2015). However, it is essential to investigate the chemical transformation, structural evolution, and removal performance of entrapped nZVI after long-term exposure in high-salinity FWW.

During long-term aging of bare nZVI in water, the core-shell structure gradually transforms into a hollow spherical shape with Fe^0 core diffusing outwardly and the iron oxide shell collapsing flakily (Liu et al., 2015; Stefaniuk et al., 2016). The corrosion products of nZVI progressively change from rapid formation of ferrihydrite and magnetite (<1 d) to slow transformation of lepidocrocite (<4 weeks), and finally to stabilization of goethite (>4 weeks) (Pullin et al., 2017). Passivated nZVI commonly shows a remarkable decrease in contaminant removal efficiency based on reduction mechanism, which is attributed to hindrance in electron transfer due to the loss of Fe^0 and increase of surface oxide layer (Calderon and Fullana, 2015; Xie and Cwiertny, 2012). However, goethite (FeOOH) as the dominant iron corrosion product on nZVI surface in the long term provides higher adsorption affinity and capacity for metals/metalloids (Yan et al., 2010). High-level chloride and bromide salts dispersed the oxide film and maintained the degradation efficiency of Fe^0 within 7 days of water exposure, whereas divalent cations (Ca^{2+}, Mg^{2+}) and alkalinity ions (HCO_3^-, OH^-) dampened nZVI reactivity via surface passivation (Xin et al., 2016).

Dong et al. (2016) observed that coating of polymeric materials, carboxymethyl cellulose (CMC), on bare nZVI surface could slow down the aging rate of nZVI and result in more crystalline lepidocrocite (γ-FeOOH) of the corrosion products after 90 days of aging in static water. Huang et al. (2016) suggested that alginate modification prevented nZVI particles from air oxidation and increased Cd removal in polluted sediments. However, there are uncertainties in structural evolution of alginate and PVA in high-salinity FWW and the corresponding effects on various removal mechanisms of entrapped nZVI upon aging.

In this study, both alginate and PVA-alginate entrapped nZVI were tested for chemical transformation, structural evolution, and metals/metalloids removal after 1 or 2 months of exposure to model FWW. The objectives of this research were to: (i) evaluate the structural and chemical changes of entrapped nZVI as it corrodes in FWW with increasing salinity; and (ii) reveal how different removal mechanisms correlate to the performance of entrapped nZVI and matrix dissolution after aging via X-ray spectroscopic analysis and speciation modelling. These findings would advance our understanding of the long-term fate of entrapped nZVI in aqueous environment and FWW treatment.

2. Experimental methods

2.1. nZVI and FWW

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%. The chemicals used in this research were reagent grade from Sigma Aldrich (viz. NaOH, HCl, KCl, NaBr, $BaCl_2 \cdot 2H_2O$, $CaCl_2 \cdot 2H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $SrCl_2 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$, NaCl, H_3BO_3, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, CrO_3, $Na_2HAsO_4 \cdot 7H_2O$, polyacrylamide, ethylene glycol, glutaraldehyde, Na-alginate, PVA, Na-citrate, citrate acid, Na_2HPO_4, NaH_2PO_4). Model FWW (representing the fluids returning to the ground surface in 1 and 90 days after well creation, referred to as Day-1 and Day-90 FWW, respectively) (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 was consistent with our previous studies (Chen et al., 2016; Chen et al., 2017; Sun et al., 2017a; Sun et al., 2017b). 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 represented the maximum concentrations reported in Marcellus fracturing wastewater (Abualfaraj et al., 2014; Shih et al., 2015). The speciation of Cu(II), Zn(II), Cr(VI), and As(V) in Day-90 model FWW was calculated using Visual MINTEQ ver. 3.0 (Table S1).

Table 1
Chemical compositions of model FWW.

	Units	Day 1	Day 90
KCl	g L^{-1}	0	31.9
NaBr	g L^{-1}	0.113	1.51
$BaCl_2 \cdot 2H_2O$	g L^{-1}	0.689	3.80
$CaCl_2 \cdot 2H_2O$	g L^{-1}	2.48	67.8
$Fe(NO_3)_3 \cdot 9H_2O$	g L^{-1}	0.140	0.844
$MgCl_2 \cdot 6H_2O$	g L^{-1}	1.02	14.2
$SrCl_2 \cdot 6H_2O$	g L^{-1}	0.476	9.56
NaCl	g L^{-1}	15.2	111
H_3BO_3	g L^{-1}	0.046	0.102
Polyacrylamide	g L^{-1}	0.8	0.8
Ethylene glycol	g L^{-1}	0.43	0.43
Glutaraldehyde	g L^{-1}	0.1	0.1
pH	–	7.2	5.9
Ionic strength	M	0.35	4.10