SEPTIC TANK EFFLUENT DENITRIFICATION WITH SULFUR/LIMESTONE PROCESSES

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ABSTRACT

Septic tanks are the second largest source of groundwater nitrate contamination in Nebraska. In this study, the feasibility of coupling a conventional lateral field with a sulfur/limestone layer to treat nitrate in septic tank effluent was investigated using column reactors to simulate the septic tank soil adsorption system. The effects of different hydraulic loading rates, nitrogen loading rates, the depth of sulfur/limestone layers, and the ratio of sulfur/limestone to gravel on reactors' performance were investigated. The profiles of ammonium, nitrite, nitrate, sulfate, calcium, and other parameters along the depth of the reactors were measured. Significant nitrification was observed in the sand layer. Significant denitrification, sulfate production, and hardness production were observed in the sulfur/limestone layer. The results showed the sulfur/limestone method was very effective in denitrification, while the high concentration of sulfate and hardness and the existence of sulfide in effluent might be limiting factors in its application.

Key words: septic tank, nitrate, denitrification, sulfur/limestone method, groundwater

INTRODUCTION

Nitrate contamination in groundwater has become an increasingly serious problem in the U.S., especially in agriculture-oriented states such as Nebraska. Septic tank systems are the most common form of on-site wastewater management systems. However, a septic tank system usually fails to treat nitrate and other contaminants, which makes septic tank systems the second largest source of nitrate contamination in groundwater. In Nebraska, approximately 30% of wastewater is treated by septic tank systems. According to the Nebraska Department of Environmental Quality (NDEQ), about 40% of these septic systems are contaminating groundwater with nitrate and other contaminants. Thus, it's imperative to remove nitrate from septic tank system effluent.

One of the most efficient methods to treat nitrate is the biological denitrification process, including both heterotrophic and autotrophic denitrification. Heterotrophic biological denitrification is effective in nitrate removal as long as there is sufficient external organic carbon to support heterotrophic bacteria for growth. However, in septic tank systems, external organic carbon, such as BOD or COD, is usually degraded very efficiently in the conventional lateral field, and nitrification also occurs very efficiently at the same time in the lateral field. Therefore, there is not enough external organic carbon source to facilitate heterotrophic denitrification occurring, leaving nitrate to leach through the septic tank systems.

In the past, researchers tried several alternatives to provide external carbon sources to facilitate the efficient occurance heterotrophic denitrification. The "peat" system utilized a layer of sphagnum peat moss below the weeping tile bed (Brooks et al., 1984). The "Ruuk" system (Laak, 1981) mixed gray water with treated black water to provide an external carbon source. The

recirculating sand filter system (Piluk and Hao, 1989) returned a portion of the treated wastewater to the soil adsorption system. However, these methods only achieved partial nitrogen removal (40-90%).

The objectives of this study are (1) to investigate the feasibility of coupling a sulfur/limestone autotrophic denitrification (SLAD) layer with a conventional lateral field to treat nitrate in septic tank effluent; and (2) to evaluate effects of different operational conditions and parameters on the reactors' performance.

The SLAD process utilizes autotrophic denitrificans (*Thiobacillus denitrificans*, and *Thiomicrospira denitrificans*) to reduce nitrate to nitrogen gas. These denitrificans can use inorganic carbon compounds (i.e., CO_2, HCO_3^-) as their carbon source, nitrate as the electron acceptor, and elemental sulfur as the electron donor. The stoichiometric equation of sulfur-based autotrophic denitrificans is as follows (Batchelor and Lawrence, 1978a, 1978b):

$$55\ S + 20\ CO_2 + 50\ NO_3^- + 38\ H_2O + 4\ NH_4^+ \rightarrow 25\ N_2 + 4\ C_5H_7NO_2 + 55\ SO_4^{2-} + 64\ H^+ \qquad (1)$$
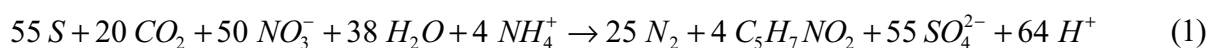
Since hydrogen ions are produced in this reaction, limestone needs to be introduced to provide alkalinity to maintain a neutral pH environment for the system.

In a septic tank system, the lateral field (the soil absorption system or the drain field) is the key component for nitrate removal. To improve nitrate removal efficiencies, a layer of sulfur/limestone (S/L) was introduced underneath the sand layer. COD removal and nitrification take place in the sand layer, as in the conventional lateral field. After nitrification, the nitrate produced will enter the SLAD layer, where denitrification takes place.

MATERIAL AND METHODS

System

Four packed-bed columns, 8 in. in diameter and 4 ft. in height, were built to simulate the lateral field (Figure 1). Each column was filled, from bottom to top, with 2 in. of soil, different heights of S/L, different heights of sand, 6 in. of gravel, and 4 in. of top soil. Different heights of S/L layers and sand layers were designed to study the optimal depth of each layer (Table 1).

The S/L layers in columns #2, #3, and #4 were completely filled with S/L. After five months of operation, column #3 was refilled with S/L (50% v/v) and gravel (50% v/v) mixture. This was designed to reduce the system capital cost because sulfur stone ($16/ton) is more expensive than gravel. Column #4 was refilled with pure sand as a control column. In this paper, we call them columns #5 and #6, respectively. The ratio of sulfur to limestone was 3:1 (volume : volume) in all the S/L layers.

The hydraulic loading rate of column #1 was the EPA standard for the septic tank system. To study the clogging effects, the hydraulic loading rates of other columns were five times larger than the EPA standard to speed up the system deterioration (Table 1).

The feed solution (raw wastewater) used in this study was the effluent from a primary sedimentation tank in a local wastewater treatment plant. Raw wastewater was pumped into the top of the gravel layer of each column, i.e., beneath the top soil cover, and then dripped down. To prevent air from penetrating into the column through the end of discharge ports, a triangle bottle was used to prevent oxygen from penetrating into the columns.

The pump used in this study was a Cole-Parmer MasterFlex pump. To simulate the influent loading peaks of a real septic tank system, a digital timer was used so that the pump ran only during the following time periods: 4:00 a.m. - 4:30 a.m., 7:00 a.m. -7:30 a.m., 10 a.m. – 11 a.m., 4:00 p.m. - 4:30 p.m., 7:00 p.m. - 7:30 p.m., and 10 p.m. – 11 p.m. (total running time: 4 hr. per day). The peak loading at 10 a.m. and 10 p.m. was used to simulate the morning and evening peak of water usage.

Sampling methods

Influent samples were taken from the raw water tank. Effluent samples were collected directly from the bottom of the columns. Sampling points were set every half-foot along the columns. Dry paper towels were put into the sampling points and taken out after 1 - 2 hours. Water in the paper towel was then squeezed out and filtered through a 0.45 μm filter membrane for analysis. Control tests showed no significant interference in analytical results was introduced by using paper towels as the sampling media.

When testing the columns, 2 - 4 sets of samples were taken in each column. The median values are presented in this paper. Average data are not used because the influent of each set might vary. However, the similarity among all the data sets of each column suggests the validity of data.

Analytical methods

A Dionex 500 IC/HPLC, equipped with an AS12A anion column or a CS14A cation column and a CD20 conductivity detector, was used to analyze NO_2^-, NO_3^-, NH_4^+, SO_4^{2-}, and Ca^{2+} of all the samples. Alkalinity, S^{2-}, COD, and pH were analyzed for influent and effluent samples. Alkalinity and S^{2-} were analyzed by the Standard Method (APHA et al., 1992). COD was analyzed by the HACH method (HACH, 1992). pH was measured using a Jenco pH electrode.

RESULTS AND DISCUSSION

COD and nitrogen removal

The influent COD was about 300 mg/L, and all effluent CODs were lower than 30 mg/L after one week of operation. The influent nitrogen was 30 - 50 mg/L as total nitrogen (TN). During the first month, there were times when the NO_3^- and NO_2^- concentrations in effluent were high (5 mg N/ L and 0.7 mg N/L, respectively). After that, the effluent NO_2^- remained lower than the detection limit (0.1 mg N /L); the effluent NO_3^- never exceeded 1 mg N/L; and the effluent NH_4^+ was always

lower than 4 mg N /L. The total nitrogen removal efficiency was > 90%. The control column only achieved about 50% nitrate removal, with the effluent nitrate concentrations of 15 - 20 mg/L (Figure 2).

Nitrification and denitrification

Nitrification is the process in which NH_4^+ is oxidized to NO_3^-. NO_2^- is an intermediate of the reaction. As shown in Figures 3 to 5, as wastewater flowed down the sand layers of the columns, NH_4^+ concentrations gradually decreased, while NO_3^- concentrations increased, suggesting that nitrification occurred in the sand layer. However, NH_4^+ concentrations could not be reduced to zero. They remained at about 2-3 mg N/L, and even increased a little bit in S/L layers. This may be caused by the anaerobic environment, or by the biological metabolism of denitrificans in the S/L layer.

Figure 4 shows two nitrite peaks along the columns. The first peak is due to nitrification, while the second is due to denitrification. Figures 4 and 5 indicate that significant denitrification did occur in the S/L layer. However, one should note that, in Figure 5, the nitrate concentration always reached its peaks before the interface of the sand layer and S/L layer, indicating that heterotrophic denitrification might also occur near the end of the sand layer.

To study the effects of initial NH_4^+ concentrations on the performance of the columns, different NH_4^+ concentration was introduced by spiking NH_4Cl in the raw wastewater. Figure 6 shows that when the initial NH_4^+ concentration was low, the sand layer could oxidize most of the NH_4^+. But when the sand layer could not oxidize all of the ammonium, the NH_4^+ concentration would not decrease in the S/L layer. This suggests that no nitrification took place in the S/L layer, which might have been caused by the anaerobic environment in the S/L layer. When the spiked NH_4^+ concentration increased to 20 mg N/L, and the corresponding total nitrogen in the raw wastewater was approximately 70 - 80 mg TN/L, the effluent NH_4^+ reached 2.0, 7.5, and 10.5 mg N/L in columns #2, #3, and #4, respectively. This suggests that when the initial total nitrogen is about 70 to 80 mg/L, column #4 with 1-foot of sand layer cannot guarantee the accomplishment of nitrification, while column #2 can still perform very well due to the longer sand layers. Since TN of 80 mg/L is a typical concentration in septic tank effluent, at least two feet of the sand layer is required in the soil adsorption system.

Fed with all the initial NH_4^+ concentrations, column #2, which had only one foot of S/L layer, reached almost total denitrification. After reaching steady state, the highest NO_2^- concentration in the effluent of column #2 remained much lower than 1 mg/L, usually lower than the detection limit. These results suggested that 1 foot of S/L layer is enough for the initial TN concentration as high as 80 mg TN/L, while the sand layer must have a length of 2 feet to complete nitrification. The standard depth of the lateral field is 2 - 4 feet. Therefore, introduction of a S/L layer underneath the

sand layer will not significantly increase the depth of the septic tank system, and thus, will not increase the construction capital cost significantly.

Column #5, which had 50% gravel in the S/L layer, also achieved a low effluent NO_3^- concentration. Since the sulfur/limestone in column #5 was taken from column #3, it already had biomass on it. Therefore, after only one week, the effluent NO_3^- concentration became 0.1 mg N/L and remained at this level. Other experiments conducted in the authors' research group showed that mixing S/L with up to 67% of gravel could achieve denitrification well (Flere and Zhang, 1998). Thus the sulfur limestone dosage can be greatly reduced to further lower the cost.

Sulfate/sulfide production

In all S/L columns, sulfate production was observed in the first half-foot of the S/L layer (Figure 7), where nitrate removal was also significant. Effluent sulfate ranged from 300 to 400 mg/L except for column #1, which will be discussed later. There was no significant difference in sulfate production among the different columns. No sulfate production was observed in the control column.

In most of the columns, as shown in Figure 7, there was a decrease of sulfate in the deeper part of the S/L layer. Since sulfide production was observed in all of the columns, it was believed that sulfate was reduced into sulfide in the S/L layer by sulfate-reducing bacteria, which utilized the organic carbon released by the endogenous respiration of autotrophic bacteria. Only the effluent sulfide was measured due to the limitation of large quantities of the sample volume. The effluent sulfide ranged from 1.5 to 10 mg/L. There was no significant difference in sulfide production among the different columns. No sulfide production was observed in the control column.

The stoichiometric equation indicates that to reduce every 1 mg of nitrate-N, 7.5 mg of SO_4^{2-} will be produced. In this study, it was found that the ratio of sulfate produced to nitrogen removed ranges from 4.0 to 9.3, with an average of 6.45 (Fig. 8). Considering that sulfide produced might be from sulfate reduction, and assuming that 10 mg/L sulfide was produced in each column, the average ratio of sulfate produced to nitrogen removed becomes 6.98, which is very close to the theoretical value. This suggests that all sulfate produced in columns #2, #3, and #4 (but not including #1) was due to autotrophic denitrification.

There was no difference in sulfate production between columns #2 and #5. Column #2 had a 100% S/L layer, while column #5 had a layer of 50% gravel plus 50% S/L. This is reasonable because the nitrogen-loading rates in both columns were the same, and the removal efficiencies were the same. Thus, the sulfate production should be the same according to the stoichiometric equation.

Calcium production

The calcium increase was observed in all S/L columns (Figure 9), especially in the first half-foot of the S/L layer, where sulfate production was also significant. The calcium came from limestone, which was used to neutralize the hydrogen ions produced in the autotrophic denitrification process. During this reaction, calcium ions are released, increasing the hardness. The effluent hardness ranged from 400 to 600 mg $CaCO_3$/L. No calcium production was observed in the control column.

Based on equation (1) and equation (2),

$$CaCO_3 + 2\,H^+ \rightarrow Ca^{2+} + H_2CO_3 \qquad (2)$$

1 mg N removed will consume 4.57 mg $CaCO_3$ alkalinity. This is equal to 1.82 mg Ca or 4.57 mg $CaCO_3$ hardness. However, the lab data shown in Figure 10 suggests that the ratio of hardness produced to nitrogen removed ranges from 8.0 to 10.3, with an average of 9.50.

Analysis of the system effluent indicated the effluent alkalinity was exclusively made up of bicarbonate and the pH in the SLAD column was between 6 and 8. Thus, what actually happened in the S/L layer should be equation (1) and equation (3):

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^- \qquad (3)$$

The ratio of hardness production to nitrogen removed, based on equations (1) and (3), is 9.14. The average ratio (9.50) obtained in this study is very close to this value, indicating the calcium produced (hardness increase) is majorly due to autotrophic denitrification.

Influence of soil cover

Column #1 had the lowest hydraulic loading rate and the lowest nitrogen removal efficiency. But in the first few months, the effluent sulfate was always higher than 1000 mg/L. This cannot be explained by equation (1). It should be noted that an insufficient COD loading rate was applied to column #1, and therefore, oxygen was not used up in the sand layer and could penetrate into the S/L layer creating an aerobic environment. Therefore, the presence of sulfur-utilizing but non-denitrifying bacteria such as *Thiobacillus thiooxidans* became possible. *Thiobacillus thiooxidans* is an autotrophic acidophilic bacterium that can reduce elemental sulfur and sulfides into sulfates and sulfuric acid under strict aerobic conditions ($S^0 + 1.5\,O_2 + H_2O \rightarrow H_2SO_4$ and $S^{2-} + 2O_2 + 2H^+ \rightarrow H_2SO_4$) on the basis of the sulfur-oxidizing enzyme and sulfite-oxidizing enzyme systems (Suzuki et. al., 1992). The microorganisms can oxidize elemental sulfur at acidic pH or at neutral pH, but favor an acidic pH which allows them to reproduce quickly. However, they can only survive under aerobic conditions. This is why in columns #2, #3, and #4, sulfate was not produced at as high of rates as in column #1, since columns #2 to #4 were under anaerobic conditions.

It was found that the EPA standard for soil cover is 1 to 5 feet, while the soil cover used in column #1 was only 4 inches. To eliminate the effects of *T. thiooxidans* on the SLAD process, a plastic mat was used over the soil cover to prevent air from getting into column #1. After one week, the effluent sulfate dropped to 600 mg/L (Figure 11), indicating oxygen penetration was the cause of the extremely high sulfate production. We can expect that oxygen penetration into the S/L layer will not happen in the field because the soil cover will be much thicker than on the columns used in this study.

pH, alkalinity and sulfur/limestone ratio

The effluent pH was stable, ranging from 6.4 to 7.6. The alkalinity in influent and effluent were 300 - 400 mg $CaCO_3$/L in all S/L columns. This obviously is due to the presence of limestone.

The ratio of sulfur/limestone used in this study was 3:1 (v/v), based on a previous study (Zhang and Lampe, 1997). Liu (1992) used a 1:1 ratio, but she also observed that most of the denitrificans grew on the surface of sulfur stones. She suggested that increasing the portion of sulfur improved the system performance. Previous study in the authors' group showed no difference in nitrate removal between SLAD systems with different S/L ratios (1:1, 2:1, 3:1, 4:1, and 5:1). Van der Hoek et al. (1992a and 1992b) observed that the consumption ratio of sulfur and limestone was 1:2, and there was no difference in nitrogen removal efficiency among three kinds of ratios (1:2, 1:1, 2:1).

Assume an operational duration of 30 years, and the loading rate, according to the EPA standard, is 32 L/m^2/d. Thus, 350,000 L wastewater will be pumped into one square meter of the SLAD system. Assuming an influent nitrogen concentration of 40 mg N/L, the SLAD system will remove 14 kg nitrate-N in 30 years. According to the stoichiometric equations (1) and (3), 2.5 kg sulfur and 9.14 kg limestone will be consumed to remove 1 kg nitrogen. Therefore, 35 kg sulfur and 128 kg limestone are needed. The specific gravity of $CaCO_3$ is 1.6, and that of S is 1.13. So the volume of sulfur is 40 liter and limestone 80 liter, which is a 1:2 ratio.

According to this study, a 0.3 m S/L layer is enough for most of the systems. Based on a 30 years of consumption, a 0.5 m S/L layer is recommended. This is 500 L/m^2. Using a safety factor of 2, about 250 liters of S/L is needed every square meter. Another 250 liters can be filled with gravel. This is a mixture of 50% gravel and 50% 1:2 S/L. which could achieve denitrification successfully, as proved by column #5 results.

CONCLUSIONS

(1) The SLAD system, combined with the soil absorption system, can remove nitrate from septic tank effluent effectively. It is a low-cost, low-maintenance system that can be easily used in small community wastewater treatment facilities. (2) Nitrification occurs mainly in the sand layer. Denitrification happens in the S/L layer. The depth of these two layers should be greater than 2 feet

and 1 foot, respectively. (3) High concentrations of sulfate and hardness, and a certain amount of sulfide, are produced in the process. This may become a concern. However, since the effluent was discharged into groundwater, hardness and sulfate should not be a serious problem. (4) The soil cover is very important in preventing air from entering the S/L layer. (5) The appropriate S/L layer can consist of 50% gravel, 16% sulfur, and 34% limestone. This calculation is based on a 30-year operational period.

ACKNOWLEDGEMENTS

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Table 1. Differences between columns.

Reactor	Sand Layer (ft)	Sulfur/Limestone (ft)	Surface Loading Rate (L/m²/d)	S/L Ration in S/L Layer (%)
#1	1.5	1.5	32	100
#2	2	1	160	100
#3	1.5	1.5	160	100
#4	1.5	2	160	100
#5	2	1	160	50
#6	3	0	160	100

Figure 1. Lab system layout.
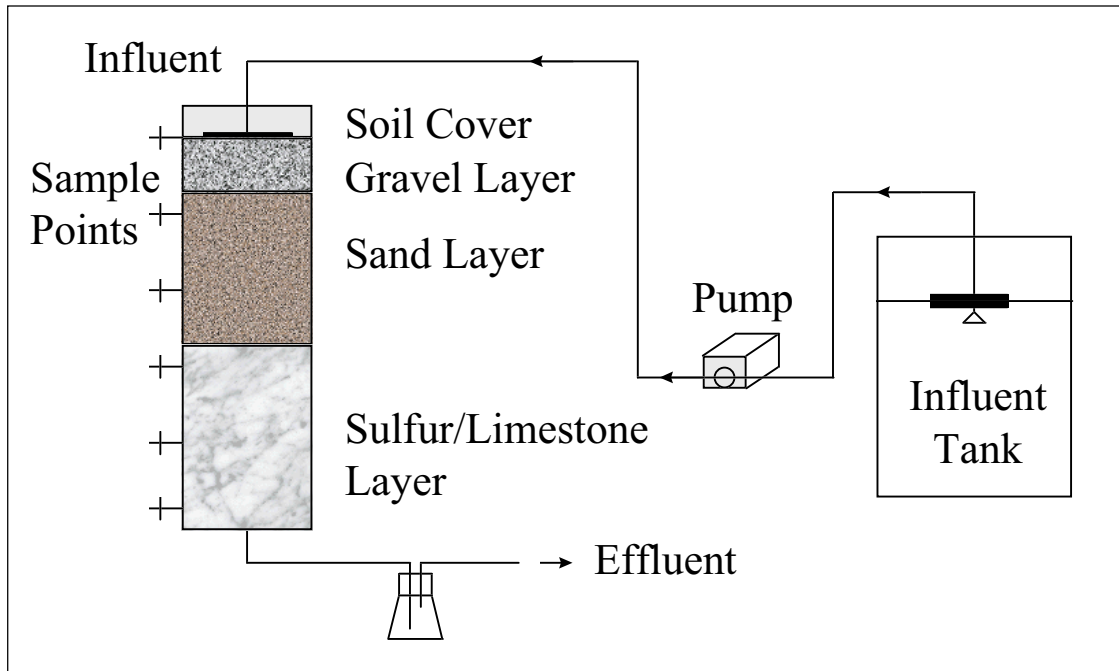
Figure 2. Time courses of nitrogen removal. Reactors #5 and #6 were run 5 months after other columns. Introducing the data of these two reactors in this figure is for the purpose of comparison.
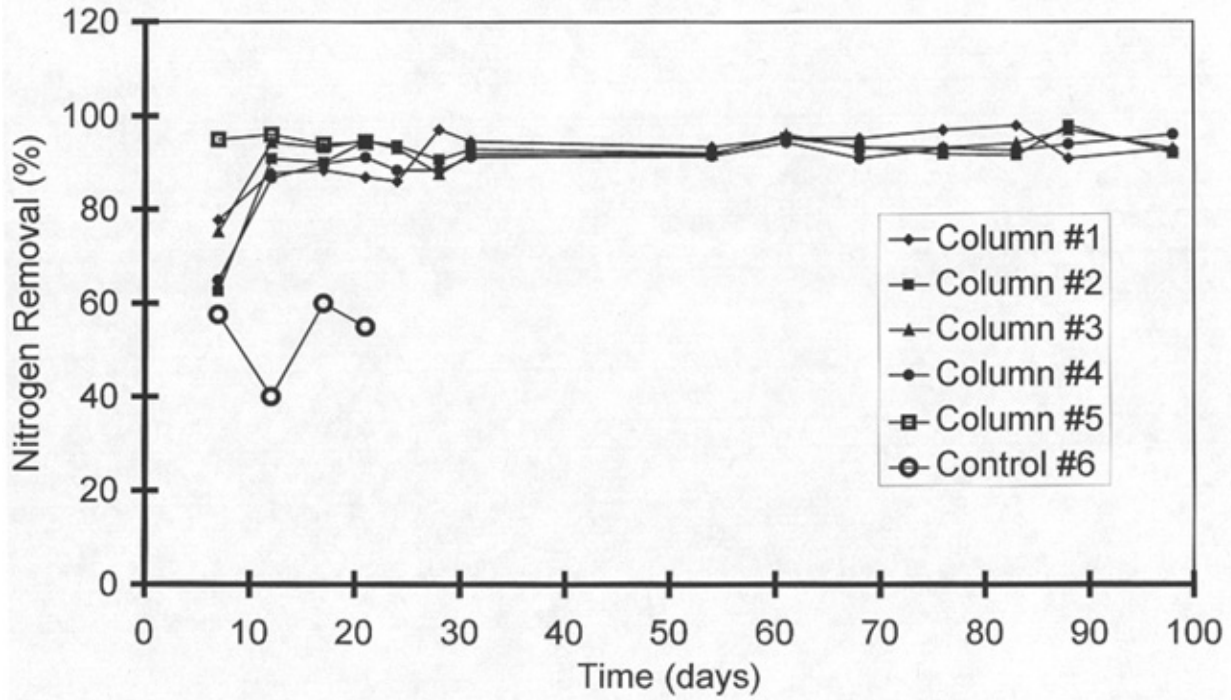
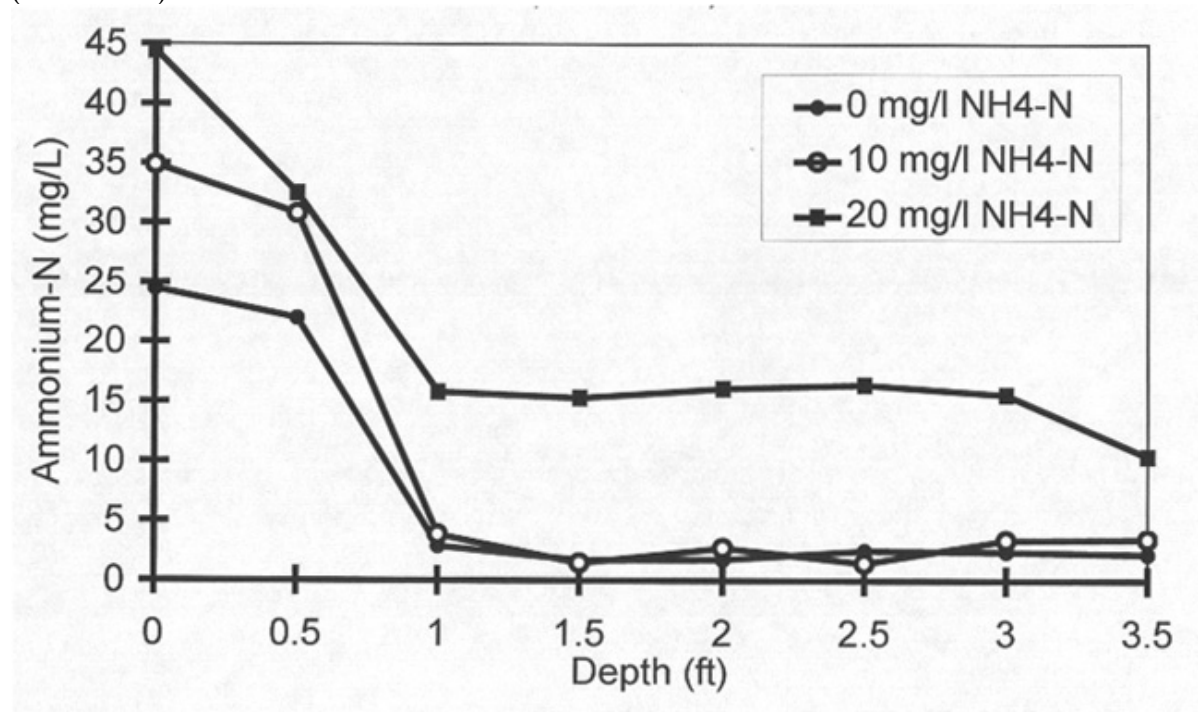**Figure 3.** Ammonium-N profiles along columns. Arrows indicate the interfaces of the sand layer and the SLAD layer.
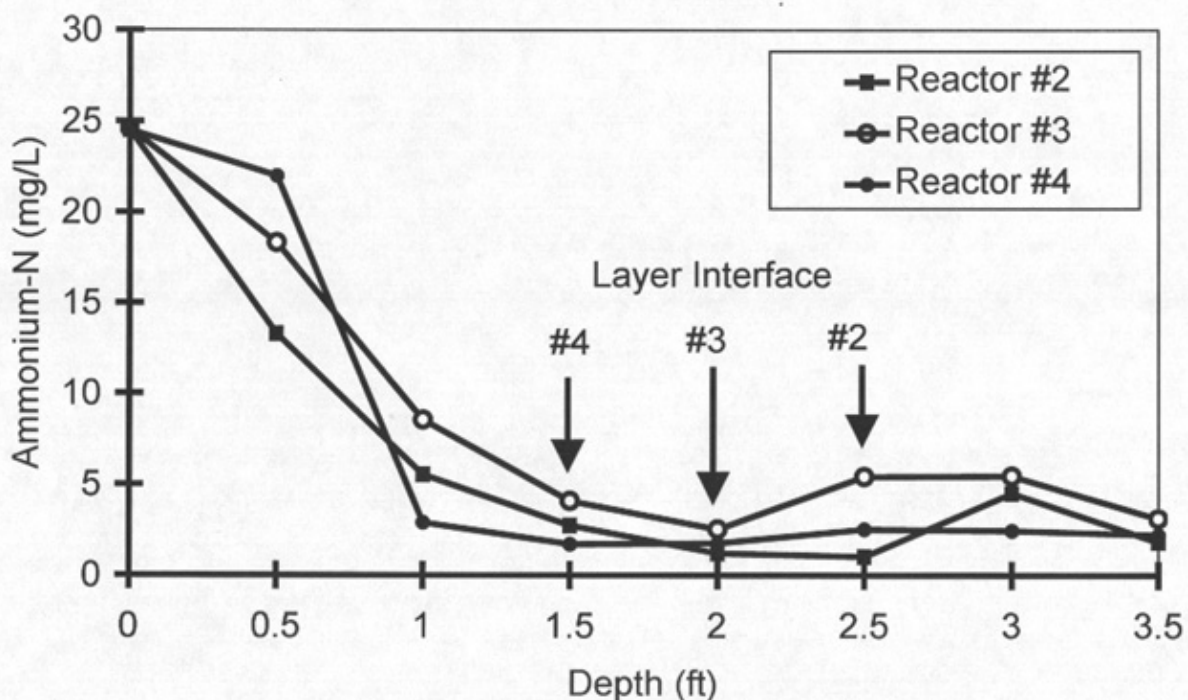
Figure 4. Nitrite-N profiles along columns. Arrows indicate the interfaces of the sand layer and the SLAD layer.
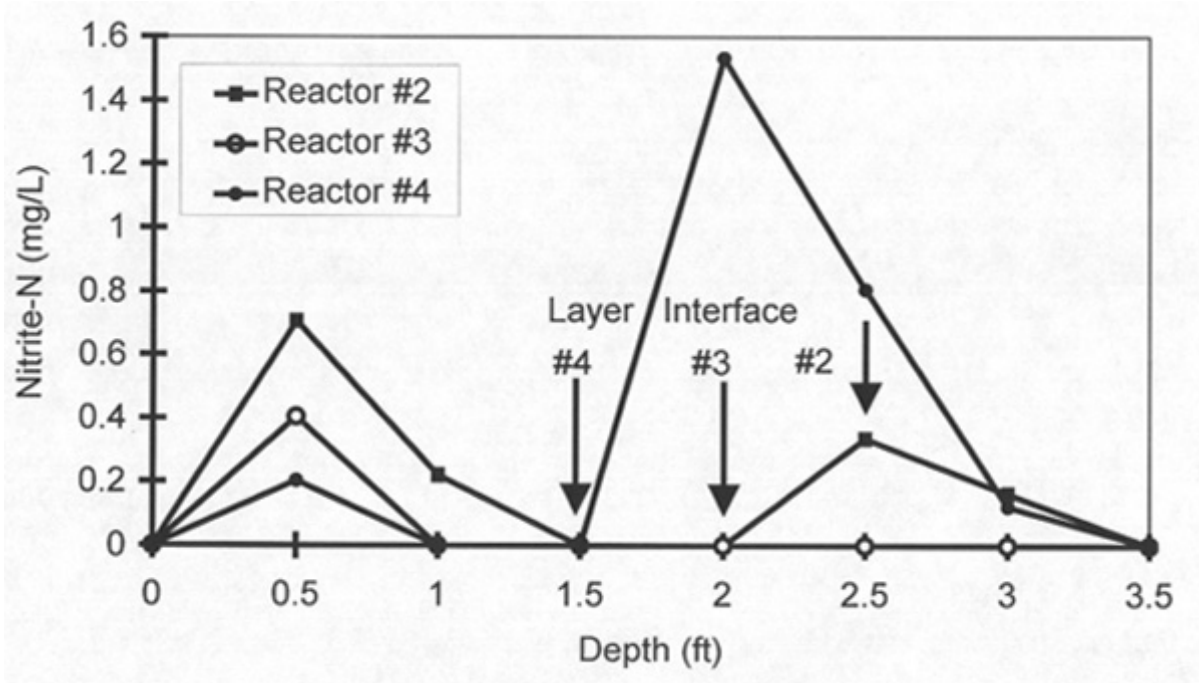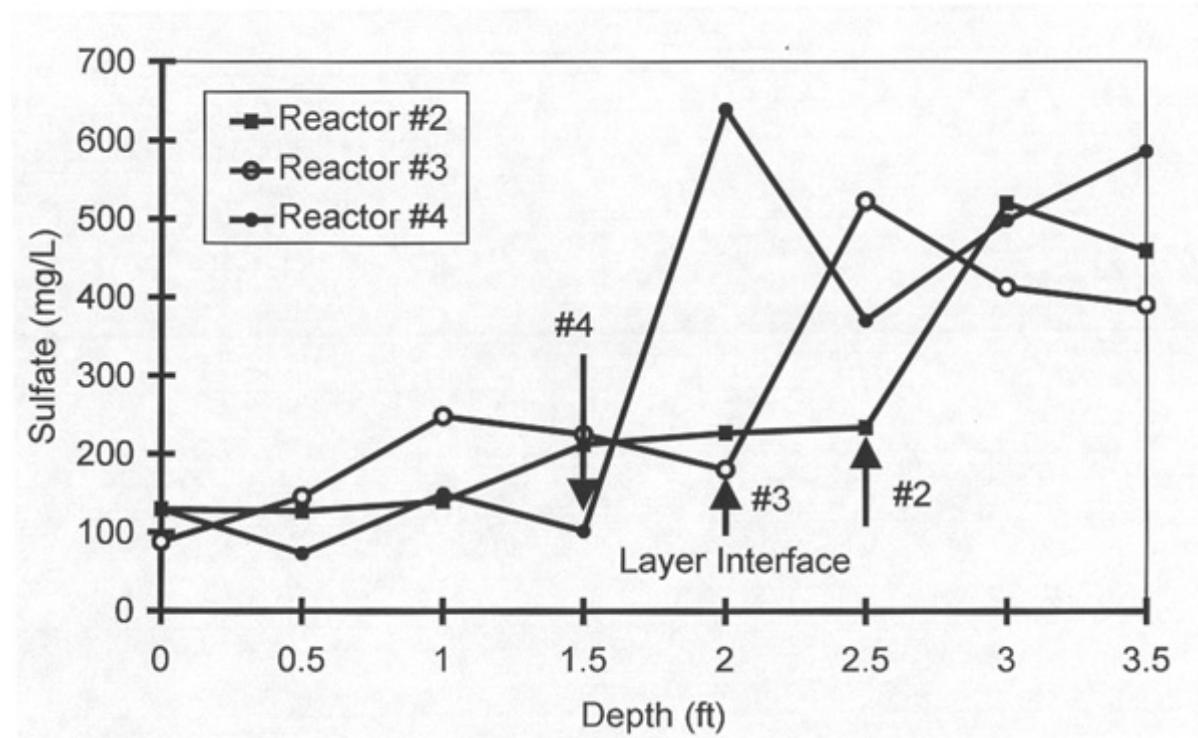

Figure 5. Nitrate-N profiles along columns. Arrows indicate the interfaces of the sand layer and the SLAD layer.
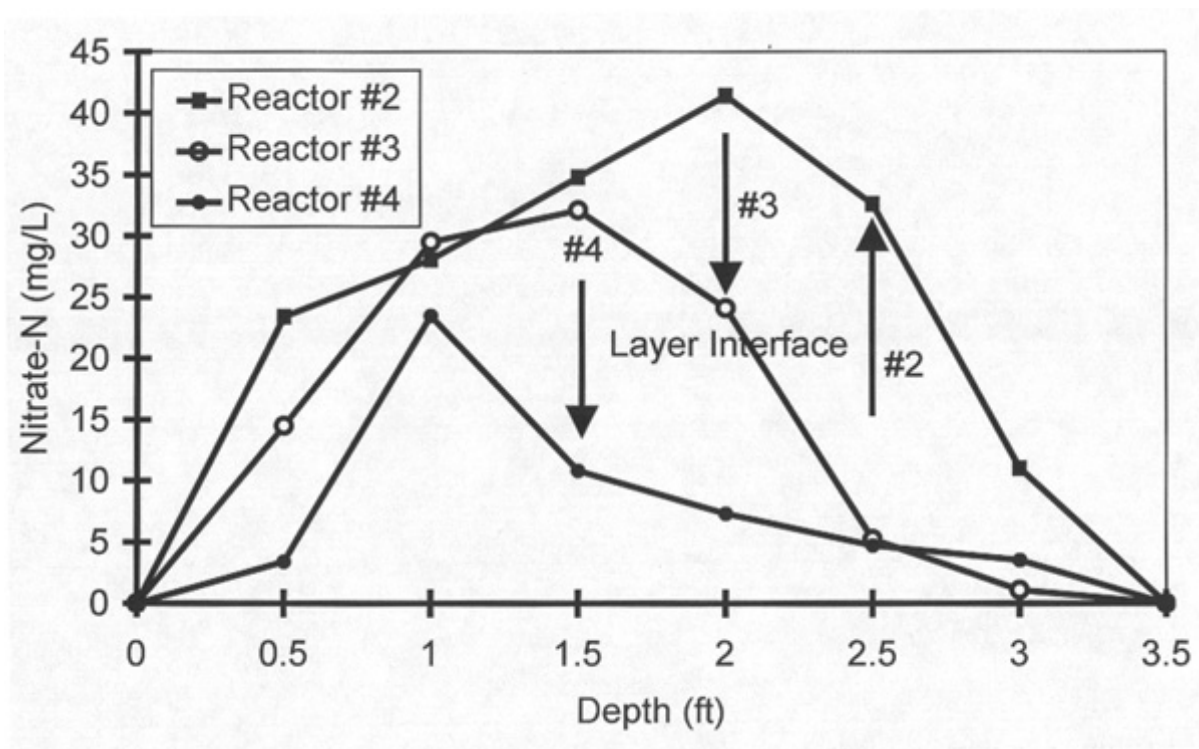
Figure 6. Effect of initial ammonium-N concentrations (ammonium-N in the raw water plus NH$_4$Cl spiked) on ammonium-N profiles. The interface of the sand layer and the SLAD layer is at 1.5 ft (Reactor #4).
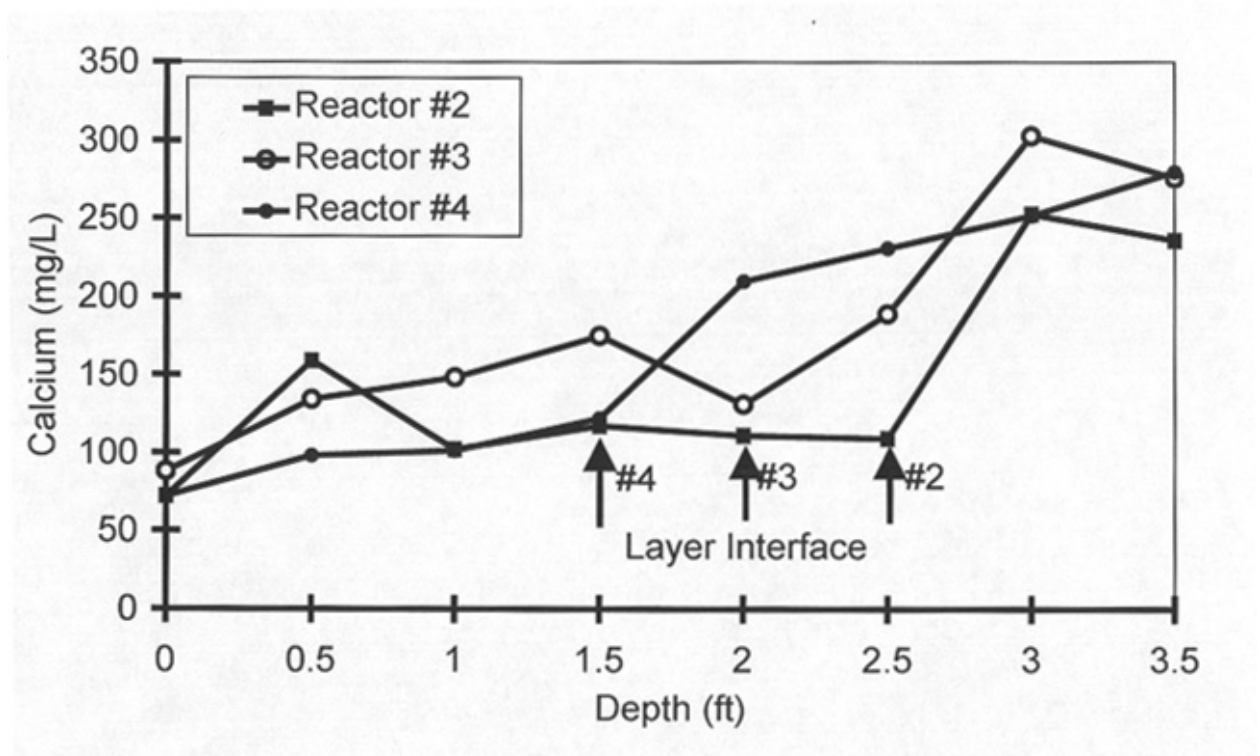

Figure 7. Sulfate profiles along columns. Arrows indicate the interfaces of the sand layer and the SLAD layer.
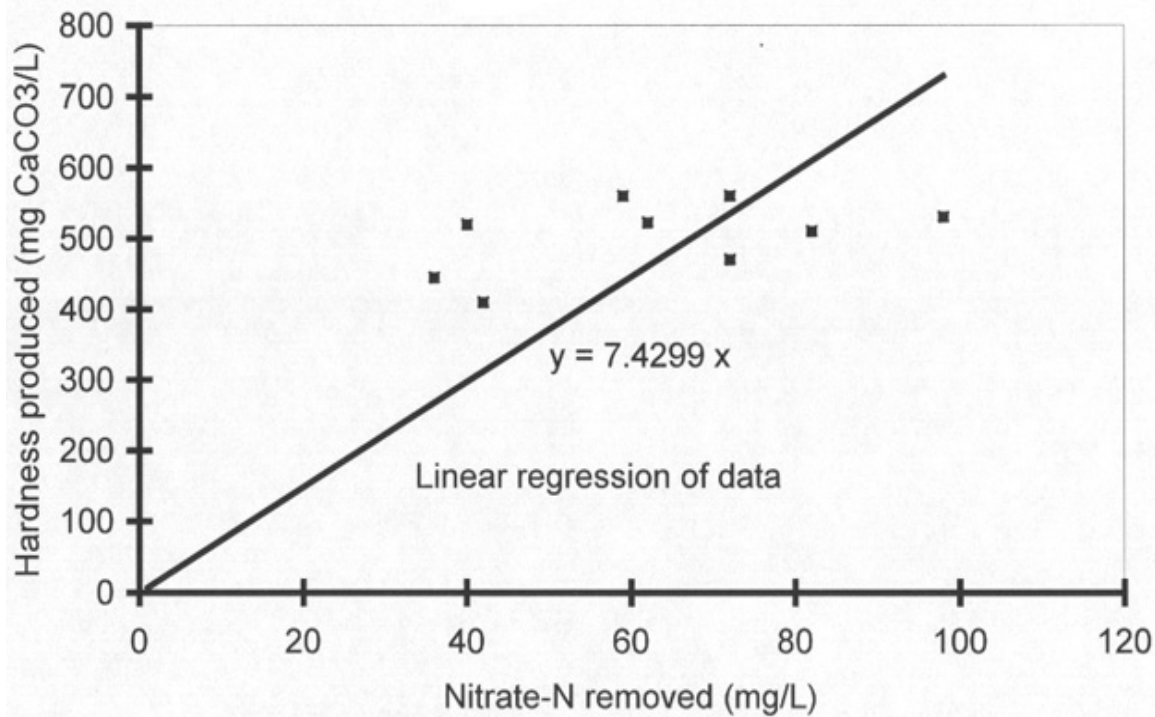
Figure 8. Relationship between sulfate produced and nitrogen removed.

$$y = 5.6164\,x$$

Linear regression of data
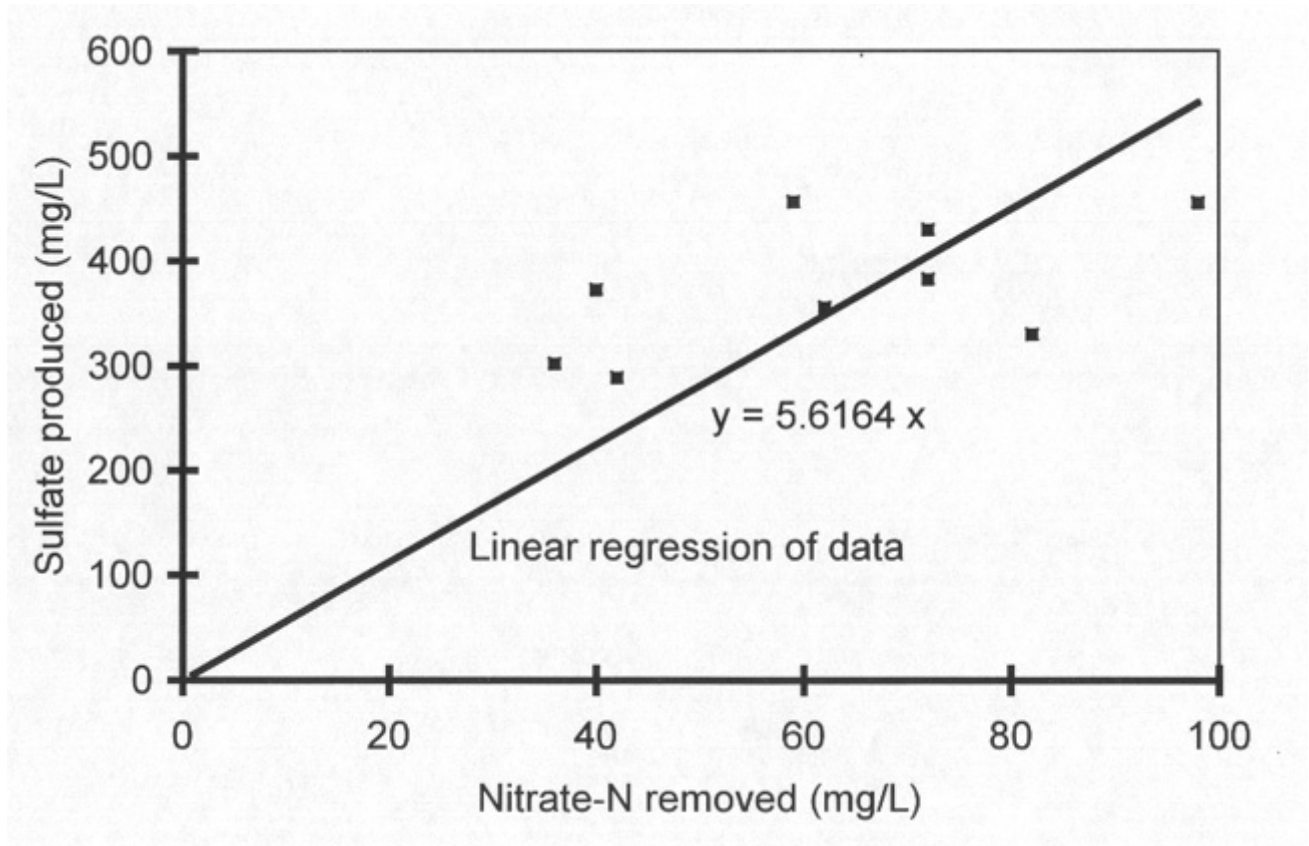
Figure 9. Calcium profiles along columns. Arrows indicate the interfaces of the sand layer and the SLAD layer.

Figure 10. Relationship between hardness produced and nitrogen removed.

Figure 11. Sulfate in column #1 effluent. Arrow indicates the day the plastic mat was added.