Denitrifying woodchip bioreactor shutdown during dry periods

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Abstract: There is a growing acceptance of denitrifying bioreactors, an innovative *in-situ* treatment technology, as an effective tool for the removal of nitrates from agricultural outflows. Denitrifying bioreactors are containers or trenches filled with various types of organic material that releases bioavailable organic carbon over a long period. Wood-particle materials, such as sawdust and woodchips, are used most frequently as fill media. The presented research focuses on wet bioreactor shutdown during dry weather periods and its impact on nitrate removal rate and fill media leaching under various inflow NO_3^--N concentrations and hydraulic retention times (HRTs). The experiment was conducted in laboratory bioreactors filled with poplar woodchips at an average temperature of 19 °C, at inflow NO_3^--N concentrations of 20 mg/L and 40 mg/L, and at HRTs ranging from 1.6–2.1 d. Three shutdowns were performed, lasting two, two and three weeks, during which the fill media were kept flooded. The steady outflow NO_3^--N concentrations of all bioreactors were below 3 mg/L. Outflow COD (chemical oxygen demand) and BOD (biochemical oxygen demand) stabilised below 400 and 200 mg/L, respectively, while TKN (total Kjeldahl nitrogen) stabilised at 1 to 2 mg/L. The shutdowns did not significantly affect either the NO_3^--N removal process or the release of organic compounds from the denitrifying bioreactor fill media. Outflow TKN concentrations after recommissioning increased to 2–3.5 mg/L, subsequently decreasing to steady values within three weeks. The water stagnating in the bioreactors during their shutdowns contained elevated concentrations of NO_3^--N, COD, BOD and TKN (4–6 mg/L, 1,200–1,600 mg/L, 600–900 mg/L and 2.5–5 mg/L, respectively), but the volume of water was small. Thus, the long-term benefits brought to the aquatic environment by denitrifying bioreactors highly exceed the occasional negative impact of discharged stagnant water.

Key Words: denitrifying woodchip bioreactor, wet shutdown, dry period, nitrates, organic matter release

INTRODUCTION

The excessive application of fertilizers and animal manure in agriculture and subsequent nitrogen losses from agricultural areas are responsible for nitrate contamination of the aquatic environment worldwide, which results in eutrophication, toxic algal blooms, hypoxia, and habitat deterioration (Galloway et al. 2003). The prevention of the nitrate pollution of water bodies is covered by the European Directive (Council of the European Communities 1991).

There is a growing acceptance of denitrifying bioreactors, an innovative *in-situ* treatment technology, as an effective tool for the removal of nitrates from agricultural outflows (Christianson and Shipper 2016). Denitrifying bioreactors are containers or trenches filled with various types of organic material that releases bioavailable organic carbon over a long period. Organic carbon has three important functions in heterotrophic denitrification, which converts nitrates to nitrogen gas. It provides an anoxic environment, acts as an electron donor, and serves as a substrate for the growth of denitrifying microorganisms (Schipper et al. 2010).

The organic fill medium is one of the most important factors controlling the denitrification process. Wood-particle materials, such as woodchips and sawdust, are used most frequently (Schipper et al. 2010). They have many advantages. They provide constant nitrate removal rates over decades (Robertson 2010), exhibit a high C:N ratio (Robertson and Anderson 1999) (which is preferred due to the need to avoid excessive nitrogen leaching), maintain high hydraulic conductivity (van Driel et al. 2006), and require minimum maintenance (Robertson 2010).

Operating conditions, including inflow nitrate concentration, HRT, and temperature, are other important factors affecting processes in denitrifying bioreactors. Their influence on nitrate removal rate was analysed by Addy et al. (2016), who applied meta-analysis approaches to data from 26 published studies dealing with 57 separate bioreactor units. They concluded that nitrate removal rate rises with increasing inflow nitrate concentration, and that furthermore this effect is fostered by a sufficient HRT (at least 6 h) and a temperature greater than 6 °C. Denitrification requires a pH ranging from 6 to 8. Denitrification rate decreases with falling pH (Paul and Clark 1996).

A sufficiently long HRT and an adequately high temperature do not only promote nitrate removal, but unfortunately also the leaching of bioreactor fill media. Cameron and Schipper (2010) assume that a longer HRT enables greater dissolution of organic carbon, and that a higher temperature supports faster microbial decomposition of fill media, releasing NH_4–N, organic nitrogen and carbon.

The operating conditions of a denitrifying bioreactor, including its shutdown during dry periods, highly depend on natural conditions (the amount of precipitation and irrigation in particular). In general, fluctuating flow rates may result in lower removal efficiency even at high HRTs (Christianson et al. 2011). During conditions of no flow or very low flow, denitrifying bioreactors can be left dry, partially flooded, or wet.

The effect of wet/dry shutdown on bioreactor function and its impact on the environment is complex. In the case that desiccation occurs, the imported dissolved oxygen may reduce denitrification to the benefit of aerobic mineralization. On the other hand, mineralization leads to oxygen consumption, and the organic carbon released after the dry period may support rapid denitrification for a limited time period after rewetting (Woli et al. 2010, Weigelhofer and Hein 2015). Consistently saturated woodchips degrade more slowly than periodically desiccated chips (Christianson et al. 2012).

The goal of the presented research was to determine how wet bioreactor shutdown during dry weather periods affects nitrate removal rate and fill media leaching under various inflow NO_3^--N concentrations and HRTs.

MATERIAL AND METHODS

The experiment was conducted in 0.3 m^3 vertical cylindrical bioreactors filled with poplar woodchips of a particle size ranging from 2 mm to 20 mm. The bioreactors were loaded with tap water enriched with potassium nitrate. A water-saturated environment was maintained in the bioreactors by a flexible pipe. The average outflow water temperature was 19 °C.

The bioreactors were operated at inflow NO_3^--N concentrations of 20 mg/L and 40 mg/L. The experiment was conducted with two replicates. After achieving steady operation, the bioreactors were shut down for various periods of time. Three shutdowns were performed, lasting two, two and three weeks. The fill media were kept flooded. At the end of the shutdowns, the bioreactors were discharged and the stagnant liquid was analyzed. Afterwards, they were filled with inflow water and operated till a new steady state was achieved. Some of these operational phases differed in HRTs, as discussed below.

Sampling was carried out on a weekly basis. The pH was measured via a Hach HQ40d multi-parameter meter (Loveland, Colorado, USA). NO_3^--N was measured by the UV absorption method with a Hach optical Nitratax plus sc Sensor (Loveland, Colorado, USA). The COD, BOD, and TKN were analysed by the following methods: COD – semi-micro method with potassium dichromate and photometric evaluation; BOD – dilution and seeding method with allylthiourea addition and five-day incubation time; TKN – acid digestion using concentrated sulphuric acid together with catalyst tablets (KJELTABS ST – Thompson & Capper Ltd) and photometric determination of the released ammonia via the photometric indophenol method. A paired *t*-test (significance level of 0.05) was used to verify the similarity of the parallel bioreactors outlet parameters.

NO_3^--N removal rates were calculated as $[\Delta c(NO_3^-\text{-N}) \cdot Q] / V$, where $\Delta c(NO_3^-\text{-N})$ was the difference between the inflow and outflow NO_3^--N concentrations (mg/L), Q was the water flow rate (L/d) and V was the bioreactor filling volume (L). Removal efficiency was calculated from the inflow and outflow NO_3^--N concentrations.

RESULTS AND DISCUSSION

Statistical analysis did not show any difference between all outlet parameters of bioreactors fed with 20 mg/L NO_3^--N and also TKN and pH of those fed with 40 mg/L NO_3^--N. The outlet NO_3^--N, COD, and BOD concentrations of the latter bioreactors differed. However, the differences were not big, as can be seen from Figures 1, 5, and 6.

Nitrate removal

The outflow NO_3^--N concentrations (Figure 1) of bioreactors with both 20 and 40 mg/L inflow NO_3^--N concentrations were below 3 mg/L during the whole experimental period. NO_3^--N removal efficiency (Figure 2) corresponded with these low values – it was 92% and 97% in average for the 20 and 40 mg/L inflow NO_3^--N concentrations, respectively. NO_3^--N removal rates (Figure 3) were high for both cases – about 5 and more than 10 mg/(L·d) for the 20 and 40 mg/L inflow NO_3^--N concentrations, respectively. The difference in the NO_3^--N removal rates was caused by the amount of NO_3^--N available for denitrification. Despite bioreactors shutdowns the rates were in the range of 2–22 mg/L/d, which was published by Schipper et al. (2010) for various wood-based materials in continuous operated bioreactors. The high NO_3^--N removal efficiencies clearly show that the rates could be even higher.

During the shutdowns, decay of organic fill media caused the outflow pH to drop from 6–7 to approx. 5 (Figure 4). Denitrifying bacteria require pH between 6 and 9. (Paul and Clark 1996) After recommissioning, pH rapidly increased. Bioreactors with higher inflow NO_3^--N concentrations recovered faster with regard to pH, probably because greater amounts of OH^- ions are produced during denitrification. Under these conditions, NO_3^--N removal rate was restored and outflow NO_3^--N concentration stabilised at its former values.

In the 17th week, HRTs of all columns were increased from 1.6 and 1.9 d in case of 20 and 40 mg/L inflow NO_3^--N concentrations, respectively, to 2.1 d for both concentrations. Longer HRT is favourable for NO_3^--N removal efficiency, but can cause deterioration in bioreactor outlet water quality in released compounds concentrations, such as COD, BOD, and TKN. (Schipper et al. 2010) The increase in HRTs in the 17th week did not affect NO_3^--N removal efficiency (Figure 2). The HRTs of 1.6 to 2.1 d were relatively long in comparison with some published papers, describing bioreactors successfully operating at HRTs of about 8 h. (Christianson et al. 2012) It can be assumed that the bioreactor operation is less stable at shorter HRTs, and thus any change in operation parameters like shutdown could probably cause longer recovery period.

Figure 1 Outflow NO_3^--N concentration

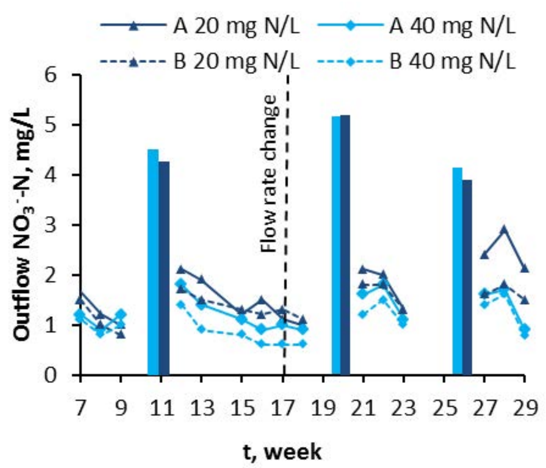


Figure 2 NO_3^--N removal efficiency

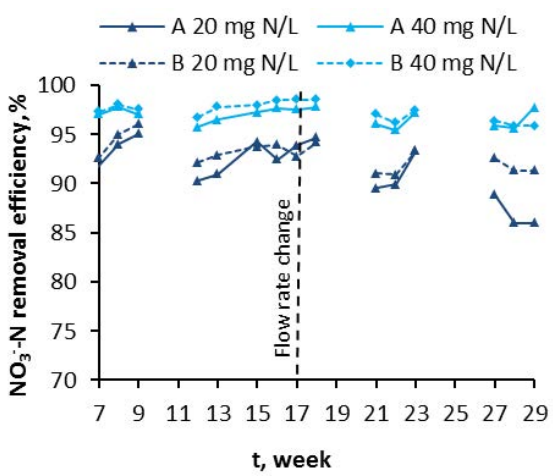


Figure 3 NO_3^--N removal rate

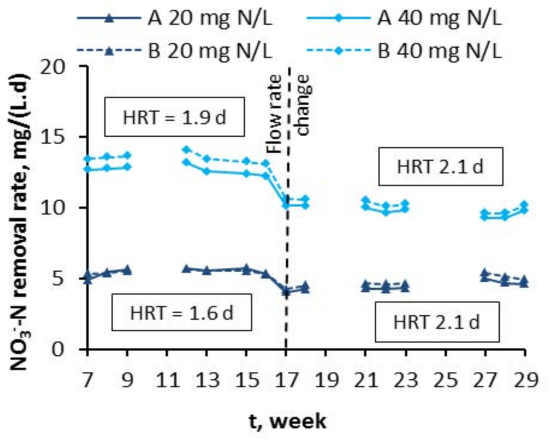
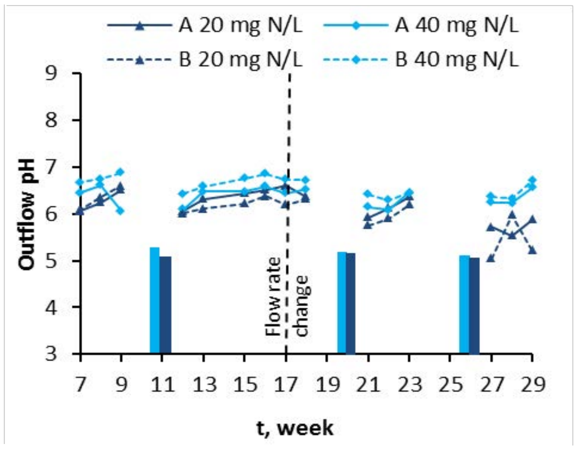


Figure 4 Outflow pH values



Release of organic substances and TKN

The presence of organic substances and TKN in outflow was caused by their release from the fill media. Outflow COD and BOD (Figure 5 and 6) stabilised below 400 and 200 mg/L, respectively, which was sufficient for denitrification. Steady outflow TKN (Figure 7) was below 2 mg/L.

The release of both COD and BOD followed a similar pattern, and after recommissioning their concentrations rapidly dropped to their former values. Shutdown caused a relatively high increase in outflow TKN. Its concentration decreased more slowly. It is evident from Figures 5–7 that there were no significant differences between shutdowns. Thus, it can be stated that the lengths of shutdowns and HRTs did not significantly affect fill media leaching after bioreactor recommissioning.

Figure 5 Outflow COD

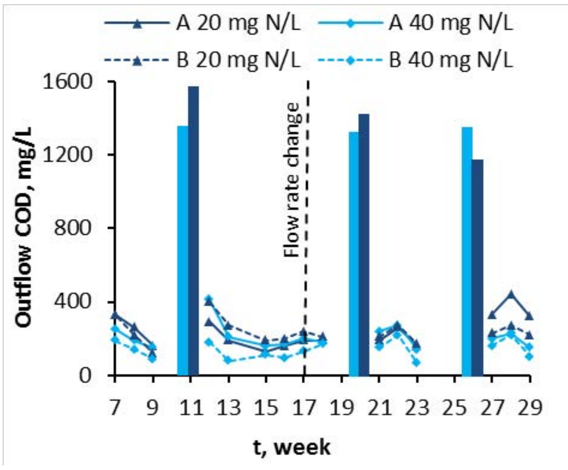


Figure 6 Outflow BOD

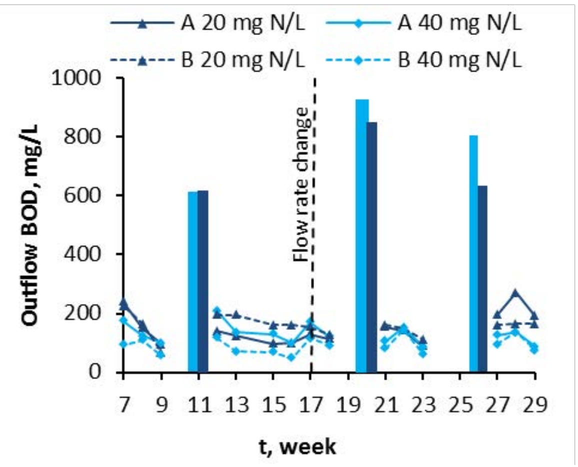
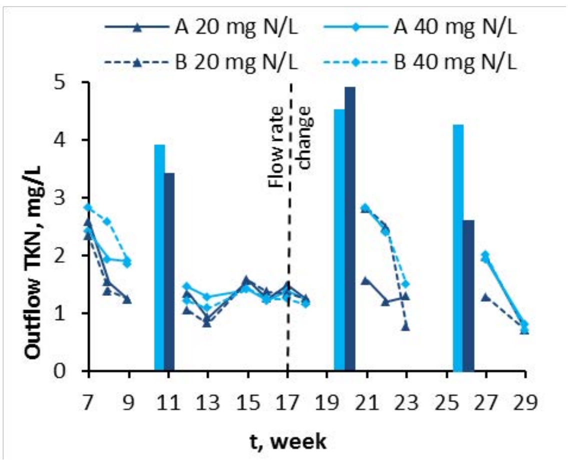


Figure 7 Outflow TKN concentrations



Stagnant water

The quality of stagnant water in the shutdown bioreactors is presented in the form of columns in Figures 1 and 4–7 (average values). The stagnant water contained elevated residual NO_3^--N concentrations (4–6 mg/L), which were probably caused by the conditions prevailing during stagnation. Denitrification was hampered by several of the assessed parameters, and by the insufficiently high pH of 5 in particular. NO_3^--N removal could also have been influenced by other factors, such as the leaching of compounds adversely affecting denitrification bacteria. The release of potentially harmful substances from wood materials has been described by several authors, such as Svensson et al. (2014). The organic matter contents and TKN in the stagnant water were relatively high: 1,200–1,600 mg/L, 600–900 mg/L, and 2.5–5 mg/L for COD, BOD, and TKN, respectively. The duration of the shutdowns (two and three weeks) did not significantly affect the release of organic compounds and TKN from the fill media. However, 29 weeks of bioreactor operation is a short time period compared with its duration in real use. The bioreactor can last for a minimum of 15 years (Schipper et al. 2010). Thus, its behaviour during shutdowns can differ after a longer period of operation. It was described at field bioreactors that concentrations of compounds leached from bioreactor fill media decrease in time. (Robertson 2010)

Besides the quality of stagnant water, its quantity is also important for the evaluation of its impact on the aquatic environment. Although the stagnant water quality was poor, its volume was quite small. At a woodchip porosity of approx. 50% and an HRT of approx. 2 d, the stagnant water volume would be equivalent to the two-day flow rate.

CONCLUSION

Wet shutdowns with a duration of 2–3 weeks under 20 and 40 mg/L inflow NO_3^--N concentrations and HRTs from 1.6 to 2.1 d did not significantly affect the NO_3^--N removal process or the release of organic compounds from denitrifying bioreactor fill media. The bioreactors returned to fully functional operation within one week of recommissioning. The release of TKN after recommissioning was higher, though its outflow concentrations decreased to steady values within three weeks.

The quality of the water stagnating in the bioreactors during their shutdowns was poor, but its volume was quite small. Thus, it can be concluded that the long-term benefits brought to the aquatic environment by denitrifying bioreactors highly exceed the negative impact of occasionally discharged stagnant water.

The tested shutdown durations were relatively short. Longer shutdowns would probably affect bioreactor operation to a larger extent. Also behaviour of the bioreactor under shorter HRT can differ. We plan to investigate both these subjects in our future research.

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