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Impact of ageing on the fate of molybdate-zerovalent iron nanohybrid and its subsequent effect on cyanobacteria (*Microcystis aeruginosa*) growth in aqueous media

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ABSTRACT

Nanoscale zerovalent iron (nZVI) has been proposed to remediate heavy metal ions in the subsurface. However, the fate of metal-nZVI hybrid has not been fully investigated. In this study, we investigated (1) the long-term removal performance of nZVI for molybdate (Mo(VI)); (2) the relationship between the ageing of Mo-nZVI hybrid in specific solution chemistries and the remobilization of Mo(VI) from the hybrid; and (3) the effects of Mo-nZVI hybrid on cyanobacteria (*Microcystis aeruginosa*). Results showed that although common ions have limited influence on the removal ratio of Mo(VI) by nZVI, they do impact the structure evolution and transformation of the Mo-nZVI nanohybrid formed thereafter. Ageing time was crucial for the chemical stabilization of Mo-nZVI hybrid, but common groundwater ions retarded the stabilizing process, which may lead to a significant remobilization of Mo(VI) from the hybrid after exposure to water bodies. While low levels of Mo(VI) ions could stimulate the growth of *M. aeruginosa*, aged Mo-nZVI hybrid inhibited the growth of *M. aeruginosa*, except when ageing occurred in the presence of HPO_4^{2-}/CO_3^{2-} (which also retarded hybrid stabilization). This study shows that nZVI can immobilize Mo(VI) ions in groundwater, and the derived metal-nZVI hybrid can effectively suppress the potential growth of *M. aeruginosa* in river water.

1. Introduction

Heavy metal pollution in natural water bodies imposes a serious health risk to human beings and the environment (Bhuiyan et al., 2010; Demirel, 2007; Duruibe et al., 2007). In recent years, China has particularly been facing an increasing threat from this problem (Hu et al., 2014), particularly in areas close to mining sites (Gong et al., 2014). Heavy metals are persistent pollutants, which can be biomagnified in living organisms (Khan et al., 2008). While the removal of (heavy) metals such as chromium (Fruchter, 2002), cadmium (Su et al., 2016, 2015a; 2014a), lead (Su et al., 2015b; Zhang et al., 2013), and arsenate/arsenic (Mohan and Pittman, 2007) from different water matrices have received a considerable amount of attention, remediation of molybdate (Mo(VI)) pollution has not been widely investigated even though there has been a consistent increase in molybdenum (Mo) utilization in lighting, advanced material-forming, and electronics industry in recent years (Braithwaite and Haber, 2013; Saji and Lee, 2012; Saji and Lopatin, 2014). Release of Mo(VI) into the environment (including water bodies) at different stages of a product's life-cycle is likely to occur, which may impact water quality. Mo(VI) is part of the nitrogen fixation process (Howarth and Cole, 1985), and can stimulate the growth of cyanobacteria, which can lead to blue-green algae blooms (Cole et al., 1993). Hence, it is essential to develop an effective but accessible technique for remediation of Mo(VI) pollution in natural waters.

Nanoscale zerovalent iron (nZVI) has been employed to remediate organic pollution, such as chlorinated compounds in groundwater (Adeleye et al., 2016a; Liu et al., 2007; Zheng et al.,

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2008), but its application towards remediating heavy metal pollution in groundwater has not been fully explored although a considerable number of papers on metal removal mechanism by nZVI has been published since 2007 (Li et al., 2014; Li and Zhang, 2007; Su et al., 2014a, 2014b; Zhang et al., 2014). Based on previous published works, metal ions or metal-containing anions are sequestered by nZVI through adsorption, precipitation/co-precipitation and reduction/oxidation (Li and Zhang, 2007; Tosco et al., 2014).

Over a short period of time (e.g. a few hours), the removal performance of nZVI for metals is not sensitive to ionic strength or the presence of common anions (Boparai et al., 2013). Thus, it is surprising that the majority of current studies have focused on the short term removal performance of nZVI (Li and Zhang, 2007; Tanboonchuy et al., 2012; Zhu et al., 2009). In the long term, the decline of Fe(0) content (Liu and Lowry, 2006), changes to the core-shell structure (Liu et al., 2015), and the different iron oxides derived from Fe(0) oxidation (Lowry and Liu, 2006) can impact the metal removal performance of nZVI as well as the removal mechanism. Although several studies investigated the transformation of nZVI in groundwater (Liu et al., 2017; Reinsch et al., 2010), to the best of our knowledge, there are no studies integrating long term metal removal performance with the transformation and aging of nZVI under specific conditions (particularly in the presence of common groundwater ions). Further, unlike with applications of nZVI in industrial wastewater treatment (Li et al., 2016), the metal-nZVI hybrid formed during the remediation groundwater pollution is nearly impossible to contain and/or remove from the matrix. As a result, the nanohybrid can be released into nearby surface waters (Lefevre et al., 2015). Thus, the fate of metal-nZVI hybrid in aqueous media must be fully investigated as an important part of any groundwater nZVI-based remediation project.

Before the nanohybrid reaches a waterbody, it undergoes ageing for different lengths of time. Different ageing times under different conditions will result in different nanohybrid compositions (Johnson et al., 2013; Lefevre et al., 2015). For instance, the nanohybrid may contain different Fe(0) amounts, various types of iron oxides, and different species of metals. Furthermore, the different compositions of nanohybrid can cause different toxic effects on ecologically important organisms, such as freshwater algae (Keller et al., 2012) and cyanobacteria (Marsalek et al., 2012). *Microcystis aeruginosa* is a common cyanobacteria in freshwater, which can produce harmful microcystin (Funari and Testai, 2008). A previous study showed that pristine nZVI can destroy cyanobacterial cells (Marsalek et al., 2012), but it remains unknown whether nZVI still possesses its inhibitory effects on cyanobacteria after particle ageing and/or adsorption of metal ions. Further, organism-derived organic matters can affect the stability and transformation of iron-based nanoparticles (Adeleye et al., 2016a), which may affect the chemical stability of the metal-nZVI hybrid in ways we currently do not know. A comprehensive study of the fate of metal-nZVI hybrid in water is therefore required in order to fully evaluate the effectiveness and implications of nZVI in remediation of metal-polluted groundwater.

In this study, we investigated the long-term (30 days) removal performance of nZVI for Mo(VI) under different environmentally-relevant conditions while monitoring the transformation of nZVI during a 30-day experiment. To simulate the release of metal-nZVI nanohybrid into a river, Mo-nZVI nanohybrid was aged for different times and then transferred into a modified river water (90% raw river water and 10% BG-11 medium), containing cyanobacteria, for another 30 days. *Chlorophyll a* (*Chl a*) was monitored for the 30 days in order to understand the effects of metal-nZVI nanohybrid on the growth of cyanobateria.

2. Materials and method

2.1. Materials and nZVI synthesis

$FeCl_3$, $NaBH_4$, $(NH_4)_2MoO_4$, NaCl, KNO_3, Na_2SO_4, H_3BO_3, $MgCl_2 \cdot 6H_2O$, Na_2CO_3, $ZnSO_4$, $Na_2HPO_4 \cdot 12H_2O$, $CaCl_2 \cdot 2H_2O$, $ZnCl_2$, citric acid, $CuCl_2$, $MnCl_2 \cdot 4H_2O$, NaOH, HCl, $CuSO_4 \cdot 5H_2O$, ferric ammonium citrate, $EDTANa_2$, $Na_2MoO_4 \cdot 2H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ were purchased from Sigma-Aldrich. All chemicals were analytical grade and used without any further purification. $FeCl_3$ and $NaBH_4$ were used for nZVI synthesis, and NaCl, Na_2SO_4, $MgCl_2 \cdot 6H_2O$, Na_2CO_3, $Na_2HPO_4 \cdot 12H_2O$ and $CaCl_2 \cdot 2H_2O$ were used to study the influence of common groundwater ions on Mo(VI) removal by nZVI. KNO_3, Na_2HPO_4, $MgSO_4 \cdot 7H_2O$, H_3BO_3, Na_2CO_3, $CaCl_2 \cdot 2H_2O$, $FeSO_4 \cdot 7H_2O$, $ZnSO_4 \cdot 7H_2O$, $MnCl_2 \cdot 4H_2O$, $CuSO_4 \cdot 5H_2O$, $Na_2MoO_4 \cdot 2H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ $EDTANa_2$, and citric acid were used to prepare BG 11 media (Dahmani et al., 2016). Deoxygenated deionized water (DDIW) was used for solution preparation in batch experiments.

The nZVI synthesis method was based on previously published methods (Su et al., 2014a, 2014b; Zhang et al., 2013) according to the following reaction:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 \downarrow + 3H_2BO_3^- + 12H^+ + 6H_2 \uparrow$$

Freshly prepared nZVI was stored in 100% ethanol. Detailed synthesis conditions and characterization of nZVI can be found in our previous studies (Su et al., 2014a, 2014b; Zhang et al., 2013).

2.2. Long-term removal experiments of Mo(VI) in DDIW

The influence of different cations (Na^+, Mg^{2+}, Ca^2) and anions (Cl^-, SO_4^{2-}, HPO_4^{2-} and CO_3^{2-}) on Mo(VI) removal by nZVI was investigated in DDIW. Experiments were carried out in 100 mL serum bottles under different conditions on a shaking table (250 rpm, 25 ± 1 °C, Shanghai Fengling Laboratory Instrument FLY-111B, China). Each bottle was filled with 500 mg/L nZVI and 20 mg/L Mo(VI) except for one set of bottles used for pure nZVI ageing. (20 mg/L Mo(VI) was selected so we could clearly see the influence of ions and nZVI transformation on removal efficiency as 500 mg/L nZVI only removed ~90% of 20 mg/L Mo(VI) in a previous study (Qian et al., 2018). Moreover, after 10-fold dilution, preliminary studies showed that 2 mg/L Mo(VI) enhanced the growth of cyanobacteria while 50 mg/L nZVI exerted no toxicity to algae (Adeleye et al., 2016b; L.M. Stevenson et al., 2017). This concentration of Mo(VI) thus allowed us to clearly see the effect of the Mo-nZVI hybrids on cyanobacteria growth.) At each sampling point (Days 5, 10, 15, 20, 25, and 30), three bottles per condition were sacrificed for aqueous Mo(VI) and Fe(II) analysis after filtration with 0.22 μm filters. Metal analysis was carried out via inductively coupled plasma optical emission spectrometry (ICP-OES; Agilent 720ES, Santa Clara, CA). After the aliquots for aqueous metal analysis were removed, the remaining suspensions in the three bottles were mixed together. One drop of mixture was collected for transmission electron microscopy (TEM; Hitachi S-3000N, Japan), and three 10 ml mixtures were collected for dosing cyanobacteria (explained later). The remaining solids were collected after centrifugation at 5000 rpm for 5 min, freeze-dried (Biocool FD-1C-50, China), and used for further analyses via high-resolution X-ray photoelectron spectroscopy (HR-XPS; Perkin Elmer PHI 5000 ESCA System, USA) and X-ray diffraction (XRD; Bruker D8 Advance, Germany) using the Reference Intensity Ratio (RIR) method (Hubbard and Snyder, 1988).