Science of the Total Environment 443 (2013) 717–724

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Effects of solution chemistry on the removal reaction between calcium carbonate-based materials and Fe(II)

Yu Wang [a], Saraya Sikora [a], Hwidong Kim [a,b], Treavor H. Boyer [a], Jean-Claude Bonzongo [a], Timothy G. Townsend [a,*]

[a] *Department of Environmental Engineering Sciences, University of Florida, P. O. Box 116450, Gainesville, FL 32611, USA*
[b] *Department of Environmental Science and Engineering, Gannon University, 109 University Square, Erie, PA, 16541, USA*

HIGHLIGHTS

- Removal of Fe(II) by limestone is not significantly affected from pH 7 to 9.
- Na^+ significantly affected removal of Fe(II) at levels of 100 mg/L and above.
- Ca^{2+} and Mn^{2+} showed effect on removal as low as 10 mg/L Ca^{2+} and 5 mg/L Mn^{2+}.
- NOM premixed with Fe(II) (10 mg/L DOC) resulted in final Fe(II) levels above GCTL.
- NOM retained 0.05 mg Fe(II)/mg C for 2/3 sources and 0.032 mg/mg for 1/3.

ARTICLE INFO

Article history:
Received 9 June 2012
Received in revised form 25 October 2012
Accepted 4 November 2012
Available online 7 December 2012

Keywords:
Calcium carbonate-based materials (CCBMs)
Competing cations
Limestone
Natural organic matter (NOM)
Iron removal
Iron mobilization

ABSTRACT

Elevated iron concentrations have been observed in the groundwater underlying and surrounding several Florida landfill sites. An in situ groundwater remediation method for iron (present as soluble ferrous iron) using a permeable reactive barrier composed of calcium carbonate-based materials (CCBMs), such as limestone, was examined as a potentially effective and low-cost treatment technique. The effects of various environmental factors (i.e., pH, co-existing cations, and natural organic matter (NOM)) on the removal reaction were investigated using laboratory batch studies. Solution pH had a minor effect on iron removal, with superior iron removal observed in the highest pH solution (pH of 9). Sodium and calcium tended to impede the iron removal process by increasing the ionic strength of the solution. Manganese competes with iron ions at the adsorption sites on CCBMs; therefore, the presence of manganese prohibits iron removal and reduces removal effectiveness. NOM was found to decrease Fe(II) uptake by CCBMs and reduce the removal effectiveness by complexing Fe(II), most likely through the carboxyl group, thereby maintaining Fe(II) mobility in the aqueous phase.

1. Introduction

Dissolved iron can be observed in groundwater surrounding and underneath landfills, often as a result of reductive dissolution of iron from compounds contained in soil minerals (Bjerg et al., 1995; deLemos et al., 2006; Di Palma and Mecozzi, 2010; Heron and Christensen, 1995; Keimowitz et al., 2005). Iron is regulated in the US through the secondary drinking water standards at a concentration of 0.3 mg/L; higher concentrations of dissolved iron in groundwater cause negative aesthetic changes in water quality, impacting odor, color, and taste, as well as allowing for the formation of iron floc in surface water as a result of oxidation of dissolved ferrous iron (United States Environmental Protection Agency US EPA, 2011). A health based guideline of 4.2 mg/L was more recently developed for Florida (Florida Department of Environmental Protection FDEP, 2005) by University of Florida researchers, a concentration often exceeded at landfill sites in the state. Reductive dissolution of iron-containing soil minerals has also been associated with arsenic (As) release due to the strong tendency of As to adsorb onto iron soil minerals (Altundogan et al., 2002; Catalano et al., 2008; Cummings et al., 1999; Keimowitz et al., 2005; Mandal and Suzuki, 2002).

The techniques commonly used for reducing iron levels in groundwater are aeration, biological treatment, and chemical treatment (Chen et al., 2011; Hashim et al., 2011; Sharma et al., 2005). Problems associated with the aforementioned techniques include: 1) toxic intermediate chemicals potentially produced during chemical reactions; 2) high operational costs often required to maintain desired physicochemical conditions; and 3) for biological treatment techniques, a relatively long period may sometimes be required until biological activity becomes adequate for remediation (Camacho et al.,

---

* Corresponding author. Tel.: +1 352 392 0846; fax: +1 352 392 3076.
E-mail address: ttown@ufl.edu (T.G. Townsend).

0048-9697/$ – see front matter © 2012 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.scitotenv.2012.11.009

2011; Hashim et al., 2011; Wilson et al., 1986). Although it has not previously been applied to subsurface iron removal, the permeable reactive barrier (PRB) technique, where contaminated waters are allowed to passively flow through a reactive media, has many benefits when applied to contaminants such as chlorinated solvents, hexavalent chromium, and petroleum hydrocarbons; benefits of this technology include reasonable cost, low exposure of workers to contaminants, and beneficial use of above ground areas because additional structures may not be needed (Gavaskar, 1999; Naftz et al., 2002). However, PRBs have some drawbacks, including unexpected generation of byproducts and a relatively low removal ratio (Naftz et al., 2002). Therefore, the choice of suitable barrier materials and an understanding of the chemical reactions between barrier materials and contaminants are critical.

It was reported that calcium carbonate-based materials (CCBMs) have a great potential to remove ferrous iron from groundwater or drinking water (Aziz et al., 2004; Mettler et al., 2009; Sim et al., 2001; Smith et al., 1993; Wilson et al., 1986). The ferrous ion (Fe(II)) can be adsorbed and/or precipitated onto the calcite surface and form calcium siderite CaFe $(CO_3)_2$ (Sharma, 2001; Wajon et al., 1985). However, in-situ pollutant removal in groundwater by PRBs may be highly dictated by a variety of environmental conditions (Sharma et al., 2005). In particular, information about the influences of environmental conditions on iron removal using the PRB–CCMBs technique is very limited.

The potential environmental factors which may affect the performance of the PRB–CCBMs technique for Fe(II) removal are pH, co-existing cations, and natural organic matter (NOM). The pH in groundwater can affect the removal effectiveness of Fe(II) since pH affects the charge of metal ions and chemical precipitation (Nano and Strathmann, 2006), with a higher pH promoting metal ion sorption (Barrow and Whelan, 1998; Benjamin and Leckie, 1981; Giusti et al., 1994) and/or accelerating ferrous hydroxide formation on the mineral surface ($pH > 9$) (Stumm and Morgan, 1996). Coexisting cations are another mitigating factor in regards to Fe(II) removal, due to competition for adsorption sites. Sodium, which is commonly found in landfill leachate and landfill contaminated groundwater (Keimowitz et al., 2005; Kjeldsen et al., 2002), can lead to reduction in the metal removal effectiveness by increasing the ionic strength (Anirudhan and Radhakrishnan, 2011). Calcium ions can be naturally released from CCBM PRBs, which may affect the removal reaction by preventing other cations from approaching the CCBM surface. Manganese, a contaminant often associated with Fe(II) contamination due to its similar tendency towards reductive dissolution in favorable conditions (Homoncik et al., 2010), can also compete with Fe(II) for adsorption sites on CCBM surfaces (Aziz et al., 2001). Numerous studies have evaluated the role of NOM in water treatment processes (Sharp et al., 2006; Wu et al., 2011). Some research has already been performed on the sorption of NOM onto CCBMs and the associated effects on metal sorption (Lee et al., 2005). It has been found that NOM can interact with metal ions through chelation and complexation and can thus cause a decrease in uptake capacity (Rose and Waite, 2003). NOM can also attach onto the mineral surface and inhibit reaction between metals and CCBMs (Lee et al., 2005).

In this research, we evaluated CCBMs as a potential barrier material for groundwater iron removal. We also assessed the effects of various environmental factors on the reaction between CCBMs and Fe(II), providing a valuable assessment of the use of CCBMs to treat ferrous iron contaminated groundwater. Specifically, our study focused on 1) understanding the effect of pH on the removal reaction between Fe(II) and limestone material, 2) exploring how the coexisting cations affect the interaction between Fe(II) and limestone material, and 3) testing the effects of NOM on the interaction between Fe(II) and limestone material. Limestone was used as a model CCBM in this work because of its low cost and accessibility, which are considerably important for a field-scale application. The key contribution that this research makes to previous literature is to systemically evaluate CCBMs as a potential PRB material for iron removal from iron-contaminated groundwater.

2. Material and methods

2.1. Experimental materials

The reactive material used in this study was limestone with a granular size of 7.0–10 mm in diameter. All experiments were conducted at room temperature (25 ± 2 °C). Limestone employed in this research contained 36.2% calcium and 1.21% Mg. Low oxygen deionized (DI) water was prepared by purging DI water with N_2 gas for at least 30 min (Airgas, 99.99% purity). $FeCl_2$, NaCl, $MnCl_2$, and $CaCl_2$ were used as additives to simulate natural groundwater conditions. Stock solution (1000 mg/L Fe(II)) was made with $FeCl_2$ and low oxygen DI water. 1000 mg/L Na, Mn, and Ca stock solutions were made with low oxygen DI water and NaCl, $MnCl_2$, and $CaCl_2$, respectively. A liquid to solid ratio to 20:1 (by mass) was utilized for all experiments.

All bottles containing limestone and experimental solutions were shaken by a horizontal rotator (Fisher model 341) at 30 rpm for the duration of their reaction time. After all batch experiments the solution was filtered through a 0.45 μm cellulose filter paper into a secondary HDPE container. Filtration occurred in the glove box to minimize oxidation. Final Fe(II) concentration was measured with a spectrophotometer (Hach DR-4000) outside the glove box.

2.2. Collection and preparation of natural organic matter

Three types of NOM were used in this study. The first organic matter source was concentrated NOM solution, which is waste brine produced from a MIEX treatment process (Apell and Boyer, 2010) and was collected from a Florida groundwater treatment plant (Cedar Key Groundwater treatment plant, FL, CKGO). The second source was landfill leachate collected from a local MSW landfill (New River Regional Landfill, FL, NRRL). The last source was Suwannee River Humic Acid (SRHA, IHSS Standard), which was purchased as a standard, originally sourced from surface water, and served as a control sample. These three varieties of NOM were chosen to investigate the effect of NOM on the removal efficiency of Fe(II) by limestone and represented NOM in groundwater, landfill leachate, and surface water.

The original CKGO and NRRL NOM solutions were filtered through a 0.45 μm cellulose filter (Fisher Sci., Inc.). Ultrafiltration was used to separate monovalent ions (Na^+, Cl^-) from NOM so a relatively pure NOM solution could be used in experiments (Bjelopavlic et al., 1999). Chin et al. (1994) observed that the typical MWCO of NOM is 1000 Da; thus, the filtrates were desalted by ultrafiltration through a membrane with a nominal cutoff molecular weight (MWCO) of 1000 Da. After the first flush through the membrane, DI water was added consecutively until the conductivity of the NOM solution was measured to be less than 100 $\mu S \cdot cm^{-1}$. The dilution of the DI water was accounted for by precise measurement of the volume added during flushing.

The UV absorbance of each NOM solution was measured on a Perkin–Elmer Lambda 800 spectrophotometer with 1 cm quartz cell at a wavelength of 254 nm. Dissolved organic carbon (DOC) concentrations were measured on a Tekmar–Dorhman Phoenix 8000 TOC (total organic carbon) analyzer. Specific UV absorbance ($SUVA_{254}$) was calculated by dividing the 254 nm UV absorbance by the DOC concentration (Boyer and Singer, 2008). UV_{254} absorbance is a measurement that is directly correlated to aromatic carbon content and the molecular weight of NOM (Chin et al., 1994; Weishaar et al., 2003).