Effect of Acid Pre-Treatment on Removal of Nitrate from Drinking Water by Sulfur-Modified Iron®

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ABSTRACT

Laboratory testing was conducted on water from Well-11 from the City of Ripon, California to determine whether acid pre-treatment could prevent precipitation of calcium carbonate in an SMI®III column without adversely affecting the ability of SMI®III to destroy nitrate. Two influent pH values were tested: pH 6 and pH 7. A control column that used groundwater as received (pH~8.3) was run for comparison. The columns ran for 32 days (~ 3,000 bed volumes) at a flowrate of 1.9 gpm/ft² (15 minute empty bed contact time, EBCT). Pre-treatment with dilute sulfuric acid prevented precipitation of calcium carbonate ($CaCO_3$). Pre-treatment to both pH 6 and pH 7 was effective. Pre-treatment to pH 6 significantly enhanced removal of nitrate, but also increased the concentration of dissolved iron. Pre-treatment to pH 7 showed no enhanced removal of nitrate and only a minor increase in dissolved iron.

STUDY OBJECTIVES

The goals of this study were to

- determine whether acid pre-treatment can prevent precipitation of $CaCO_3$
- determine the effect of pre-treatment on nitrate removal
- evaluate the effect of pre-treatment on iron and other water quality parameters

BACKGROUND

Field pilot tests using SMI®III were recently conducted by/for the City of Ripon to assess the ability of SMI®III to remove nitrate. The results were positive, but showed that SMI®III lost effectiveness due to clumping of the SMI®III media. Tests of the spent media, conducted by Lawrence Livermore National Laboratory (LLNL), indicated that the cause of the clumping was precipitation of calcium carbonate ($CaCO_3$). Therefore, if precipitation of $CaCO_3$ can be prevented, the SMI®III media should not clump and should retain its ability to remove nitrate.

SMI®III is an iron-based granular media (US Patents 6,093,328; 5,866,014 and 5,575,919) that has been developed for the removal of nitrate, arsenic and other compounds from water. It is certified by the National Sanitation Federation for use in drinking water treatment.

SMI®III can remove nitrate from water via chemical reduction of nitrate to ammonia and other products (Eqn. 1). Laboratory testing conducted by PRIMA Environmental has shown that not all of the nitrate lost can be accounted for as ammonia, suggesting that another compound, possibly nitrogen gas, is also formed. Nitrite, a potential intermediate of nitrate reduction, is sometimes detected, but does not account for most of the nitrate removed. These observations are consistent with literature reports that identify ammonia as an end-product of nitrate reduction by zero-valent iron (a material similar to SMI®III) and nitrogen gas as end-product of nitrate reduction by zero-valent metals in the presence of sulfur compounds (Siantar et al, 1996; Huang, et al 1998, and Dzlewinski and Marczak, 2000).

$$NO_3^- + SMI^{®}III \rightarrow NH_4^+/NH_3 + N_2\ (?) \qquad \text{Eqn. 1}$$

nitrate *ammonium/ammonia* *nitrogen*

References

Siantar, D.P.; C.G. Schreier; M. Reinhard. "Treatment of 1,2-Dibromo-3-chloropropane- and Nitrate-contaminated Water with Zero-Valent Iron or Hydrogen/Palladium Catalysts," Water Res., ***1996, 30***(10), 2315-2322,.

Huang, C.-P.; H.-W. Wang; P.-C. Chiu. "Nitrate Reduction by Metallic Iron," Water Res., ***1998, 32***(8), 2257.

Dzlewinski, J. and S. Marczak. "Fighting the Nitrates," Chemical Innovation, ***April 2000***, 33.

PROCEDURES

Three columns were constructed using clear Schedule 40 PVC pipe. The columns were approximately 7 feet tall with a bed depth of about 4 ft. The bottom (influent end) was equipped with a pressure gauge (0-30 psi) and a valve that allowed water to flow through the column or to by-pass the column. Column parameters are summarized in Table 1. The columns were run continuously upflow for 32 days. Dilute sulfuric acid solution was added about 15 seconds prior to water entering the columns. Well-water was stored in 55-gallon drums. The columns were fluffed approximately once per day for 10 minutes. Bed expansion varied by a few inches from day to day, but was generally about 60%.

SMI-III® Column Tests

Table 1. SMI-III® Column Test Parameters

Parameter	Control Column	pH 6 Column	pH 7 Column
Amount SMI-III®, lbs (kg)	3.5 (1.6)	3.5 (1.6)	3.5 (1.6)
Bed height, inches (cm)	45 (114)	49 (124)	46 (117)
Column diameter, inches (cm)	1 (2.54)	1 (2.54)	1 (2.54)
Operational flowrate, mL/min (gpm/ft²)	40 (2)	40 (2)	40 (2)
Operational EBCT, min	14.4	15.7	14.8
Influent pH	7.78-8.38	5.34-6.65	6.49-7.46
Bed volumes/day	100	92	97
Total bed volumes	~ 3,000	~ 3,000	~ 3,000
Fluff flowrate, mL/min (gpm/ft²)	450-650 (22-32)	450-650 (22-32)	450-650 (22-32)
Fluff height, inches (cm)	79 (200)	77.5 (197)	71 (180)

RESULTS

pH (Figure 1). The influent pH of the acid-treated columns varied somewhat, but was still different enough to demonstrate the effects of pH. Better control can be achieved in larger scale field applications through the use of pH controllers. The effluent pH decreased by up to 0.7 pH units in the control column, but increased by 0.7 units in the pH 7 column and by 1.5 pH units in the pH 6 column. The increase is presumably due to corrosion of iron, which can consume acid, while the decrease may be due to precipitation of calcium carbonate.

Calcium (Figure 2). Up to 32,000 mg/L (48%) of calcium was removed from the control column, but < 1% was removed from the pH 6 and pH 7 columns. This clearly indicates that calcium carbonate—the apparent source of clogging in the field tests—did not precipitate in the columns pre-treated with acid.

Figure 1. Effect on pH.

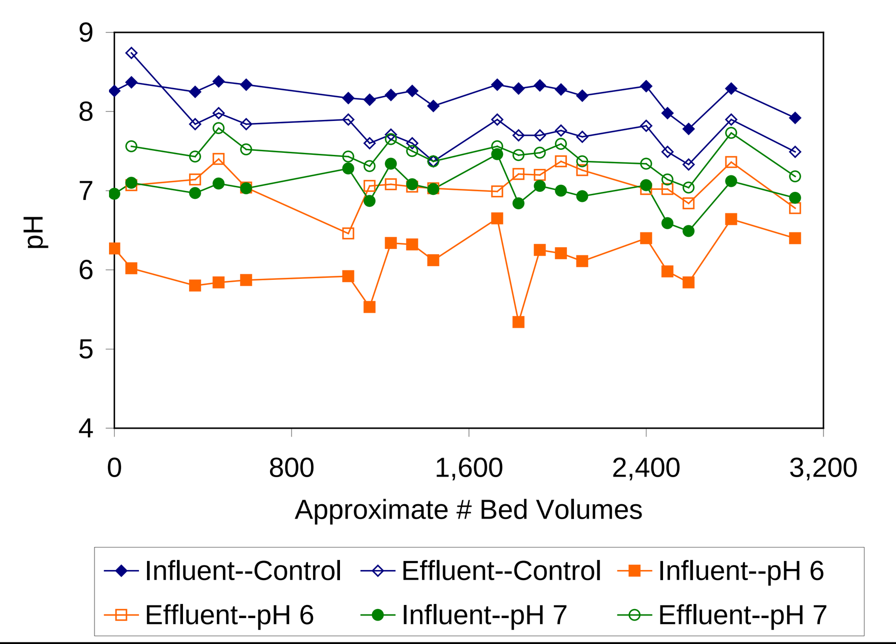


Figure 2. Effect on Calcium.

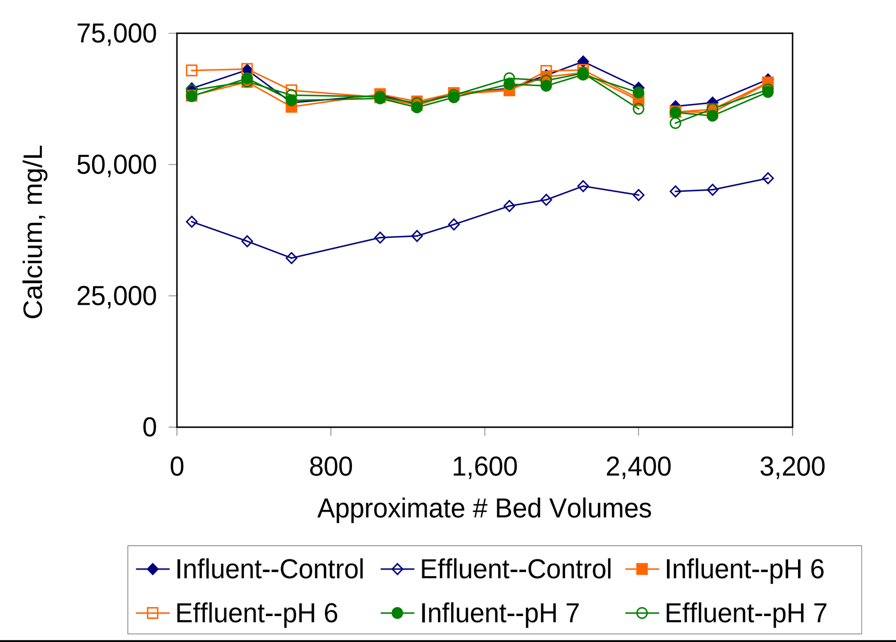


Figure 3. Effect on Nitrate.

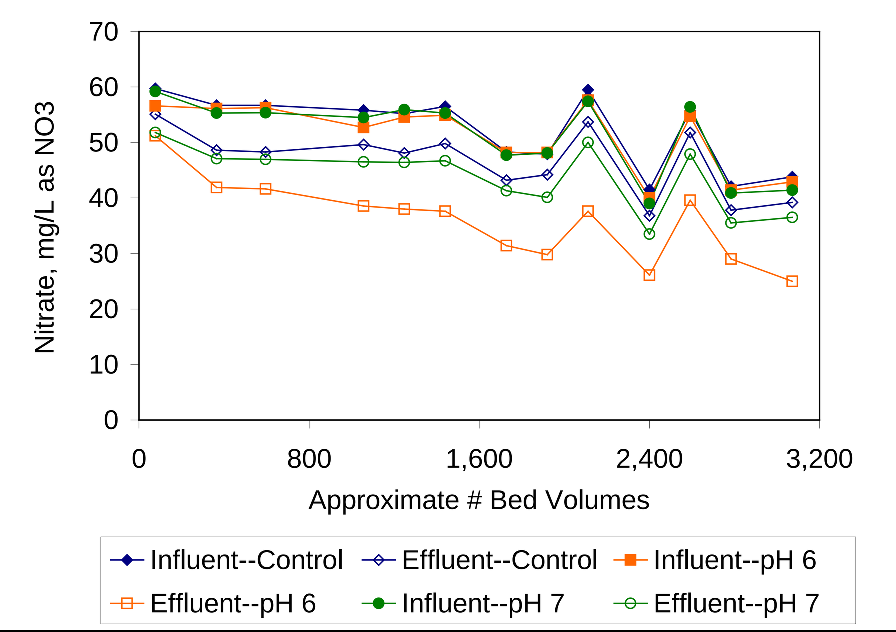
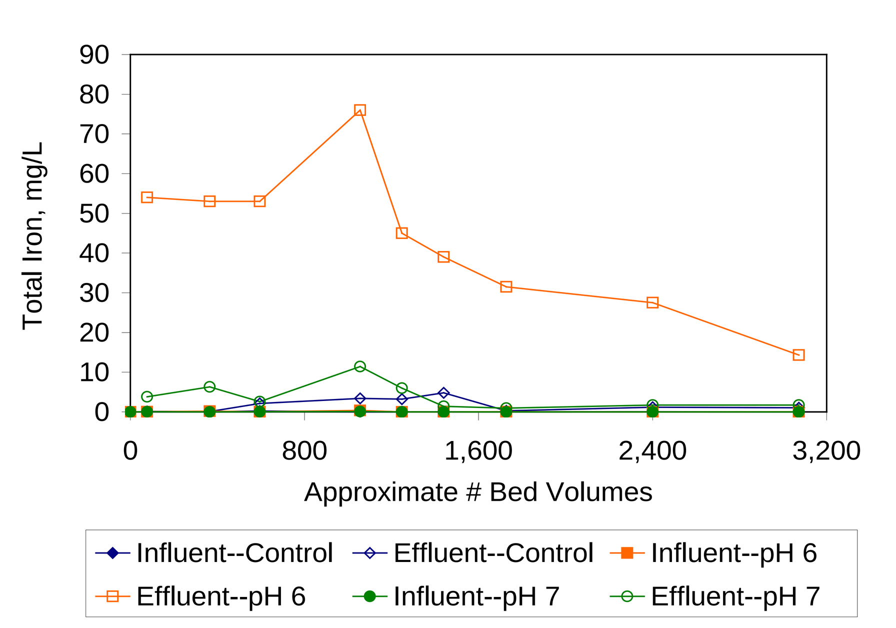


Figure 4. Effect on Iron.



Nitrate (Figure 3). The Control and pH 7 columns behaved similarly, each removing about 5-9 mg/L of nitrate for 3,100 bed volumes. In contrast, the pH 6 removed up to 14-20 mg/L of nitrate. This clearly indicates that lower pH can enhance the effectiveness of SMI®III for nitrate removal.

Nitrite. Nitrite was measured in some samples. Influent concentrations ranged from < 0.5 to 2.5 mg/L as nitrite, while effluent concentrations ranged from < 0.5 mg/L to 4.4 mg/L as nitrite. In some cases, the influent concentration exceeded the effluent concentration, while in other cases, the effluent concentration was higher. This may be possible if nitrite is an intermediate of nitrate reduction. In most cases, nitrite accounted for < 15% of the nitrate removed, confirming that nitrite is not the primary end-product of nitrate reduction by SMI®III.

Iron (Figure 4). Less than 0.03 mg/L of dissolved iron was detected in any influent. The effluent concentration of iron in the control and pH 7 columns varied over the first 1,500 bed volumes, then stabilized at about 1-1.7 mg/L. The effluent concentration from the pH 6 column was initially very high but steadily declined after 1,000 bed volumes. The decline is probably due to the somewhat higher pH after 1,000 bed volumes.

CONCLUSIONS AND FUTURE WORK

- Acid pre-treatment can prevent precipitation of CaCO3 in SMI-III® beds
- Acid pre-treatment can significantly enhance removal of nitrate, but may also increase the concentration of dissolved iron
- Nitrite may be produced, but is not the primary end-product of nitrate removal

A field pilot test to optimize the influent pH to maximize nitrate removal while minimizing the amount of iron produced is schedule to begin Summer 2006.