



# Nanoscale zero-valent iron for metal/metalloid removal from model hydraulic fracturing wastewater



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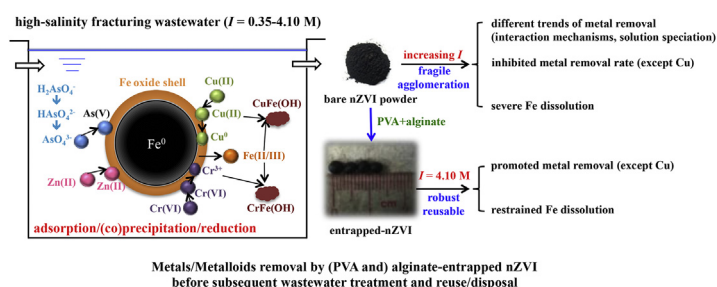
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## HIGHLIGHTS

- nZVI could remove Cu(II), Zn(II), Cr(VI), and As(V) from fracturing wastewaters.
- High salinity enhanced Fe dissolution and reduced removal rates except Cu(II).
- nZVI entrapment mitigated Fe dissolution and improved metal(loid) removal.
- Removal efficiency varied with interaction mechanisms and solution speciation.

## GRAPHICAL ABSTRACT



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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<sup>-1</sup>. 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 to 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<sup>2+</sup> to ZnCl<sub>3</sub><sup>-</sup> and ZnCl<sub>4</sub><sup>2-</sup>; from CrO<sub>4</sub><sup>2-</sup> to CaCrO<sub>4</sub> complex). Bare nZVI was susceptible to variations in wastewater

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chemistry while entrapped nZVI was more stable and environmentally benign, which could be used to remove metals/metalloids before subsequent treatment for reuse/disposal.

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## 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, 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<sup>-1</sup>), metals/metalloids (up to 116 mg L<sup>-1</sup> Cu, 247 mg L<sup>-1</sup> Zn, 2.2 mg L<sup>-1</sup> Cr, 1.1 mg L<sup>-1</sup> As), and organic compounds (such as hydrocarbons, benzenes, heterochlorides, 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<sup>-3</sup>). 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<sup>-1</sup> Cu) (Li et al., 2014b), Cr (0.00082–0.0012 USD g<sup>-1</sup> Cr) (Li et al., 2007), and As (0.00078 USD g<sup>-1</sup> As) (Tanboonchuy et al., 2011) than reverse osmosis (up to 0.57 USD g<sup>-1</sup> As and 0.03 USD g<sup>-1</sup> Cu), ion exchange (up to 0.07 USD g<sup>-1</sup> As, 0.04 USD g<sup>-1</sup> Cr, and 0.004 USD g<sup>-1</sup> Cu) and activated carbon adsorption (up to 0.38

USD g<sup>-1</sup> Cr and 0.04 USD g<sup>-1</sup> 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<sup>-1</sup>) 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<sup>-1</sup>), Cu (67 mg L<sup>-1</sup>), Zn (10 mg L<sup>-1</sup>), and Cr (<10 mg L<sup>-1</sup>). The nZVI reactor (0.22 g L<sup>-1</sup>) was also able to remove greater than 96% of Cu (70 mg L<sup>-1</sup>) 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 ( $I = 0.35\text{--}4.10\text{ M}$ ) (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, Farrell 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<sup>2+</sup> 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

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