Technical Paper

Denitrification of Groundwater in the Biofilm Reactor with a Specific Biomass Support Material[†]

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[†] Dedicated to the memory of Prof. Dr. Davorin Dolar

Abstract

This study demonstrated the feasibility of a fixed-bed reactor system with a specific biomass support material for groundwater treatment. The denitrification rate increased up to a maximal value of 1.3 $gNO_3\text{-}N\cdot m^{-2}\cdot day^{-1}$ with increasing nitrogen loading rate. Kinetic analysis of the system confirmed a half-order denitrification kinetic region in the NO_x-N concentration range from 0.25 $mg\cdot L^{-1}$ to 16 $mg\cdot L^{-1}$, with the half-order reaction coefficient $k_{1/2}$ of 0.35 $g^{0.5}\cdot m^{-0.5}\cdot day^{-1}$ when the carbon source was in excess. Under the experimental conditions, drinking water quality was achieved at a nitrogen loading lower than 1.9 $gNO_3\text{-}N\cdot m^{-2}\cdot day^{-1}$ with an influent COD/N ratio of 3.7 if acetate was used as the carbon source. The system is fairly robust; it can be operated in a simple manner at low hydraulic loadings without recirculation flow and without backwashing.

Key words: biofilm reactor, denitrification, external carbon substrate, groundwater, kinetics

1. Introduction

The nitrate ion is a common groundwater contaminant that can cause health problems in infants and animals. In the light of growing requirements to minimize the content of the nitrate ion in drinking water, denitrifying reactors are becoming increasingly important. In combination with an effective system for disinfection, biological denitrification can be an appropriate solution for groundwater treatment.[1] In the biological denitrification process, nitrate is reduced via nitrite to nitrogen gas by using biodegradable carbon compounds as an energy source. If the carbon/nitrogen (COD/N) ratio in the treated water is low, external carbon sources such as acetate, methanol or ethanol have been added in some cases.

Biological denitrification could be achieved either in the activated sludge or in the biofilm system. Biofilm reactors are the favoured bioreactors for denitrification because they may be made much more compact. The most efficient type of biofilm reactors are the fluidized-bed type, because of their high biomass hold-up and high denitrification rate. Nevertheless, the operation of fluid-bed reactors is connected with some disadvantages: uncertain control of stable fluidization, high energy input for recirculation, and problematic particle/biomass separation.[2,3] Fixed-bed reactors are usually less efficient but very simple in operation. In order to avoid the main disadvantages of fixed-bed reactors, namely the clogging of the biofilm support media, an appropriate type of packing material must be selected.

The objective of this paper was to evaluate the operating performance of a fixed-bed biofilm reactor with a specific packing material by comparing the results obtained with data available in the literature for existing biofilm systems; additionally the kinetic aspects of the groundwater denitrification process were emphasized.

2. Materials and Methods

2.1. Support Media

The biomass support media used in this study was developed in the National Institute of Chemistry, Slovenia. The support media material was a mixture of PVC plastic and powdered activated carbon (PAC). Addition of activated carbon increased the total pore area (measured by: Micromeritics Pore Sizer 9310) from 12.8 $m^2\cdot g^{-1}$ (PVC) to 31.4 $m^2\cdot g^{-1}$ (PVC + PAC). This material is inert/neutral, resistant to abrasion, and with a high ability to support the biofilm. The shape and the size of the particles provided a high specific surface area and a high void volume (high biomass-holding capacity/no biomass clogging).

The characteristics of the support media are presented in Table 1.

Table 1. Characteristics of the biomass support media

Material: PVC plastic + activated carbon
Shape: cylinders with longitudinal external fins
Diameter/length (cm): 3.0/4.0
Total pore area ($m^2 \cdot g^{-1}$): 31.4
Specific surface area ($m^2 \cdot m^{-3}$): 165
Void space (%): 88
Bulk density ($g \cdot cm^{-3}$): 1.05

2.2. Reactor Set-up

Figure 1 shows a schematic diagram of the fixed-bed column used in the denitrification studies. A peristaltic pump (Bűhler) was used to provide the feed from the wastewater reservoir to the plexiglass column (diameter = 12 cm, length = 100 cm). The column was packed with 10 L of the biomass support media. A pulse pump (Prominent) was used for the backwashing of the reactor. Excess biomass was collected in the settler (volume = 1.5 L).

All experiments were performed at an ambient temperature of 20°C.

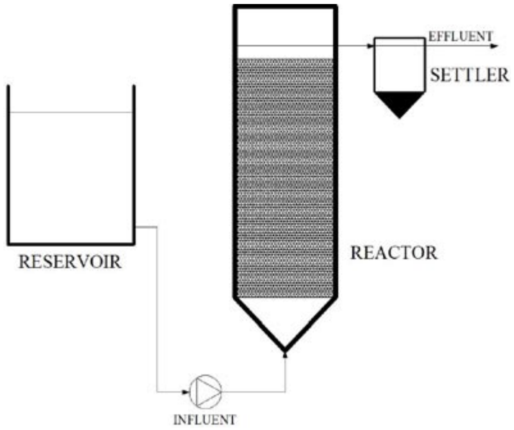

Figure 1. Schematic diagram of the experimental set-up.

2.3. Wastewater

Nitrate wastewater, simulating polluted groundwater with a concentration up to 45 $mgNO_3\text{-}N \cdot L^{-1}$, was used in the experiments. Potassium nitrate (KNO_3, p.a. grade), dissolved in tap water, was used as the NO_3-N source, and the carbon source was supplemented using sodium acetate ($CH_3COONa \cdot 3H_2O$, industrial grade). Potassium phosphate (KH_2PO_4, p.a. grade) was added to the solution to eliminate nutrient deficiency.

2.4. Analytical Procedure

Samples of influent and effluent were collected daily and filtered through membranes of 0.45 μm pore size. Filtrates were analysed for COD, NO_3-N and NO_2-N. All analyses were performed according to Standard Methods.[4] All data reported in our study refer to steady-state conditions.

3. Results and Discussion

The biomass support media performance was evaluated in the first set of experiments. The carbon source (acetate) in the nitrate wastewater was in excess, with the COD/NO_3-N ratio maintained at a constant value of 5.5. The reactor was inoculated with municipal wastewater before the experiments started.

In Figure 2 the denitrification rate is plotted as a function of NO_3-N loading rate. In the loading rate range from 0.3 $gNO_3\text{-}N \cdot m^{-2} \cdot day^{-1}$ to 2.5 $gNO_3\text{-}N \cdot m^{-2} \cdot day^{-1}$ the denitrification rate increased with increasing load. The system was operated without backwashing; no clogging with excessive biomass was observed. The highest denitrification rate obtained in our study was 1.3 $gNO_3\text{-}N \cdot m^{-2} \cdot day^{-1}$ ($0.21\ g^{0.5} \cdot L^{-0.5} \cdot day^{-1}$). The shape of the curve was comparable with the shape of the curve obtained in a highly loaded system (20.0 - 50.0 $gNO_3\text{-}N \cdot m^{-2} \cdot day^{-1}$) with glass raschig rings as the support material and sodium acetate as the carbon source.[5] Denitrification rates obtained in a highly loaded system were much higher (up to 47.2 $gNO_3\text{-}N \cdot m^{-2} \cdot day^{-}1$) but the system required intensive periodic backwashing due to excessive biomass accumulation.

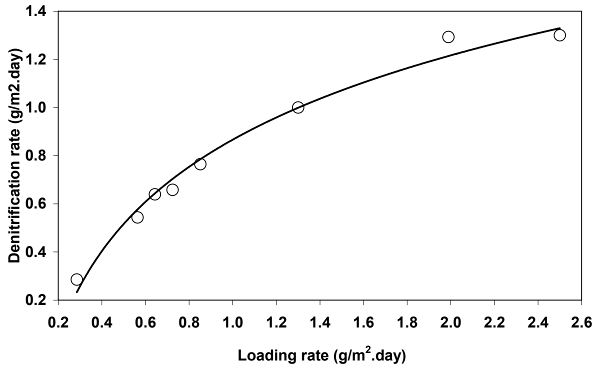

Figure 2. Denitrification rate versus nitrogen loading rate

Highly loaded denitrification systems are able to enhance high nitrogen removal rates and result in removal efficiencies greater than 99%.[5] In groundwater treatment, the operating conditions are usually limited by the required effluent quality set with regard to environmental regulations. The results presented in Figure 3 show that at an increasing loading rate the concentration of nitrate and nitrite in the effluent increased significantly. Similar results were found in a fixed-bed system packed with Pall rings and with molasses as the carbon source.[6] In order to avoid public health damage the following nitrate, nitrite and organic substrate concentration guidelines for drinking water were established in the EU[7]: $NO_3 < 50$ mg·L^{-1} (NO_3-N < 11 mg·L^{-1}), $NO_2 < 0.1$ mg·L^{-1} (NO_2-N < 0.03 mg·L^{-1}) and TOC < 4 mg·L^{-1} (COD < 11 mg·L^{-1}); these numbers represent the concentration region in which systems for groundwater treatment must be operated.

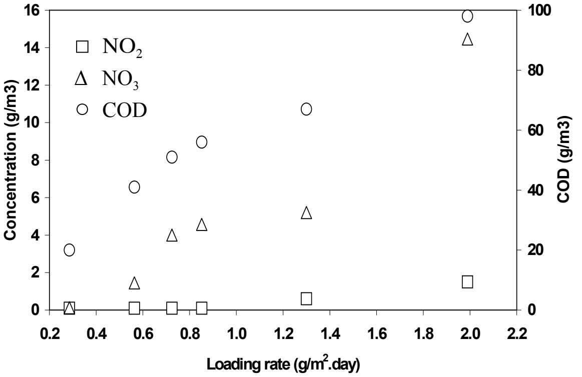

Figure 3. Concentration of nitrate, nitrite and residual COD in the effluent at increasing loading rate.

Theoretical analysis of biofilm processes is much more complicated than that of the activated sludge process. The expression for the overall reaction combines biofilm kinetics and transport phenomena in the biofilm pores.[8] Haremoes[9] showed that the denitrification rate in the low substrate concentration region can be expressed as the half-order reaction:

$$r_{dn} = k_{1/2} \cdot C^{0.5} \qquad (1)$$

where $k_{1/2}$ is the half-order reaction coefficient and C is the concentration of residual nitrogen in the bulk liquid (residual nitrogen: NO_2-N + NO_3-N = NO_x-N). Equation 1 corresponds to the thick biofilm condition where the biofilm is not fully penetrated by the substrate.[6] In Figure 4 the denitrification rate is plotted as a function of the square root of the NO_x-N concentration in the effluent. The denitrification rate kinetic was of half-order in the NO_x-N concentration range from 0.25 mg·L^{-1} to 16 mg·L^{-1} when the carbon source was in excess. The half-order reaction coefficient $k_{1/2}$ obtained in our study was 0.35 g$^{0.5}$·m$^{-0.5}$·day^{-1} (0.058 g$^{0.5}$·L$^{-0.5}$·day^{-1}). This value is similar to the value of 0.23 g$^{0.5}$·m$^{-0.5}$·day^{-1} obtained in a system packed with Pall rings (specific surface area: 190 m^2·m^3) and with molasses as the carbon source[6], but lower than the value of 1.2 g$^{0.5}$·m$^{-0.5}$·day^{-1} obtained in a fluid-bed system with polystyrene beads (specific surface area: 1200 m^2·m^3) and with ethanol as the carbon source.[10]

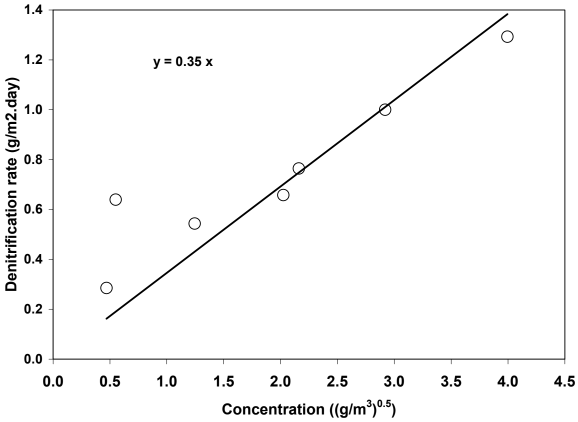

Figure 4. Denitrification rate versus square root of NO_x-N concentration.

De Mendonca and coworkers[11] found that $k_{1/2}$ is a function of a hydraulic loading. Doubling the hydraulic loading from 3.63 m·h^{-1} to 7.24 m·h^{-1} was associated with an increase in $k_{1/2}$ from 0.023 g$^{0.5}$·L$^{-0.5}$·day^{-1} to 0.063 g$^{0.5}$·L$^{-0.5}$·day^{-1}. This could be the reason for the high $k_{1/2}$ value of 1.2 g$^{0.5}$·m$^{-0.5}$·day^{-1} (system with polystyrene beads)[8] obtained at a hydraulic loading of 8.0 m·h^{-1} (0.5 m·h^{-1} influent flow + 7.5 m·h^{-1} recirculation flow). A value of $k_{1/2}$ of 0.23 g$^{0.5}$·m$^{-0.5}$·day^{-1} (system with Pall rings)[5] was obtained at the hydraulic loading of 0.05 m·h^{-1}. The $k_{1/2}$ value of 0.35 g$^{0.5}$·m$^{-0.5}$·day^{-1} from the present study was obtained at a hydraulic loading of 0.2 m·h^{-1}.

Above a certain concentration of NO_x-N the denitrification reaction proceeded as a zero-order reaction due to full penetration of nitrogen into the biofilm and the zero order reaction coefficient k_0 represents the maximum denitrification rate.[8] A k_0 value of 1.42 gNO_3-N·m^{-2}·day^{-1} (1.7 gNO_3-N·L^{-1}·day^{-1}) was obtained in the system with polystyrene beads at a concentration higher than 1.4 mgNO_x-N·L^{-1}, a k_0 value of 1.9 gNO_3-N·m^{-2}·day^{-1} (0.36 gNO_3-N·L^{-1}·day^{-1}) was obtained in the system packed with Pall rings at a concentration higher than 60 mgNO_x-N·L^{-1}, and a k_0 value of 1.3 gNO_3-N·m^{-2}·day^{-1} (0.21 gNO_3-N·L^{-1}·day^{-1}) was obtained in our system at a concentration higher than 16 mgNO_x-N·L^{-1}. In the system with polystyrene beads the drinking water effluent quality (NO_x-N < 11 mg·L^{-1}) was achieved in the k_0 region at a maximal denitrification rate. In the system packed with Pall rings and in our system drinking water effluent quality was achieved in the $k_{1/2}$ region at a denitrification rate of 0.8 gNO_3-N·m^{-2}·day^{-1} (0.15 gNO_3-N·L^{-1}·day^{-1}) and 1.16 g NO_3-N·m^{-2}·day^{-1} (0.19 gNO_3-N·L^{-1}·day^{-1}) respectively. A loading rate of about 1.9 gNO_3-N·m^{-2}·day^{-1} (Figure 2) must be applied in our system in order to achieve the required denitrification rate. Figure 3 shows that at this loading rate the residual effluent COD exceeded the drinking water guideline (COD < 11 mg·L^{-1}) when the carbon source in the influent was in excess. It is important to determine the optimal influent COD/N ratio, because a higher-than-necessary COD/N ratio leads to a higher residual effluent COD.

A second set of experiments was conducted in order to examine the influence of influent COD/N ratio on denitrification kinetics and effluent quality with sodium acetate which is the preferable carbon source for groundwater treatment (readily available, nontoxic, and safer to handle and store than the more flammable alternatives, methanol and ethanol). The excess biomass remaining from the first set of the experiments was eliminated from the reactor by intensive backwashing. During the experiments the system was operated without backwashing; no clogging with excessive biomass was observed. The COD/N ratio in the influent was gradually increased at a constant nitrogen load lower than 1.9 gNO_3-$N{\cdot}m^{-2}{\cdot}day^{-1}$. Figure 5 shows the concentration of nitrate, nitrite and residual COD in the effluent at different influent COD/N ratios. It may be noted from this figure that the minimal concentration of nitrate, nitrite and COD was achieved at an influent COD/N ratio of 3.7. Higher ratios lead to a higher residual effluent COD and lower ratios lead to incomplete denitrification.

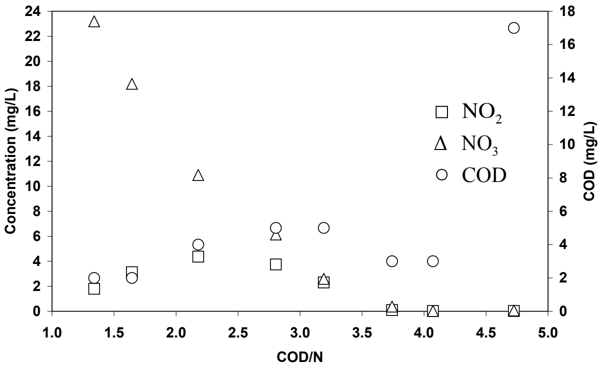

Figure 5. Effluent quality with different influent COD/N ratios.

A higher average effluent nitrite concentration was also found in the packed-bed system with Biolite (expanded clay with grain size of 2 – 4 mm) when acetate was used as a carbon source[12]. A volumetric denitrification rate of about 0.2 gNO_3-$N{\cdot}L^{-1}{\cdot}day^{-1}$ was achieved at a hydraulic loading of about 1 $m{\cdot}h^{-1}$ and influent COD/N ratio lower than 3; this system required intensive periodic backwashing due to excessive biomass accumulation[12]. The optimal influent COD/N ratio of 3.7 determined in the present study is comparable with the value of 3.6 obtained in a highly loaded system with glass raschig rings as the support material and sodium acetate as the carbon source and is approximately twice as high as the theoretical acetate COD/N ratio of 1.9.[5] The influence of the influent COD/N ratio on the effluent quality in the system with Pall rings and molasses as the carbon source and in the system with polystyrene beads and ethanol as the carbon source was not presented in the relevant papers[6,10].

4. Conclusions

This study demonstrates the feasibility of a fixed-bed reactor system with specific biomass support material for groundwater treatment. The kinetic analysis of the system confirmed a half-order denitrification kinetic region in the NO_x-N concentration range from 0.25 $mg{\cdot}L^{-1}$ to 16 $mg{\cdot}L^{-1}$ with the half-order reaction coefficient $k_{1/2}$ of 0.35 $g^{0.5}{\cdot}m^{-0.5}{\cdot}day^{-1}$ (0.06 $g^{0.5}{\cdot}L^{-0.5}{\cdot}day^{-1}$). The drinking water quality was achieved at a nitrogen loading lower than 1.9 gNO_3-$N{\cdot}m^{-2}{\cdot}day^{-1}$ (0.31 $g^{0.5}{\cdot}L^{-0.5}{\cdot}day^{-1}$) with the influent COD/N ratio of 3.7 if acetate was used as the carbon source. The system is fairly robust; it can be operated in a simple manner at low hydraulic loadings without recirculation flow and without backwashing.

5. Acknowledgements

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6. References

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Povzetek

Preučevali smo delovanje laboratorijskega pilotnega reaktorja s pritrjeno biomaso za denitrifikacijo podtalnice. Specifičen nosilec biomase, ki smo uporabili v reaktorju, smo razvili na Kemijskem inštitutu, Ljubljana.

V koncentracijskem območju NO_x-N od 0.25 mg·L^{-1} do 16 mg·L^{-1} je reaktor deloval v režimu kinetike polovičnega reda s konstanto hitrosti $k_{1/2} = 0.35\ g^{0.5}\cdot m^{-0.5}\cdot dan^{-1}$ ($0.058\ g^{0.5}\cdot L^{-0.5}\cdot dan^{-1}$). Predpisane vrednost parametrov za pitno vodo smo dosegli pri obremenitvi nižji od 1.9 gNO_3-N·m^{-2}·dan^{-1} ($0.31\ g^{0.5}\cdot L^{-0.5}\cdot dan^{-1}$). Optimalno razmerje KPK/N v toku je 3,7, če smo kot zunanji vir ogljika uporabili acetat. Delovanje rektorja s specifičnim nosilcem biomase je enostavno, povratno spiranje ni potrebno, ker se tudi pri nizkih obtočnih hitrostih sloj nosilca ni mašil z odvečno biomaso.