

Assessing the Potential of Zero-valent Iron to reduce Nitrate Mobility in Soils

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Abstract

Finding ways to reduce non-point nitrate pollution of groundwater is of major significance because of the potential economic and environmental implications such contamination has on communities that rely on groundwater for drinking water. Much of this contamination is largely due to the high mobility of nitrate in the environment, particularly in soils. Reducing the mobility of nitrate in soils is therefore critical in controlling nitrate contamination. In this study an abiotically-mediated reduction approach using zero-valent iron as a nitrate reductant is being assessed as a potential method for reducing nitrate mobility in soils. A series of laboratory-scale batch and column experiments were designed and are currently being conducted to determine important factors for developing larger plot- and field-scale studies. Results so far indicate that in the presence of zero-valent iron, nitrate is reduced to ammonium. The ammonium produced is partitioned between the soil surface and the solution phase. The amount of ammonium partitioned to the soil surface is dependent on the cation exchange capacity of the soil as well as the concentration of ammonium in the solution phase. For a given rate of zero-valent iron, nitrate reduction was greater for a soil containing system compared to a soil-free system. Nitrate reduction was also accompanied by a decrease in dissolved oxygen (for closed system) and an increase in pH with the magnitude and rate of change being dependent on the amount of nitrate reduction and zero-valent iron in the system. In addition to ammonium as a product of reduction, visual observation indicated iron-oxide formation. No detectable quantity of iron was found in solution except in the presence of the complexing agent EDTA. Addition of EDTA also resulted in increased nitrate reduction.

1. Introduction

Recent studies of nitrate concentrations in Texas groundwater wells show that nitrate levels, particularly in the western half of the state, were substantially higher than the maximum contamination limit (10 mg NO₃-N/ L) [1]. Hudak (1999), suggested a surface origin for the nitrate contamination in at least six of nine aquifers tested, most likely from agricultural land use which occupies 77% of land statewide [2]. The results of this are consistent with those of numerous studies worldwide [3, 4, 5] with inorganic nitrogen fertilizers and soil organic N believed to be the primary sources of nitrate contamination. Best management practices including irrigation and fertilizer management have received significant attention as ways to control nitrate loss but their effectiveness is often significantly affected by rainfall and or farmers' hesitancy to change management practices. Alternative approaches are therefore worth studying. Jia et al. (2004) reported an electro-kinetic approach to retaining nitrate in the root zone. In the current proposed research an abiotically-mediated reduction approach will be investigated.

The ability of zero-valent iron (Fe^0) to chemically reduce nitrate and chlorinated organic contaminants has long been known [7, 8] and has been successfully utilized in several pilot-scale and full-scale groundwater remediation efforts to remove these contaminants [9]. Nitrate reduction by Fe^0 is a redox reaction in which the oxidation of Fe^0 to Fe^{2+} or Fe^{3+} releases electrons which are accepted by nitrate, leading to the reduction of nitrate to ammonium [10, 11, 12]. Nitrate reduction to ammonium of 70 -100 % has been reported in groundwater [12, 13]. It is the Fe^{2+} or Fe^{3+} and NH_4^+ produced during the reaction and their fate that are significant in the retardation of N mobility.

Soils generally have significantly higher cation-retention capacity than anion-retention capacity, and therefore, would retain NH_4^+ more readily than NO_3^- . Hence ammonium is less likely to leach in soils. Ammonium is also preferentially fixed by micro-organisms, rendering the NH_4^+ unavailable for leaching. The NH_4^+ can also enhance microbial denitrification. The Fe^{2+} produced can be further oxidized to less soluble Fe^{3+} , providing more electrons for nitrate reduction. Additionally, the Fe^{2+} or Fe^{3+} can be easily hydrolyzed and precipitated to form reactive Fe-(hydroxides) which can enhance reduction as well as increase the soil retention capacity of nutrients. Complexation of Fe^{2+} or Fe^{3+} by organic matter can result in complexes that are more resistant to mineralization of organic-N.

Little is known about abiotically-mediated nitrate reduction in soils. To our knowledge, this is the first study seeking to evaluate the potential use of zero-valent iron to reduce nitrate mobility in soils. Initial work will therefore be geared towards determining factors important for developing plot-scale or field-scale studies.

2. Research Objectives

As previously mentioned much of this work is and will be primarily focused on determining important factors for the development of larger scale experiments. The objectives are to:

- (a) Determine the rate of nitrate reduction and subsequent production of ammonium and oxidized iron in soils.
- (b) Quantify nitrate reduction as a function of nitrate input concentration and zero-valent iron application rate.
- (c) Estimate reducing longevity (“life”) of zero-valent iron in the soil.
- (d) Determine the fate of residual zero-valent iron and the products of reduction.
- (e) Develop a mass balance for nitrate, zero-valent iron and reduction products.

3. Materials and Methods

Six soils from varying geographical locations across Texas and having different properties (Table 1) were selected for this study.

Table 1. Summary of soil properties. *Courtesy: Soil Characterization Laboratory, TAES.*

	pHH ₂ O	CEC ¹ cmol/kg	B. D. ² g/cm ³	B. sat ³ -----%	Clay	Sand	Silt	O.C. ⁴ -----%
Soil 1	4.6	23.5	1.46	74	31.5	22.2	46.3	0.13
Soil 2	4.8	6	1.37	27	7.9	36.1	56	1.79
Soil 3	8.3	31.3	1.42	100	48.3	30.3	21.4	0.43
Soil 4	8.0	53.3	1.29	100	56.5	8.9	34.6	2.20
Soil 5	9.1	2.8	1.52	100	3.3	92.5	4.2	0.13
Soil 6	6.0	2.4	1.41	71	2.7	91.9	5.4	0.31

¹ Cation exchange capacity

² Bulk density

³ Base Saturation

⁴ Organic Carbon

3.1 Chemicals

All chemicals used were reagent grade. For preparation of nitrate solution, pre-determined quantities of KNO₃ were dissolved in a 50 mM KCl background electrolyte solution. The electrolyte solution, rather than deionized water, was used because it was more representative of the natural soil environment. In experiments where EDTA was used, the 50mM KCl was substituted with an equivalent concentration of EDTA. No effort was made to control oxygen level in these current experiments presented. Zero-valent iron (H-200, HEPUREsm) was obtained from Hepure Technologies; physical properties of the zero-valent iron are summarized in Table 2. A Na⁺-saturated cation exchange resin was used as an additional exchange surface for comparison with the soil. The Na⁺-saturated resin was prepared via Na⁺-H⁺ ion exchange of an H⁺-saturated resin (550 cmol⁻/ kg) under alkaline pH.

Table 2. Physical properties of H-200 zero-valent iron. *Courtesy of Hepure technology*

Apparent Density (g/ cm ³)	2.55
Surface area (m ² /g)	0.1
Particle size	
< 45 μm	10 %
< 85 μm	50 %
< 140 μm	90 %

3.2 Batch Experiments

Two types of batch experiments were conducted: (a) open-system and (b) closed-system batch experiments. In the open-system experiments 250 ml centrifuge bottles were used as batch reactors. Two holes were punched into the cap of each reactor to facilitate gaseous exchange with the external environment. In the closed-system experiment, no such gaseous exchange was facilitated. Additionally, for the closed system depending on

the total volume of solution used, either 250 ml centrifuge bottles or 50 ml tubes were used as batch reactors.

In nitrate reduction experiments, predetermined quantities of zero-valent iron, soil and nitrate solution were added to the batch reactors and allowed to equilibrate for varying time intervals on a rotary shaker at 250 rpm. At each interval, a reactor was sacrificed, and the pH and dissolved oxygen of the suspension was measured. The suspension was subsequently centrifuged at 2500 rpm for 5 minutes and an aliquot of supernatant filtered through 0.45 μm nylon syringe filters and refrigerated for analysis of nitrate, ammonium and dissolved iron. The remaining supernatant was discarded and a known quantity of 2M KCl was added to the residual (soil or resin + residual Fe^0) and shaken for 30 minutes to determine the quantity of ammonium and or nitrate partitioned to the exchange sites of the soil or exchange resin. The resulting residual + 2M KCl suspension was centrifuged and filtered as described above; an aliquot was saved and stored at 4 $^{\circ}\text{C}$ for later analysis.

3.3 Column Experiments

While much of the methods for the batch experiments have been completed, methodology for the column experiments is still being refined; hence, the methods described below include conceptual ideas that have been completed.

Eighteen inch long vertically mounted columns will be used. The internal diameter of the columns was approximately 1 inch. Each column will be packed to a depth of 8 inches according to its respective bulk density (Table 1). A predetermined quantity of Fe^0 will be incorporated into the top 5 inches of soil before being added to the column. For each soil type, a blank and three Fe^0 iron-containing columns (triplicates) will be used. Filter paper will be put at the base of the column to prevent loss of soil and at the on top of the soil to prevent sealing of pores upon impact of water. Nitrate solution will be applied in two pore volume intervals to the top of the column at a rate consistent with different rainfall intensities. The columns will be allowed to drain freely and drainage solution will be collected at the base of the column and refrigerated for analysis of ammonium and nitrate. The pH of the drainage solution will also be measured. After each two pore volumes the column will be flushed with a known volume of 50mM KCl to remove nitrate and ammonium from the soil pores. The drainage solution from flushing will also be collected and stored for analysis. At the end of the leaching experiments the soil in the column will be sectioned into different depth intervals. The nitrate and ammonium on the soil surface will be measured by extracting ammonium and nitrate with 2M KCl and analyzing the extract.

Nitrate-N and Ammonium-N were and will be analyzed colorimetrically using a Technicon II autoanalyzer. Released iron was measured using atomic absorption spectroscopy. pH and dissolved oxygen (DO) was measured using an accumet pH-DO meter.

4. Results and Future Work

4.1 Nitrate Reduction by zero-valent iron using batch experiments

Nitrate in soils can be completely reduced to ammonium in the presence of zero-valent iron (Figure 1). Figure 1 also suggests that the rate reduction increases as the Fe⁰: soil ratio increases. For example, after 5 h, nitrate concentration was reduced from an initial concentration of 60 mg/L to below 10 mg/L by a Fe⁰: soil ratio of 1:1 (5:5) comparing to about 30 mg/L for a ratio of 1:9. The reduction from NO₃-N to NH₄-N appears to be direct with a stoichiometric conversion ratio of 1:1. This can be seen more clearly in Figure 2 where at any given time total N (NH₄-N + NO₃-N) remained at 60 mg/L the concentration of the input nitrate solution. Nitrate reduction to ammonium was also accompanied by an increase in pH and a decrease in DO concentration (Figure 3) indicating a consumption of H⁺ and O₂.

It was not initially clear whether the change in pH and DO was due to the actual reduction process or whether it was due to the fact that these initial experiments were conducted in the closed-batch system. Table 3 shows the results of an open-batch system. These results suggest that although the reduction process may consume both H⁺ and oxygen in an open-system the oxygen can be replenished, maintaining the DO concentration. The consumption of H⁺ is most likely utilized in the formation of NH₄⁺ from NO₃⁻. Table 3 also shows that nitrate reduction is possible at much lower Fe⁰:soil ratio than those shown in Figure 1.

Further work will be conducted to determine the lowest, as well as the most economically feasible Fe⁰: soil ratio. One major consequence of reducing the Fe⁰: soil ratio is the increase likelihood of surface passivation effects arising from iron-oxide precipitation. Figure 4 shows the effect of the addition of the metal complexing agent EDTA to the system. In contrast to KCl, in the presence of EDTA no precipitation of iron was observed. The lack of iron precipitation is due to the complexation of the iron to form a Fe-EDTA complex, which is confirmed by analysis of solutions for total iron using atomic absorption spectroscopy. No Fe was detected in the presence of KCl while as much as 1000 ppm Fe was detected in the presence of EDTA. There was evidence indicating that in the presence of EDTA nitrate reduction may increase several folds (Figure 5).

Also apparent from Figure 5 is the fact that even in the presence of KCl, nitrate reduction was several folds higher than that in exchange resin and Fe-only samples. The actual reason for this is not definitive. One possible explanation is that the Fe released during nitrate reduction is precipitated onto the surface of the soil rather than the residual zero-valent iron; and therefore, passivation effects are reduced. Further evidence is needed to prove this. Selective dissolution technique will be used to compare pre-reduction and post reduction soil iron content.

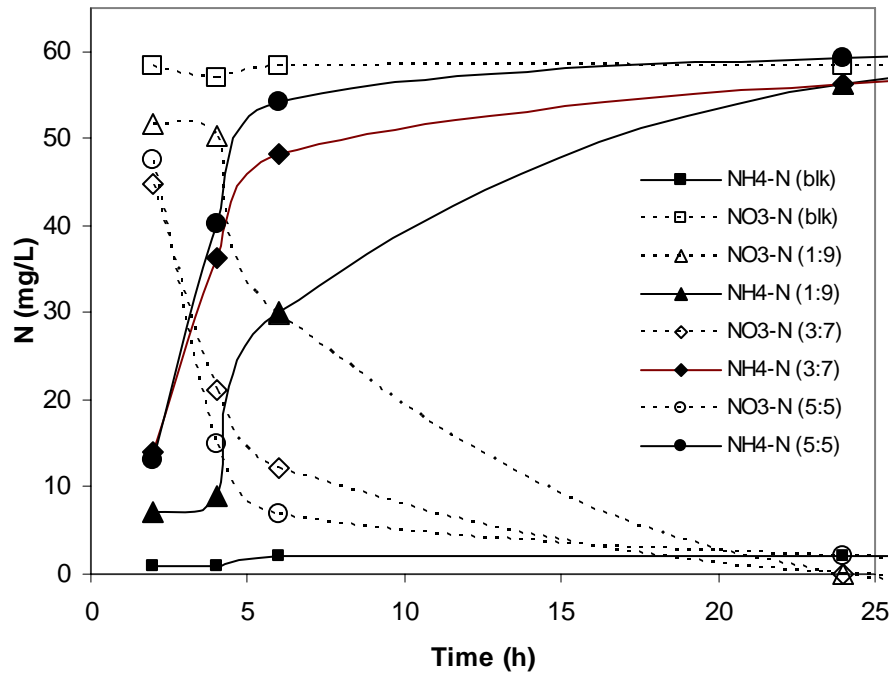


Figure 1. Nitrate-N reduction and accompanied Ammonium-N production in Soil 1 at different Fe⁰:soil ratio.

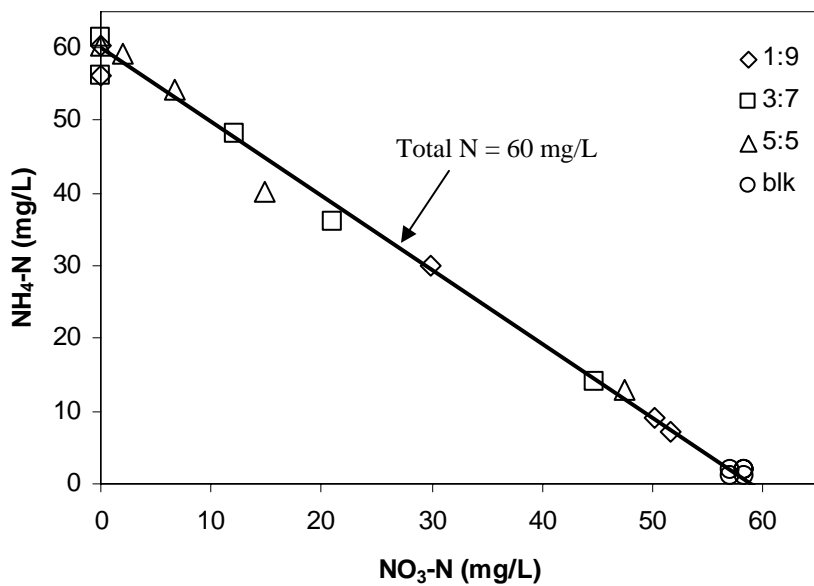


Figure 2. Total NH₄-N in Soil 1 system as a function of total NO₃-N. The fact that point follow 60 mg/L line is suggest direct conversion of NO₃-N to NH₄-N.

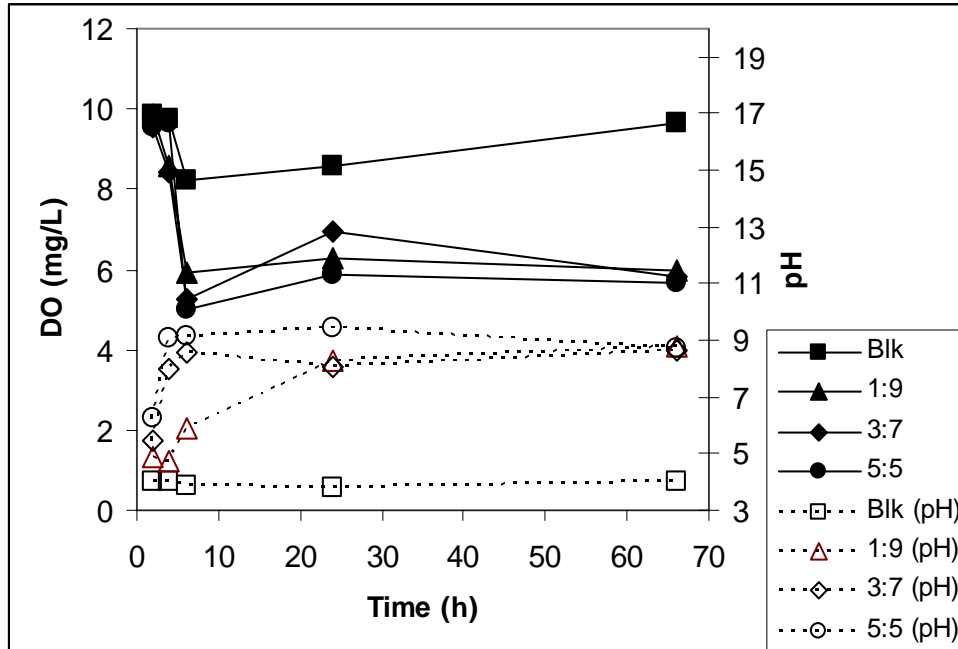


Figure 3. Changes in pH (broken lines) and DO (solid lines) with time for Soil 1 system.

Table 3. Measured pH, nitrate-N, ammonium-N, and DO concentrations in a open-batch system using Soil 1. Input nitrate-N concentration = 40 mg/L.

Fe ⁰ :					ex-NH ₄ -
Soil	pH	DO	NO ₃ -N	NH ₄ -N	N ²
			-----mg/L-----		
(g : g)		-----			
0:10	3.8	8.3	40.4	nd ¹	nd
1:100	4.2	8.2	40.4	2.1	nd
1:40	5.8	8.0	21.6	19.3	2.1
1:20	7.3	8.1	nd	38.7	3.4

¹below detection limit

²Ammonium-N on exchange sites

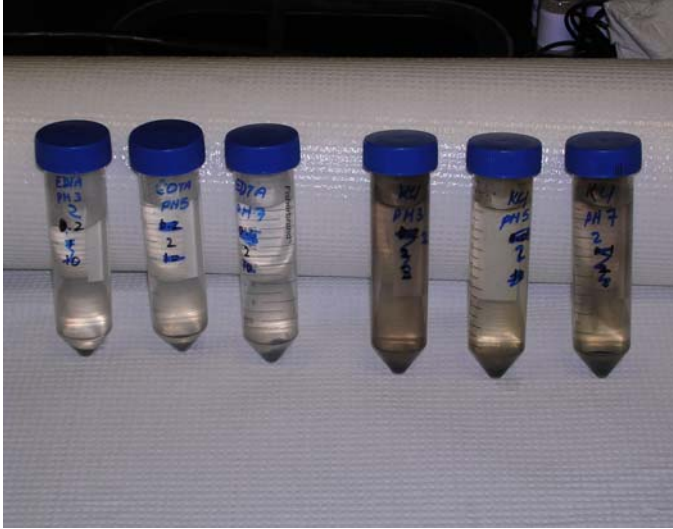


Figure 4. Effect of EDTA on iron-oxide precipitation. Cloudiness in tubes to the right (KCl as background electrolyte) is due to precipitation of iron-oxide. Tubes on the left (EDTA as electrolyte) show no evidence of precipitation.

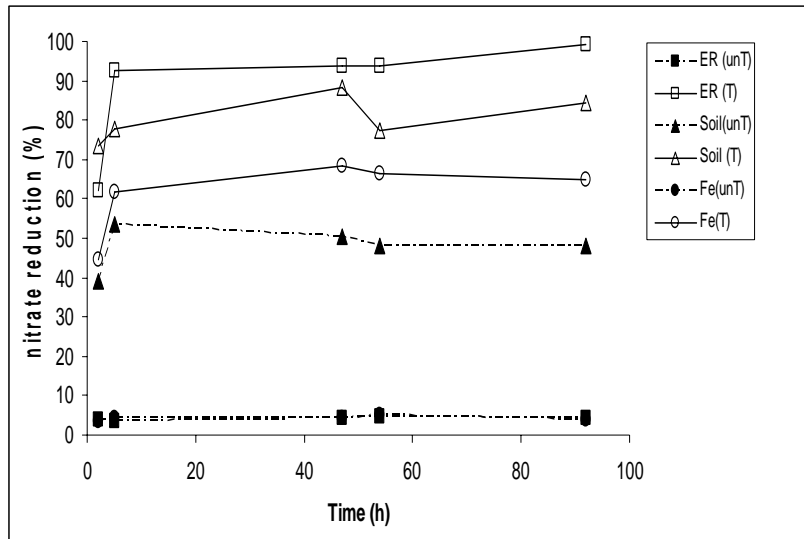


Figure 5. Effect of EDTA on nitrate reduction. ER- exchange resin; Soil – Soil 1; Fe- zero-valent iron without soil; unT- in the presence of KCl; T- in the presence of EDTA.

4.2. Ammonium partitioning between solution and soil surface

Figure 6 shows that over time the concentration of ammonium on the exchange surface increases. This is consistent with an increase in nitrate reduction and ammonium production. Figure 7 indicates that the concentration of ammonium-N on the soil exchange surface is negatively related to the nitrate and positively related to ammonium-N concentration. This indicates that as reduction proceeds, ammonium is partitioned to the soil surface exchange sites and can be trapped. There is also the potential for this ammonium to become fixed in the interlayer of some clays.

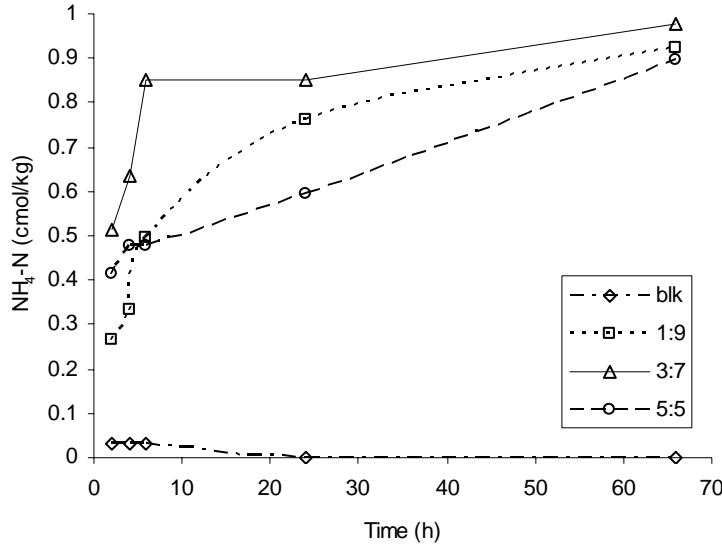


Figure 6. Concentration of ammonium-N on the soil surface.

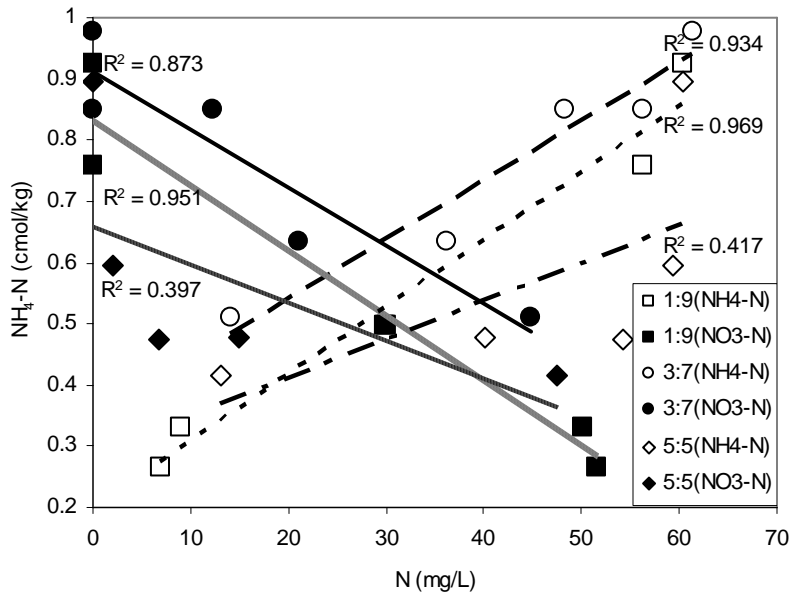


Figure 7. Correlation between N in solution and ammonium-N on the exchange sites.

4.3 Nitrate reduction in column studies

Nitrate concentration as a function of pore volumes is shown in Figure 8. Total reduction of a 160 mg/L nitrate solution was accomplished after 8 pore volumes indicating that even in the absence of stirring nitrate reduction is significant. Comparison with the blank shows that there was some evidence of nitrate reduction even in the blank. This was probably due to microbially-mediated denitrification. Autoclaving of sample or the use of a biocide will be used in up coming experiments for comparison. Even in the considering the reduction in the blank column there is an addition loss of 80 mg/L which was clearly attributable to the presence of the zero-valent iron (Figure 9).

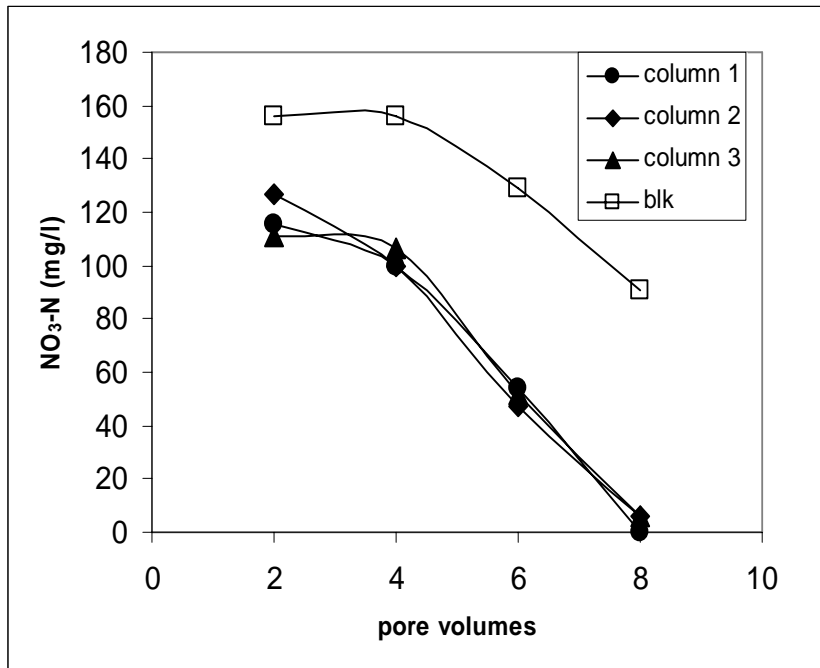


Figure 8. Concentration of nitrate in column discharge for Soil 2.

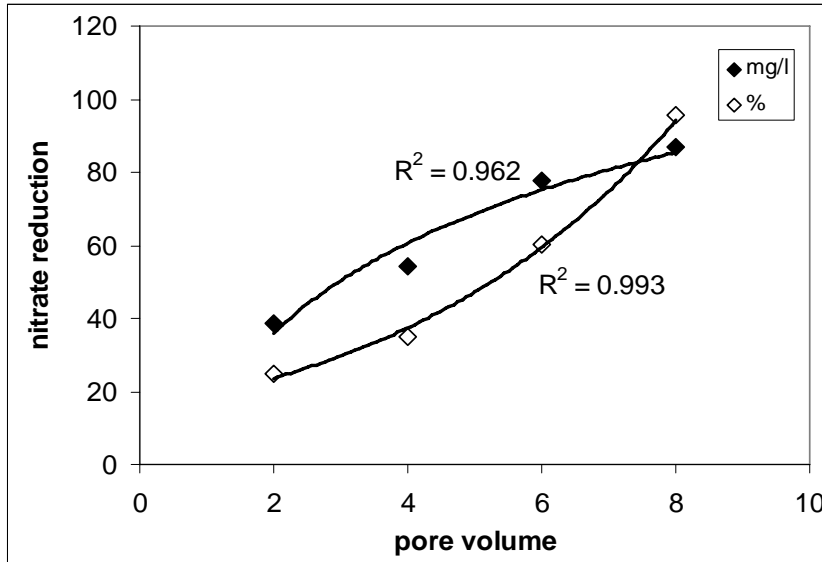


Figure 9. Nitrate concentration in nitrate discharge excluding reduction observed in blank.

Conclusion

Zero-valent iron reduction shows potential for reducing nitrate mobility in soils through the partitioning of the produced ammonium-N to soil surface exchange sites. Further work is needed to determine optimal parameters for nitrate reduction in these systems as it appears to be different than in a pure Fe^0 -solution system.

We anticipate that much of the remaining work will be completed by years ending and by then we should have finalized our conclusions and be ready to move on to the next phase of research.

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