

REMOVAL OF NITRATE/ATRAZINE CONTAMINATION WITH ZERO-VALENT IRON-PROMOTED PROCESSES

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ABSTRACT

This research project is designed to study the feasibility of removing or remediating nitrate/atrazine in groundwater using iron powder treatment. Iron powder was selected because it is cheap and nontoxic. Three different types of iron powders were used in this research. They were lab grade iron powder (about 0.02 micron in size), industrial grade iron powder (about 0.5 micron in size), and rusted industrial grade iron powder (about 0.5 micron in size). In the batch studies conducted, best nitrate removal was obtained using rusted iron powder (nearly 70% removal at approximately neutral pH). However, more atrazine was removed when lab grade iron powder was used (about 75% removal). During the column studies, it was found mixing two parts of fine sand with one part of iron powder prevented plugging and improved removal efficiency. More than 98% of the atrazine were removed by lab grade iron powder with less than two days detention time. On the other hand, nitrate removals were dependent on pH. High nitrate removals were observed at low and high pHs while less than 50% removals were observed near neutral pH.

Key words: *iron powder, zero-valent iron, atrazine, nitrate, remediation*

INTRODUCTION

Nitrate contamination in groundwater and surface water is a serious problem. In Nebraska, nitrate contamination of groundwater and surface water are commonly found in areas where commercial fertilizers are applied. In northern Holt County, Nebraska, about 50% of the applied nitrogen fertilizer had leached to the groundwater (Exner and Spalding, 1991). In the northern side of the Platte River in the Central Nebraska Platte Valley, more than 202,000 contiguous hectares have been contaminated with nitrates.

Atrazine is a major herbicide used throughout the United States to control weeds in agricultural fields. The EPA estimated that about 55 million pounds of atrazine were used in 1992 (Lin et al, 1995). Most sites of atrazine contamination are directly linked to farming practices and the impact of runoff from the farmland.

Nitrate and atrazine contamination in groundwater is a problem of great concern. The remediation of contaminated areas in the subsurface (both soils and groundwater) has been and will continue to be the most costly and time-consuming part of any site cleanup. After the source of contamination has been removed and treated, contaminated soil and groundwater may remain and require treatment. Traditional pump-and-treat systems only treat the symptom (solubilized contaminants) and not the cause, due to the limited capability of hydraulic pressure to move contaminants from soil into groundwater and to the collection point. This limitation is especially acute in fine-grained soils such as clay. Treatment methods such as *in situ* bioremediation or *in situ* chemical treatment face similar problems of moving nutrients, inoculated bacteria, and treatment chemicals through soil to the proximity of contaminants using hydraulic pressure. Because of this, there is a

need for technologies to remediate contaminants in saturated soil *in situ*.

In nitrate treatment, oxidative dissolution of Fe^0 takes place resulting in the formation of Fe^{2+} ions. The redox couple formed by the zero-valent metal iron Fe^0 and the dissolved Fe^{2+} ions ($\text{Fe}^0 \Rightarrow \text{Fe}^{2+} + 2\text{e}^-$) has a standard reduction potential of 0.44V (Stumm and Morgan, 1996). This makes Fe^0 a reducing agent to many redox labile substances. For example, a likely nitrate/nitrogen transformation reaction under the influence of Fe^0 is as follows: $\text{Fe}^0 \Rightarrow \text{Fe}^{2+} + 2\text{e}^-$, $E^\circ = 0.44 \text{ V}$; $2\text{NO}_3^- + 12\text{H}^+ + 10\text{e}^- \Rightarrow \text{N}_2(\text{g}) + 6\text{H}_2\text{O}$, $E^\circ = 1.24 \text{ V}$; the combined reaction: $5\text{Fe}^0 + 2\text{NO}_3^- + 12\text{H}^+ \Rightarrow 5\text{Fe}^{2+} + \text{N}_2(\text{g}) + 6\text{H}_2\text{O}$, $E_{\text{rxn}} = 1.68 \text{ V}$. The combined reaction has a positive electrode potential of 1.68V and therefore is likely to be thermodynamically favorable under most conditions.

In atrazine treatment, Pulgarin et al. (1995) demonstrated that atrazine underwent rapid degradation in the presence of Fe^0 at a pH of 1.5 with sunlight. No degradation was observed when experiments were conducted in the dark. Singh et al. (1996) indicated that most atrazine were adsorbed to the iron surface under neutral pH conditions. These researchers also indicated that more than 70% percent of the atrazine adsorbed can potentially be desorbed, while about 20% is bounded by the iron surface (very difficult to be desorbed).

The objective of this research was to determine the feasibility of a zero-valent iron promoted process in removing nitrate and atrazine simultaneously. Also, the conditions at which optimal removal is achieved was studied.

MATERIALS AND METHODS

Materials

Three forms of iron powder were used in the batch and column studies: lab grade iron powder from Fisher, Inc. (40 mesh, about 0.02 mm in diameter); industrial grade iron powder from U.S. Metals (about 0.5 mm in diameter); and rusted industrial grade iron powder (about 0.5 mm in diameter). Rusting was achieved by soaking the industrial grade iron powder for one hour in a 1N sulfuric acid solution and rinsing the iron powder until the pH of the rinse water was about neutral pH. The washed iron powder was then air dried overnight and rust was formed.

Batch Studies

Batch experiments were conducted in a 160 mL dilution bottle. Each bottle consisted of 150 mL of nitrate and/or atrazine contaminated solution with 5% (w/v) of different types of iron powders. To ensure mass transfer was not limited, complete mixing was provided by rotating the bottles in a 1 ft by 1.5 ft box at 30 rpm for a period of three days. This constant mixing insures that all the atrazine and nitrates would have access to the available iron sites. All batch samples were conducted in duplicates.

Column Studies

For the column studies, several bench scale reactors, 1.5-inch diameter by 5- to 12-inch lengths, were constructed to simulate the remediation process (Figure 1). Influent feed was delivered to the columns using a small positive displacement pump manufactured by Barnant Co. Several runs were made using the various types of iron powder and sand mixtures. Figure 1 shows the schematic of a typical column reactor used. Influent feed consisting of either 30 mg/L of Nitrate-N, 20 µg/L of atrazine, or both was delivered to the columns with the small positive displacement pump.

Analytical Methods

Samples were obtained for both the column and batch studies and analyzed for pH, redox, atrazine, NO_3^- -N, NO_2^- -N, NH_4^+ -N, Fe^{2+} , and total dissolved iron. pH and redox potential were measured using electrode methods. NO_3^- -N and NH_4^+ -N were measured with ion-selective electrodes and meters in accordance with Standard Methods (1992). Total dissolved iron was measured with an atomic adsorption spectrometer. Atrazine was measured using gas chromatography. NO_2^- -N and Fe^{2+} were measured using the HACH colorimetric methods.

RESULTS

Batch Studies

Batch No. 1

Experiments were conducted in 160 ml glass bottles with lab grade iron powder. For these batch experiments, each bottle was filled with a 5% (w/v) of the lab grade iron and different types of feed solutions [nitrate solution (30 mg/L as N), atrazine solution (20 µg/L) or both]. These bottles were rotated for three days at about 30 rpm to ensure complete mixing. A summary of the results is provided in Table 1. Although lab grade iron powder was relatively effective in reducing the atrazine concentrations, it did not work well for NO_3^- -N removal at initial pHs of about 6. Previous studies by Zawaideh et.al. (1997) indicated efficient nitrate removal at low (<2) or high (>11) pHs. Atrazine removal rate was about 75% in the batch solution with only 20 mg/L of atrazine and about 51-66% in the solution containing both NO_3^- -N and atrazine. This indicates that the presence of NO_3^- -N may interfere with the atrazine removal process. In all the batch samples, the final total dissolved iron concentration was less than 0.11 mg/L. pH rise was about 2.5 to 3.5 units (comparable to the previous column studies). Final redox readings ranged from about 5 to -30 mV.

Batch No.2

The experimental conditions were similar to Batch No.1 except that industrial grade iron powder was used for these batches. A summary of the results is provided in Table 2. When industrial grade iron was used, lower removal efficiencies were observed for both atrazine and NO_3^- -N. Final pH and final redox readings appeared to be slightly higher than those in Batch No.1

involving the lab grade iron powder. Final redox readings were also slightly higher than those in the batches where lab grade iron powder was used. Total dissolved iron concentrations were less than 0.1 mg/L in all samples. Again, atrazine removals were less in the solution containing both atrazine and nitrate as compared to the solution containing only atrazine.

Batch No. 3

The experimental conditions were similar to Batch No. 1 except that rusted industrial grade iron powder was used for these batches. A summary of the results is provided in Table 3. When rusted iron powder was used, NO_3^- -N removal efficiencies improved substantially to about 75%. Higher atrazine removals were also observed in batch experiments with only atrazine present as compared to both atrazine and nitrate. Final redox potential and pH appeared to be much lower for the solution containing rusted iron powder and atrazine only. The final pH and redox conditions are more conducive to corrosion as indicated by a typical pH-redox diagram for an iron/water system. This results in detection of a higher concentration of Fe^{2+} . In the sample containing atrazine only, pH rose about 2 units while a 4.5 to 5 unit increase was observed in samples containing NO_3^- -N and atrazine.

Batch No. 4

This batch experiment was conducted to determine the effects of pH on the atrazine removal using industrial grade iron powder. Feed solution containing 2.5 mg/L atrazine with 10% iron powder at pH 3, 5, 7, 9, and 11 were used. pH adjustments were made with either hydrochloric acid or sodium hydroxide. These bottles were rotated for five days at about 30 rpm to ensure complete mixing. The results confirmed that industrial grade iron powder does not work well in removing atrazine. Removals ranged from 20 - 30%. The removal efficiencies were slightly higher at the higher pH. pH increased 0.1 and 4.15 units for the pH 11 and pH 3 samples, respectively.

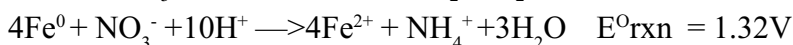
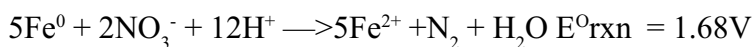
Column Studies

The following provides the results of the column studies conducted. Column Studies No. 1 to No. 4 were conducted with various forms of iron powder using 20 $\mu\text{g/L}$ of atrazine as the feed. Column studies Nos. 5 to 8 were conducted using a feed solution containing 30 mg/L NO_3^- -N and 20 $\mu\text{g/L}$ atrazine. Tables 4 and 5 present the results obtained from the column studies.

DISCUSSION

Figure 2 shows the nitrate and atrazine removal using the various types of iron powder in the batch experiments. Rusted iron powder works better for nitrate removal and lab grade iron powder works better for atrazine removal. Industrial-grade powder achieved less than 20% removal for atrazine and nitrate. Figure 3 shows the results of the pH increase after the three-day experimental period for the various iron powders. When only atrazine is used as the feed, pHs were generally 1 to 2 units lower than when nitrate or nitrate/atrazine were used. Two possible reactions involving

zero-valent iron and nitrate in water are shown below:



In both reactions, hydrogen ions are used up. This explains why the pH rise is slightly lower when nitrate is not present in the feed solution.

In column studies No.1 to No.4, where only atrazine was fed to the reactors, more than 98% of the atrazine was removed using lab-grade iron mixed with sand (1 part iron to 2 parts sand by weight). When industrial grade iron powder was used, the atrazine removal efficiencies were generally less than 20%, i.e., similar to the run where only sand was used. By using rusted iron powder, the atrazine removal efficiencies improved a little. About 37% was removed with an HRT of 1.34 days. The results are similar to those in batch studies where atrazine is mostly removed by lab-grade iron powder. From the trend observed in these experiments, it appeared that increasing the HRT may improve the removal efficiencies.

In column studies No.5 and No.6, feed solution containing both nitrate and atrazine was used. When lab grade iron powder was used, atrazine removals were more than 98% with short HRTs (0.7 to 1.8 days), while nitrate removals were less than 50%. Because previous studies indicated that HEPES (an organic buffer) improved nitrate removals, 0.01mM of HEPES was included in the feed solution. Also because lab-grade iron powder was very expensive (\$20/lb), industrial-grade iron powder was used in column study No.6. Although more than 99% of influent nitrate was removed, only about 20% of the atrazine was removed.

In column studies No.7 and 8, much longer HRTs were used. For the column with industrial-grade iron powder, more than 95% of nitrate and about 60% of atrazine were removed at HRTs of 7-8 days. When rusted iron powder was used, the results were better. About 99% of nitrate and 90% of atrazine was removed. The data obtained from column studies No. 7 and 8 are presented in Figures 4 and 5. The results indicate that rusted iron powder works better for both nitrate and atrazine removals. Therefore, under field conditions and over a long period of time, the formation of rust is likely to assist in the removal of nitrate and atrazine. Also, the used of the less expensive industrial-grade iron powder can remove both nitrate and atrazine if high HRTs (7-8 days) are provided. If zero-valent iron powder and sand are mixed and used as a treatment wall in the field, the actual HRTs would likely be higher order magnitudes than those in the column studies due to the low hydraulic gradient and the permeability in most groundwater systems.

SUMMARY

Based on the preliminary results of this research, it appeared that iron powder can simultaneously remove nitrate and atrazine when high HRTs are provided. Under most natural conditions, rusting is a very thermodynamically favorable reaction. Therefore nitrate and atrazine removals

should be improved when rusting occurs, as shown by this study. The following are some of the additional findings of this research: i) mixing sand with iron powder can prevent plugging problems; ii) the presence of nitrate can interfere with atrazine removals; and iii) high nitrate removals are observed when rust, low pH conditions, and HEPES are present.

ACKNOWLEDGMENTS

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REFERENCES

- APHA., AWWA., and WEF (1992). Standard Methods for the Examination of Water and Wastewater. 18th Ed.. American Public Health Association, American Water Works Association, and Water Environmental Federation, Washington, D.C.
- Exner, M.E., and R.F. Spalding, (1990). Occurrence of pesticides and nitrate in Nebraska ground water, Water Center Pub., No.1, Institute of Agriculture and Natural Resources, Univ. of Nebraska-Lincoln.
- Hach Water Analysis Handbook. (1992). 2nd Ed.. Hach Company, Loveland, Colorado.
- Lin, B.H., M. Padgitt, L. Bull, H. Delvo, D. Shank, and H. Taylor, (1995). Pesticide and Fertilizer use and trends in agriculture. Agricultural Economic Report, No. 717, USDA., Washington D.C.
- Pulgarin, C., J.P. Schwitzguebel, P. Peringer, G.M. Pajonk, J. Bandara, and J. Kiwi, (1995). Abiotic degradation of atrazine on zero-valent iron activated by visible light. Preprints of papers presented at the 209th ACS National Meeting, Anaheim, CA, April 1995. 35:767-770
- Singh, J., P.J. Shea, S.D. Comfort, T.C. Zhang, S.H. Lakhwindar, and D.S. Hage. Transformation of atrazine and nitrate in contaminated water by iron promoted processes. Proceedings of the WEFTEC'96 69th annual Conference & Exposition, Dallas TX, October, 1996, Vol. 3. P143-150
- Stumm, W., and J.J. Morgan, (1996). Aquatic Chemistry, 3rd Ed., Wiley-Interscience, NY, 1996.
- Zawaideh, L.L., C.F. Chew, and T.C. Zhang, (1997). Remediation of nitrate-contaminated water and soil by Fe⁰-promoted processes. Proceedings of the 12th Annual Conference on Hazardous Waste Research, May 19-22, Kansas City, MO, 1997, P77-97.

Table 1. Results for batch no. 1 (lab-grade iron powder).

Description (Feed Solution)	Initial pH	Final pH	Initial redox (mV)	Final redox (mV)	Percent NO ₃ ⁻ -N removed	Percent atrazine removed	Fe ²⁺ (mg/L)	Total Fe(mg/L)
Iron, 30 mg/L NO ₃ ⁻ -N	5.8	9.3	230	-30	18		<0.1	0.09
Iron, 30 mg/L NO ₃ ⁻ -N	5.6	9.35	230	-38	18		<0.1	0.07
Iron, 20 µg/L atrazine	5.7	8.3	195	-90		76	<0.1	0.07
Iron, 20 µg/L atrazine	5.5	8.32	200	-92		75	<0.1	0.10
Iron, 30 mg/L NO ₃ ⁻ -N, 20 µg/L atrazine	5.65	9.28	220	-25	17	66	<0.1	0.11
Iron, 30 mg/L NO ₃ ⁻ -N, 20 µg/L atrazine	5.5	9.22	235	-26	19	51	<0.1	0.08

Table 2. Results for batch no. 2 (industrial-grade iron powder).

Description (Feed Solution)	Initial pH	Final pH	Initial redox (mV)	Final redox (mV)	Percent NO ₃ ⁻ -N removed	Percent atrazine removed	Fe ²⁺ (mg/L)	Total Fe(mg/L)
Iron, 30 mg/L NO ₃ ⁻ -N	6.2	10.35	260	0	4		<0.1	0.04
Iron, 30 mg/L NO ₃ ⁻ -N	6.1	10.25	280	5	6		<0.1	0.02
Iron, 20 µg/L atrazine	6.25	9.15	265	-30		18	<0.1	0.03
Iron, 20 µg/L atrazine	6.05	10.25	290	3		17	<0.1	0.04
Iron, 30 mg/L NO ₃ ⁻ -N, 20 µg/L atrazine	6.2	10.13	260	-2	8	9	<0.1	0.03
Iron, 30 mg/L NO ₃ ⁻ -N, 20 µg/L atrazine	6.1	10.10	270	-5	12	0	<0.1	0.08

Table 3. Results for batch no. 3 (rusted iron powder).

Description (Feed Solution)	Initial pH	Final pH	Initial redox (mV)	Final redox (mV)	Percent NO ₃ ⁻ -N removed	Percent atrazine removed	Fe ²⁺ (mg/L)	Total Fe(mg/L)
Iron, 30 mg/L NO ₃ ⁻ -N	5.65	10.55	260	-50	70		<0.1	0.09
Iron, 30 mg/L NO ₃ ⁻ -N	5.7	10.43	275	-61	71		<0.1	0.07
Iron, 20 µg/L atrazine	5.7	7.62	260	-420		37	1.2	2.4
Iron, 20 µg/L atrazine	5.5	7.14	280	-470		38	1.5	2.53
Iron, 30 mg/L NO ₃ ⁻ -N, 20 µg/L atrazine	5.7	10.35	275	-62	71	6	<0.1	0.11
Iron, 30 mg/L NO ₃ ⁻ -N, 20 µg/L atrazine	5.5	10.20	295	-70	76	16	<0.1	0.08

Table 4. Summary of the results for column studies Nos. 1 to 4.

Description	Media	HRTs (Days)	Removal (%)
Column Study No. 1	100% industrial -grade iron powder	0.3	7%
		0.8	24%
		7.5	56%
Column Study No. 2	100% sand	1.8	10%
	90% sand mixed with 10% industrial-grade iron powder	1.8	6%
	80% sand mixed with 20% industrial-grade iron powder	1.8	17%
Column Study No. 3	66% sand mixed with 33% lab-grade iron powder	0.7	99%
		1.1	99%
		1.8	98%
Column Study No. 4	66% sand mixed with 33% rusted iron powder	0.28	6%
		0.5	10%
		0.7	15%
		1.1	30%
		1.3	37%

Table 5. Summary of the results for column studies Nos. 5 to 8.

Description	Media	HRTs (Days)	Atrazine Removal	Nitrate Removal
Column Study No. 5	66% sand mixed with 33% lab-grade iron powder	0.7 1.8	98% 99%	11% 45%
Column Study No. 6 (feed also contained 0.01 mN of HEPES)	66% sand mixed with 33% industrial-grade iron powder	0.18 0.27 0.35 0.43 0.65 0.96 1.16 1.8 2.25	20% 15% 19% 15% 17% 30% 21% 20% 20%	90% 92% 97% 98% 99% 99% 99% 99% 99%
Column Study No. 7	66% sand mixed with 33% industrial-grade iron powder	0.14 0.21 0.28 0.36 0.53 0.67 1.12 1.45 8 8.2	11% 10% 9% 10% 12% 11% 19% 24% 55% 64%	15% 17% 18% 18% 23% 21% 46% 50% 98% 96%
Column Study No. 8	66% sand mixed with 33% rusted iron powder	0.28 0.5 0.7 1.1 1.3 7.5 7.5	10% 14% 10% 10% 11% 93% 88%	77% 82% 97% 99% 99% 99% 99%

Figure 1. Column reactor setup.

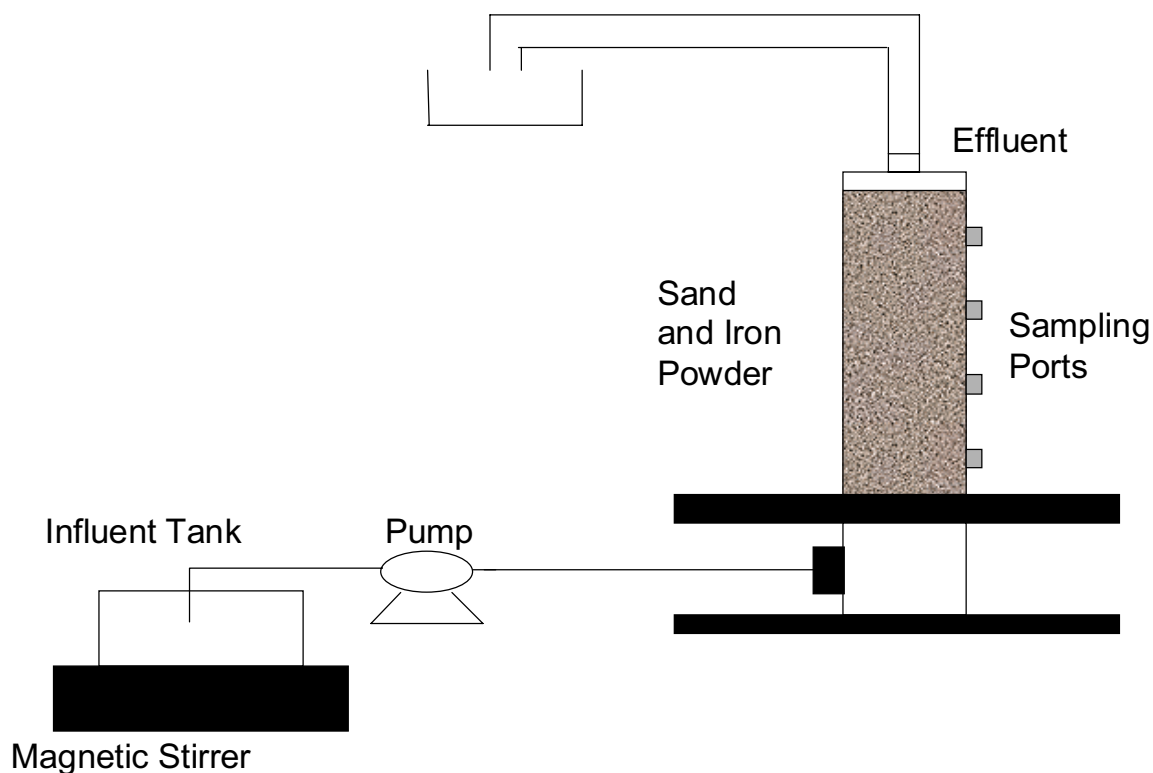


Figure 2. Results from batch studies conducted with industrial-grade iron powder, rusted industrial-grade iron powder, and lab-grade iron powder.

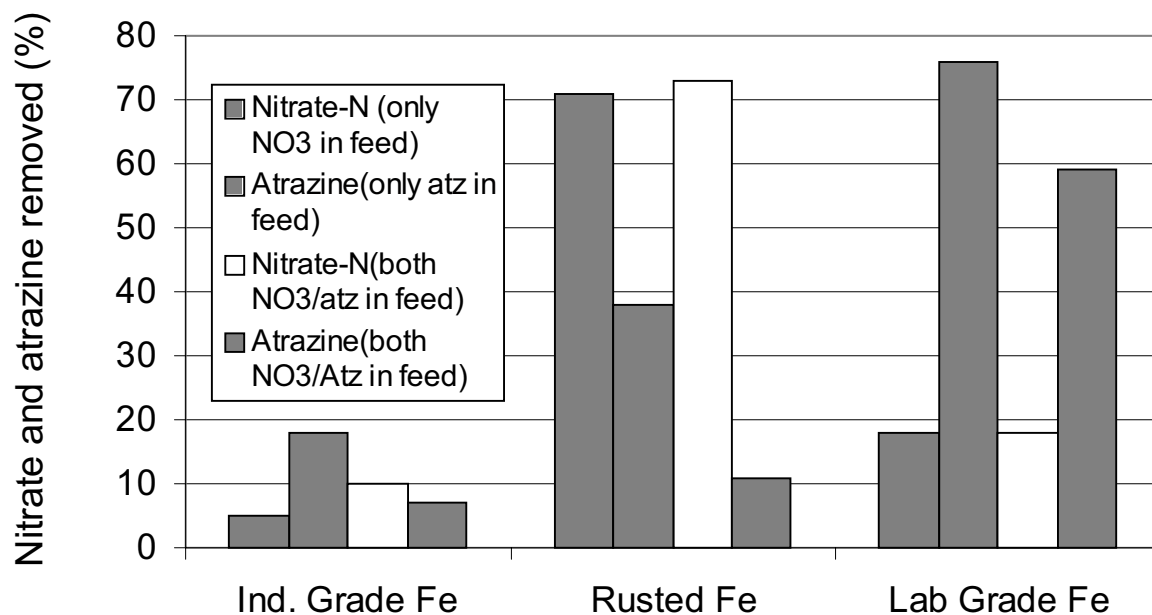


Figure 3. pH results from batch studies conducted with industrial-grade iron powder, rusted industrial-grade iron powder, and lab-grade iron powder.

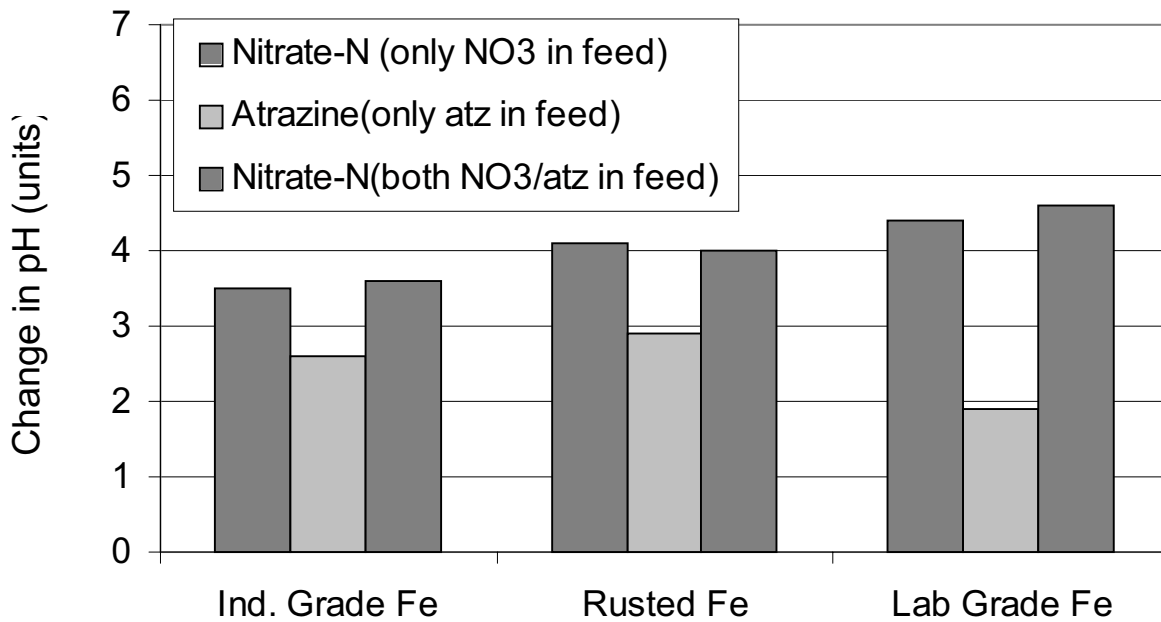


Figure 4. Atrazine removals in column reactors with industrial-grade and rusted industrial-grade iron powder.

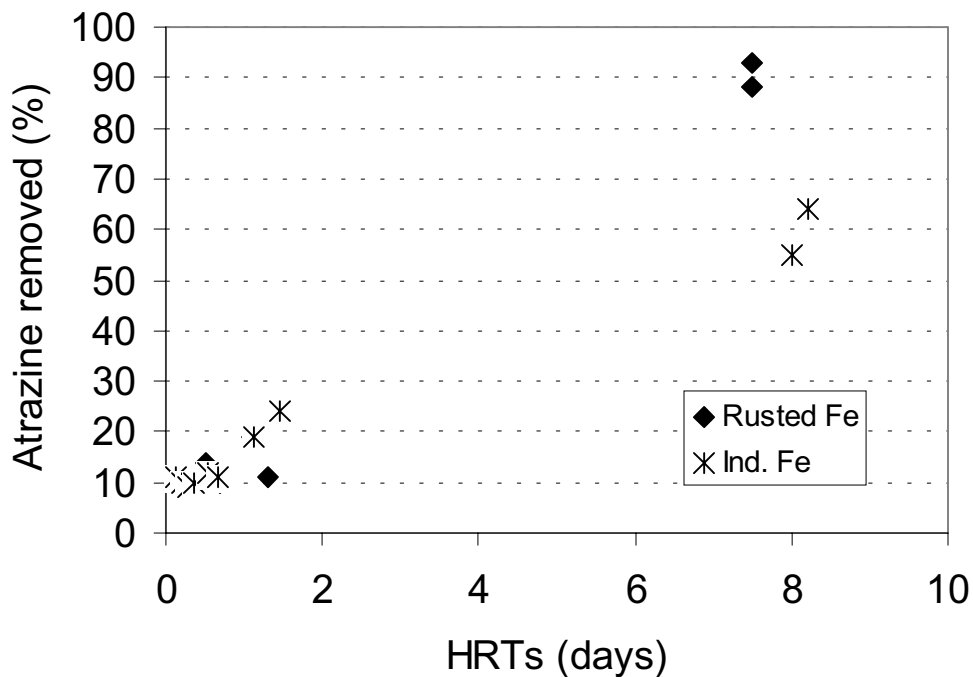


Figure 5. Nitrate removals in column reactors with industrial-grade and rusted industrial-grade iron powder.

