Nitrate removal from waste rock drainage with denitrifying bioreactors at the Kiruna iron ore mine

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Abstract

The ultimate source of most nitrogen in mine drainage is the ammonium nitrate – based explosives used in the excavation of the mine. This study reports on the performance of a full-scale woodchip denitrifying bioreactor installed for nitrate removal at LKAB's iron ore mine in Kiruna, Sweden. In the bioreactor, nitrate removal was at a rate of 70–80% during the first year (2018–2019) but decreased to 28% by 2021. The decrease in treatment efficiency with time is believed to be controlled at least partially by the low water temperature (average 3 °C) and a decrease in available organic carbon for denitrification.

Keywords: Bioreactor, woodchip, denitrification, passive treatment, bioremediation

Introduction

The ultimate source of most nitrogen in mine drainage is the ammonium nitrate-based explosives used in the excavation of the mine. Waste rock often contains adsorbed nitrogen compounds (nitrate and ammonium) that are residues from the detonation of the explosives. The percolation of rain and snowmelt through the deposits will leach the nitrogen compounds from waste rock, potentially contaminating groundwater and surface water recipients. The effect of nitrogen releases on aquatic ecosystems is commonly associated with either eutrophication or oxygen consumption by ammonium (NH_4^+) oxidation. However, ecosystem effects may also be associated with the toxicity of nonionized ammonia (NH_3) to aquatic organisms (Canadian Council of Ministers of the Environment 2010).

The potentially adverse effects of nitrogen releases on aquatic ecosystems in northern Sweden have prompted the development of treatment methods for NO_3^- removal, the predominant nitrogen form in most mine waters. Woodchip bioreactors have been designed and developed for NO_3^- removal through denitrification (Nordström & Herbert 2018; Nordström et al. 2021). Denitrification is a microbial process that requires anoxic conditions and organic matter, which serves as both a carbon and energy source for denitrifying bacteria. The overall reaction for denitrification is provided in reaction 1, indicating the consumption of organic matter ("CH_2O") and the production of bicarbonate (HCO_3^-), carbonic acid (H_2CO_3) and nitrogen gas (N_2). The reaction is hence net alkalinity-producing.

$$4NO_3^- + 5CH_2O \rightarrow 2N_2(g) + 4HCO_3^- + H_2CO_3 + 2H_2O \quad (1)$$

While reaction 1 is the overall reaction, the removal of NO^{3-} by denitrification is a sequential process producing partially-reduced nitrogen species in the following sequence:

$$NO_3^- \rightarrow NO_2\text{-} \rightarrow NO \rightarrow N_2O(g) \rightarrow N_2(g) \quad (2)$$

This is relevant as the intermediate compounds are generally undesirable by-products of incomplete denitrification. For example, the incomplete reduction of NO_3^- to nitrite (NO_2^-) provides only temporary removal of NO_3^-, since NO_2^- will re-oxidize to NO_3^- in the presence of oxygen. Also, nitrous oxide (N_2O) is a potent greenhouse gas.

This study reports on the performance of a full-scale woodchip denitrifying bioreactor installed for nitrogen removal from waste rock drainage at LKAB's iron ore mine in Kiruna, Sweden. Samples and analyses for the period 2018–2021 are presented, with the primary focus on nitrogen removal.

Methods

Bioreactor construction and mine drainage collection

In 2018, three woodchip bioreactors were installed at the Kiruna site for treating nitrate-rich waste rock drainage from the "Triangle area" waste rock pile. The three bioreactors were positioned at the northeast apex of the waste rock pile, which was triangular in shape when viewed from above and had a surface area of 0.56 km2. At the time of bioreactor construction, the waste rock dump was still being used for rock disposal, which upon completion would hold ca. 59 million tons waste rock (LKAB, pers. com.). Since the installation of the bioreactors was not considered in the original design of the triangle area waste rock pile, an adequate drainage system was not in place at the time of bioreactor construction that would enable the treatment of all drainage water from the pile. Instead, the bioreactors were designed to intercept only a smaller portion (i.e. 0.5 L/s each, see below) of the entire drainage production from the waste rock pile, which was estimated to 6.4 L/s (long-term average).

Drainage water, originally derived from rain and snowmelt that percolated through the waste rock pile, flowed into the underlying groundwater, and was collected in a subsurface reservoir at the base of the waste rock pile. The reservoir had a total volume of ca. 390 m^3, was filled with crushed rock (diameter 100–200 mm) and insulated from above to prevent freezing. The drainage-rich groundwater, which had been collected in the reservoir, was pumped from a pumping chamber (1600 mm diameter) to the bioreactors.

The denitrifying bioreactors installed at the Kiruna site consisted of large oblong excavations filled with woodchips. The excavations were approximately 44 m long and 7 m wide at the upper surface, but tapered to a width of 2 m at the base of the excavation, at 2.1 m depth (Fig. 1). These dimensions were selected to provide a theoretical 72-hour hydraulic residence time (HRT; flow 0.5 L/s, porosity 0.56), which was assumed sufficient for an almost complete removal of nitrate (cf. Nordström & Herbert 2017, 2018). The excavation was lined with an impermeable geomembrane (HDPE plastic) and then filled with pine woodchips (approximately 30 × 30 × 10 mm) mixed with a small amount of active sewage sludge (100:1 woodchip:sludge volume ratio).

The large amount of organic material in the bioreactor functioned as a carbon and energy source for the denitrifying bacteria. As denitrifying bacteria require anoxic conditions for performing denitrification, the surface of the bioreactor was covered with 0.4 m soil and inner walls were constructed so that water flow was directed to the deeper sections of the system where there was no contact with atmospheric oxygen. Finally, the bioreactor was covered with 1 m peat for insulation.

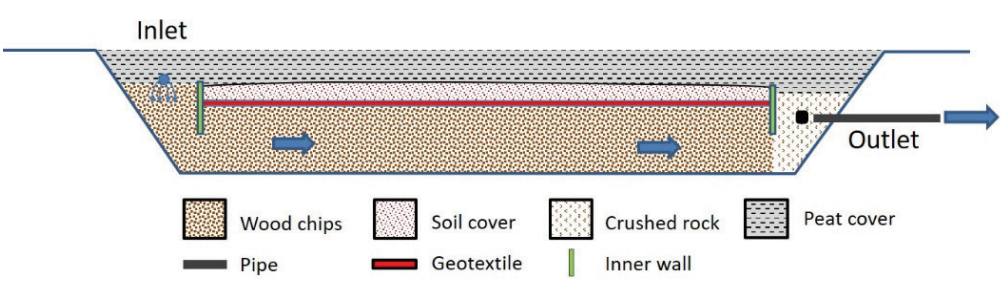

Figure 1 *Generalized cross-section of woodchip bioreactor, with flow direction indicated. The bioreactor surface is 44 m long and the depth is 2.1 m*

Bioreactor monitoring and water sampling

This study focuses on one of the three bioreactors, BR3, since this bioreactor was utilized the most during the period 2018–2021 for water treatment. The outlet of BR3 consisted of a monitoring chamber (1600 mm diameter) that was equipped with an H-flume for water flow measurements. Water depth in the H-flume was continuously monitored with an ultrasound sensor; water discharge was then calculated from water depth measurements based on a calibration curve. The automated flow measurements were brought on-line in June 2019, so only manual flow measurements were available prior to this time.

Four thermistors were installed in the woodchips of BR3, but only two of these will be discussed in this study: thermistor T1 was installed at a distance of ca. 8 m from the inlet and thermistor T4 was installed at ca. 34 m from the inlet. Both were situated 0.5 m above the base of the bioreactor.

Nitrogen removal from BR3 and general water chemistry was monitored by sampling water from the pumping chamber, which was considered representative of the water quality at the bioreactor inlet, and in the monitoring chamber at the outlet of BR3. Water samples were generally collected twice per week during 2018 – 2019 and once per week during 2020 – 2021. In general, no sampling occurred from October until April – May of the following year, due to the inaccessibility of the field site under heavy snow conditions. All water samples were analyzed by LKAB, which has an accredited laboratory for chemical analyses.

Bioreactor operations

In general, waste rock drainage was continuously pumped to bioreactor BR3 during 2018 – 2021, with the exception of a period of no flow between February and May 2021 and a number of brief periods of pump malfunction.

Results and Discussion

To evaluate the effectiveness of woodchip bioreactor BR3, the temperature and water flows at which the system was operated are first discussed. Nitrate removal in BR3 is then presented, along with data on several other compounds. Finally, overall bioreactor performance and application of technology at different field sites are discussed.

Water flow and temperature

During the period September 2018 – December 2021, the porewater temperature in BR3 generally varied between 0.5 and 6 °C with an average temperature of 3.3 °C (see Fig. 2a). The lowest temperatures were always measured in late spring with the occurrence of snowmelt; since BR3 had a permeable surface, snowmelt infiltrated into the bioreactor during this period and temporarily resulted in temperatures < 1 °C. For 2020 and 2021, inlet water temperatures during the summer months were generally greater than temperatures in BR3. Hence, temperature time series (Fig. 2a) indicated that the inlet water lost its heat to the bioreactor during the summer months (i.e. temperature at T4 was less than at T1) while the heat in the bioreactor was transferred to the inlet water during the fall months (i.e. temperature in T4 was greater than at T1).

Water flow though BR3 varied from 0 to ca. 1.4 L/s during the period 2019–2021, with a mean flow of 0.29 L/s (see Fig. 2b). This mean flow corresponds to a theoretical HRT of 5.1 d. For the individual years 2019, 2020 and 2021, the mean flows were 0.24, 0.36, and 0.28 L/s, respectively. The greatest flows were measured in conjunction with snowmelt, since melting snow infiltrated uncontrollably into BR3 providing flows in excess of the design flow (0.5 L/s). In general, flow rates were maintained at levels below the design flow since complete nitrate removal was not observed (see below), and a longer HRT was expected to result in better performance.

Inlet water composition

Waste rock drainage from the Triangle area waste rock pile had a neutral pH and an alkalinity of ca. 100 mg/L HCO_3^-, with relatively high Ca and SO_4^{2-} concentrations but low Fe concentrations. As an example, average inlet and outlet concentrations from BR3 during 2019 are presented in Table 1 (general trends are applicable for all years

in period 2018–2021). The concentrations in Table 1 are fairly representative of waste rock drainage at the Kiruna mine and reflect mineral weathering and nitrogen leaching from the waste rock. While little data is available on the specific mineralogy of the Triangle area waste rock pile, the mineral assemblage is expected to be similar to the assemblage observed in the iron ore. The iron ore mineral is magnetite. Major silicate minerals in the Kiruna iron ore are calcic amphibole (actinolite), mica (phlogopite), quartz, and feldspar (albite). Carbonates (i.e. calcite, Fe-bearing dolomite and ankerite) occur as fracture filling, and sulfates and phosphates (gypsum and anhydrite, and apatite and monazite, respectively) are localized as secondary minerals in fractures (Nordstrand 2012). Hence, much of the Ca and SO_4^{2-} in the mine drainage is probably derived from the soluble minerals gypsum and anhydrite. The inlet water is consistently undersaturated with respect to gypsum ($CaSO_4{\cdot}2H_2O$; saturation index ca. −0.4), indicating that gypsum equilibrium is not controlling the solubility of Ca and SO_4^{2-}.

Water sampling indicated that nitrogen concentrations in the inlet water to the three bioreactors varied from 10 to 110 mg/L nitrate-nitrogen (NO_3^--N) during 2018–2023 (see Fig. 2c), with the lower concentrations occurring during periods of flushing after intense rainfall and snowmelt. Concentrations of NO_2^--N and NH_4^+-N were generally below the detection limit.

The trend of decreasing nitrogen concentrations in the waste rock drainage (i.e. bioreactor inlet, Fig. 2c) probably reflects waste rock leaching caused by the preceding year's precipitation combined with dilution from the current year's precipitation. For example, 2017 was a particularly wet year (annual precipitation at 126% of long-term average) and 2018 was a very dry year (annual precipitation at 82% of long-term average; 2019 and 2020 were closer to average at 115% and 119%, respectively). Hence, the highest nitrogen concentrations in the time series were observed during 2018.

Outlet water after treatment in BR3

In BR3, denitrification resulted in a decrease in nitrogen concentrations in the drainage water (see Fig. 2c) but rarely completely removed NO_3^--N to under the detection limit. During 2018–2019, there was a relatively high degree of nitrate removal (70–77%; calculated as sum of all N species in outlet divided by NO_3^--N concentration in inlet × 100), even though there was evidence of incomplete denitrification since NO_2^--N was commonly detected at the outlet (Fig. 2c). In general, NH_4^+-N concentrations in the outlet were < 0.3 mg/L. In the subsequent years, NO_3^- removal decreased to 28–55% with only very low NO_2^--N concentrations in the outlet. Nordström et al. (2021) observed a similar change in NO_2^--N concentrations with time in a woodchip bioreactor and attributed this to a shift in the structure of the N-reducing bacterial community over time (i.e. increased

Table 1 *Mean concentrations of major components and some minor components in inlet water and outlet from BR3 during 2019. All concentrations in mg/L except Al, Cu, Fe, Mn, P and Zn which are in µg/L*

** indicates significant difference (P<0.05) between median values of inlet and BR3 concentrations, based on a paired-sample Wilcoxon signed rank test. NO_2^- and NH_4^+ are excluded from the determination of significance since inlet concentrations were below detection limits*

Compound	Inlet	BR3	Compound	Inlet	BR3	Compound	Inlet	BR3
pH*	7.0	7.3	Ca	302	298	Al*	5.3	4.6
Alkalinity[1]*	108	322	K	28	28	Cu*	4.6	0.24
DOC2*	2.9	15.3	Mg	45	44	Fe*	0.006	0.070
SO_4^{2-}	669	654	Na	108	104	Mn*	58	106
Cl^-	102	99	NO_2^--N	<0.015	7.6	P*	4.1	15
NO_3—N*	61	4.5	NH_4^+-N	<0.015	0.36	Zn*	32	4.0

[1]Concentration as mg/L HCO_3^-

[2]Dissolved organic carbon

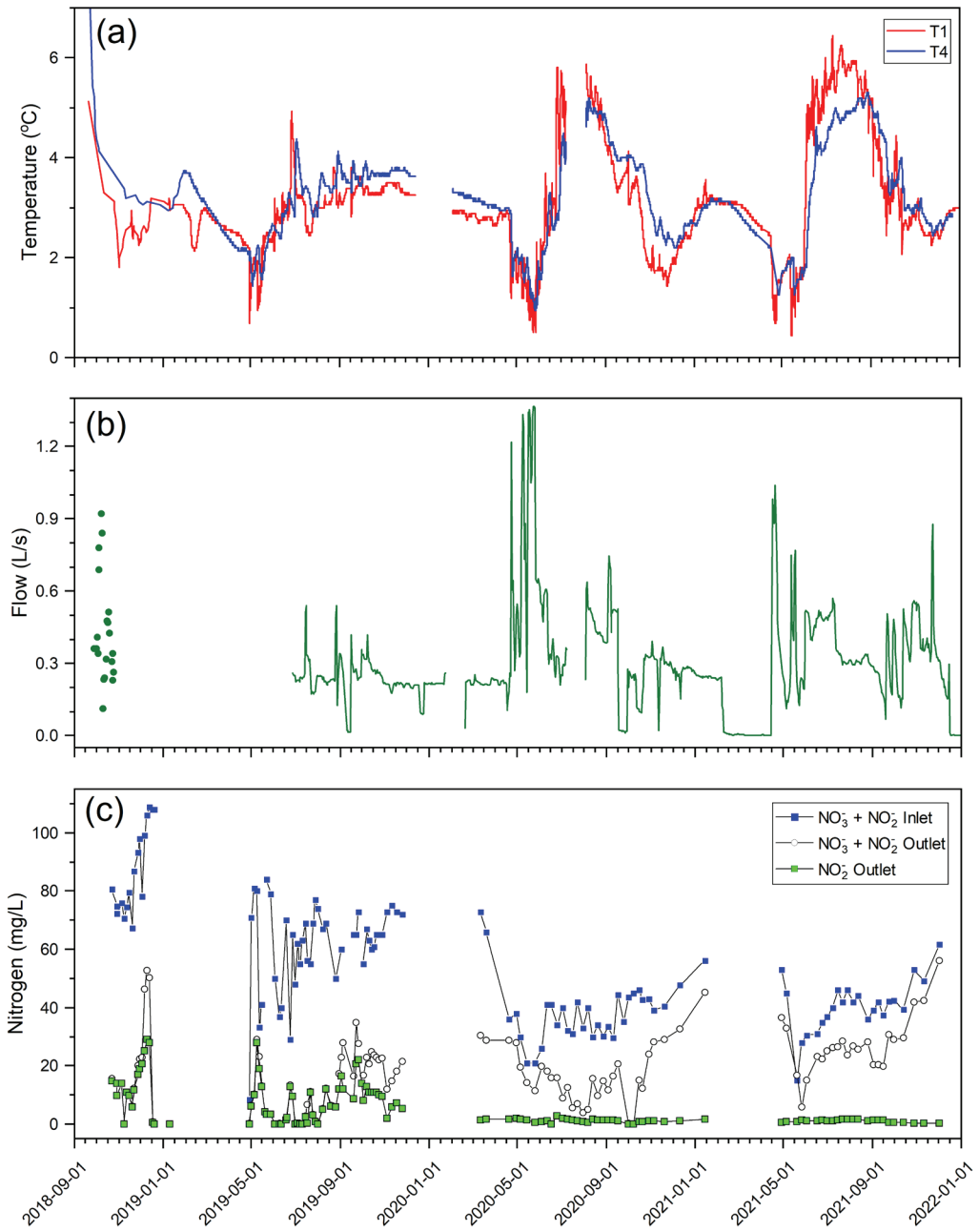

Figure 2 *Monitoring data from woodchip bioreactor BR3 for 2018–2021. (a) Pore water temperature at position T1 (closest inlet) and T4 (closest outlet), (b) average daily water flow from bioreactor, (c) concentrations of nitrogen species at bioreactor inlet and outlet. Automated flow measurements started 2020-06–29; prior to this date, only manual measurements were available (green circles)*

relative abundance of organisms that have the capacity for $NO2_2^-$ reduction). Over a period of 4 years (2018–2021), 28 450 m^3 of mine drainage was treated in BR3. This water contained in total 1560 kg of N, where 900 kg of N was removed by denitrification.

Water flow through BR3 did not significantly ($P>0.05$) change the concentrations of the major cations and anions (water quality with 2019 as example is shown in Table 1), with the exception alkalinity (as HCO_3^-), NO_3^- and dissolved organic carbon (DOC) (see Table 1). As indicated in reaction 1, alkalinity is produced by denitrification; while DOC is consumed by denitrification, DOC is also released through the hydrolysis of lignocellulosic biomass (i.e. woodchips) in the bioreactor. The saturation indices of common secondary minerals indicate that all such phases are undersaturated in the BR3 effluent (including gypsum), except for calcite ($CaCO_3$). However, based on the insignificant difference in the median Ca concentrations at the inlet and outlet of BR3, it is unlikely that calcite precipitation is an important sink for Ca.

Application of woodchip bioreactors at other mine sites

The success of a denitrifying woodchip bioreactor is determined by several factors, which are explained in the list below. This short list should be considered if bioreactors are constructed at other mine sites.

- *Mine drainage composition.* Low pH and high iron concentrations would impede bioreactor performance. Since denitrification occurs optimally at neutral pH conditions, acidic mine waters would first require acid neutralization. Also, since a woodchip bioreactor is an effective sediment filter, iron precipitation at the surface of a bioreactor would rapidly clog the substrate. Either iron removal would need to precede bioreactor treatment, or the woodchip surface layer would need to be replaced often.
- *Bioreactor construction.* Pine woodchips are readily available in northern Scandinavia and have proven to be suitable reactive material because hydrolysis of pine does not result in an excessive release of DOC nor in the production of high levels NH_4^+ through dissimilatory nitrate reduction to ammonium (Nordström & Herbert 2017). For bioreactor construction in other locations, the suitability of alternative carbon sources will need to be tested in the laboratory, primarily in terms of nitrate removal rates as well as DOC and NH_4^+ production.
- *Number of bioreactors.* The number of bioreactors constructed needs to be scaled to the expected flow of waste rock drainage to be treated, which is partially determined by the surface area of the waste rock deposit and the infiltration rate. For very large flows, the construction of numerous bioreactors may be impractical and other treatment methods (e.g. treatment with a moving bed biofilm reactor) may need to be considered.
- *Temperature and other operating conditions.* The processes of denitrification and lignocellulosic hydrolysis are kinetically controlled and temperature dependent. For bioreactor operation under non-optimal conditions (e.g., low temperature), the HRT of the bioreactor needs to be regulated to allow for adequate nitrate removal. For operation in warmer climates, a shorter HRT than applied in this study (ca. 5 days) could potentially be used.

Conclusions

This study demonstrated that a woodchip bioreactor could remove nitrate from neutral pH mine drainage by denitrification at low temperature (average 3 °C), but that nitrate removal decreased over a period of four years. The decrease in treatment efficiency with time is believed to be controlled at least partially by the low water temperature and the decrease in available organic carbon for denitrification. For greater nitrate removal, the bioreactor can be operated at longer HRTs or can be supplemented with an external carbon source (e.g. acetate).

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