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Original Research Article

Removal of Nitrate from Groundwater Using a Hydrogen-Based Membrane Biofilm Reactor: The Effects of Hydrogen Pressure and Hydraulic Retention Time

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ABSTRACT

The membrane biofilm reactor (MBfR) is a novel system that uses membranes to supply dissolved gas directly to a biofilm growing on the membrane surface. In this study, hydrogen-based MBfR was used to remove nitrate from groundwater. The continuous flow MBfR reactor was operated under varying hydrogen (H_2) pressures and hydraulic retention times (HRT) at constant nitrate concentration of 10 mg L^{-1} over 81 days with nitrate containing simulated groundwater. The study was composed two parts. In the first part of the study, the effect of H_2 pressure on nitrate removal was investigated. The results showed that nitrate reduction rate improved as H_2 pressure was increased from 2 to 5 psi, and over 98% of total nitrogen removal rate was achieved. In the second part of study, effect of HRT on nitrate removal was investigated under 5 psi H_2 pressure. Our results showed stable nitrate removals under varying HRTs and decreasing HRT from 12 h to 1 h did not adversely affect the reactor performance, however, 0.5 HRT adversely affected the nitrate removal performance. The maximum nitrate removal flux of 3.01 g NO_3 (0,659 g NO_3) was reached. This research showed that H_2 based MBfR is effective for removing nitrate from the contaminated groundwater.

Keywords: Groundwater, Drinking water, Denitrification

INTRODUCTION

Increase in population and developments in industrialization have resulted in higher use of chemicals leading to faster transport rates between environmental compartments such as ground waters which drinking water is mainly produced. So many pollutants are known as danger for ground waters even if in micro levels such as; oxidized pollutants, chlorinated solvents, heavy metals and pesticides (Nerenberg and Rittmann 2004; Chung *et al.* 2008). These pollutants are mainly the reason for industrial, municipal, and agricultural activities. In this respect, increasing chemical pressure on drinking water sources should be taken into account especially to be able to meet drinking water needs. Thus, due to the harmful effect on human health, the contamination of drinking water sources with inorganic compounds such as nitrate is a matter of concern. People who get water from groundwater sources such as shallow wells have an increased risk of exposure to nitrate-rich groundwater. In Turkey, according to the TS266 the maximum contaminant limit for nitrate in drinking water was set at 50 mg L^{-1} nitrate (NO_3^-) (TS266, 1984; Bouchard *et al.* 1992).

Nitrate contamination is a widespread problem for drinking water around the world. Nitrogen is mainly found in ground waters as mainly in the form of nitrate (NO_3^-) and nitrite (NO_2^-). Contamination of ground waters with nitrate mainly the reason for the usage of nitrogen fertilizers and the irrigation with domestic wastewater (Shrimali and Singh 2001). Nitrate should be regulated in drinking water since the excess levels can cause methemologlobinemia or blue baby disease in humans (Bae *et al.* 2002). Nitrate removal in biological systems involves denitrification processes which require anaerobic conditions. Denitrification occurs in two ways according to the carbon source, heterotrophic and autotrophic; respectively. In heterotrophic denitrification processes, electron donor source is normally organic compounds. However, due to a very low organic carbon sources in ground waters nitrate cannot be removed effectively through heterotrophic biological methods. Hopefully, autotrophic denitrification has advantages over the heterotrophic denitrification, such as usage of inorganic electron donor which makes biomass yields low (Shin *et al.* 2007). Autotrophic denitrification using attached or suspended growth profile has been the most popular treatment configuration. In attached growth processes normally occur between microorganisms and a surface that allow microorganism to make biofilm (Hasar 2009a). Membrane biofilm reactors (MBfRs) are among the attached growth biological treatment applications which are newly adapted technologies that allow biofilm growing on the membrane. This configuration of the MBfR allows gaseous substrate to move across the membrane for gas delivery and support biofilm formation on the outer surface of the membrane. This exciting new technology for removal of contaminants from ground waters has been among the most promising trends.

In this study, hydrogen-based MBfR was used to remove nitrate from groundwater. Hydrogen is the ideal electron donor that has been used in most MBfR studies due to the inherent advantages over other organic donors. H_2 is non-toxic to human and cost effective. Supporting autotrophic bacteria eliminates the need for an organic carbon source since the growth rate of autotrophic bacteria is slow; amount of produced microorganism per

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removed substrate is rather scarce. So H_2 produces far less excess biomass than organic donors. On the other hand, its low water solubility prevent the residuals in the water which means it cannot be over-dosed to increase effluent BOD and be wasted at the same time (Ritmann 2006). Additionally, it was reported in a study that use of H_2 as gaseous substrate reduce the cost about 3-15 times compared to other common organic donors used (Lee and Rittmann 2002). For these reasons, this research based on nitrate reduction in which H_2 gas was used as electron donor source in MBfR reactor. MBfR was operated under varying HRT and H_2 pressures to determine optimum operational conditions for maximum nitrate removal from ground waters.

MATERIALS AND METHODS

H_2-MBfR System

The H_2-MBfR used in this study is shown in Figure 1. H_2 gas and a membrane that allows microorganism accumulation represent the MBfR's main components. The main membrane module contained a bundle of 40 hydrophobic hollow-fiber membranes (Zena Membran, Czech Republic) inside a glass pipe shell. Pure H_2 was supplied to the inside hollow fibers through the manifold at the base with the pressure ranged from 2 to 5 Psi. Summary of MBfR characteristics was shown in Table 1.

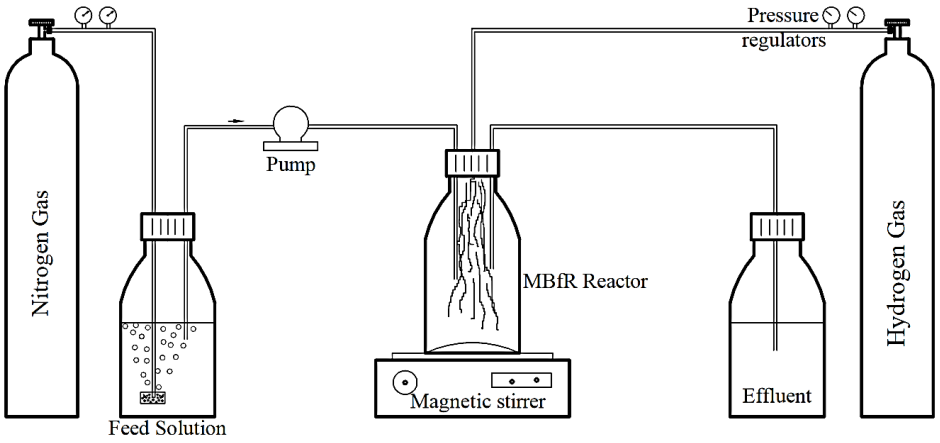

Figure 1. Schematic of the hydrogen-based membrane biofilm reactor used to investigate nitrate removal flux.

Table 1. Physical characteristics of the main module of the MBfR.

Characteristics	Value
Country/Region	Czech Republic
Company	Zena Membran
Type	Polypropylene hollow fibre membrane
Number of hollow fibers	40
Active length of fiber (cm)	10
Pore size (micron)	0.1
Fiber inside diameter (micron)	240
Fiber outside diameter (micron)	310
MBfR Reactor volume (mL)	300

The MBfR was inoculated with mixed culture taken from Kayseri Domestic Wastewater Treatment Plant in Turkey. Experiments were initiated with sludge inoculation to the MBfR. Biofilms were allowed to grow to steady state for operating conditions. This study had two main parts and MBfR was operated at seven different periods. In all operational conditions, pH, temperature and nitrate concentrations kept constant. The operating periods of the study were shown in Table 2.

Table 2. Operational conditions of H_2-based MBfR.

Parameters	Periods						
	I	II	III	IV	V	VI	VII
HRT (hours)	12	12	12	6	3	1	0.5
H_2 pressure (psi)	2	3	5	5	5	5	5
Operation period (day)	0-8	8-23	25-30	30-40	40-56	56-69	69-73
Temperature (°C)	30	30	30	30	30	30	30
pH	7-7.20	7-7.20	7-7.20	7-7.20	7-7.20	7-7.20	7-7.20
NO_3-N (mg/L)	2.25	2.25	2.25	2.25	2.25	2.25	2.25
Dissolved O_2 (mg/L)	0.2-0.8	0.2-0.8	0.2-0.8	0.2-0.8	0.2-0.8	0.2-0.8	0.2-0.8

In the first part of the study (Periods I-II-III), the effect of H_2 pressure on reactor performance was investigated. In period I, the reactor was fed with synthetic media containing nitrogen concentration of 2.25 mg NO_3-N /L and H_2 pressure was set 2 psi. Subsequently, H_2 pressure was increased stepwise from period I to III, corresponding to 2, 3, and 5 psi, respectively. In the second part of the study, effect of decreasing HRT was investigated. In this part, MBfR was operated at constant H_2 pressure of 5 psi. In subsequent periods (Periods IV-V-VI-VII), HRT was decreased stepwise from period IV to VIII, corresponding to 12, 6, 3, 1, and 0.5 h, respectively. All assays were run in triplicate and the data illustrated in all figures were the mean values of the measurements.

Simulated ground water

The MBfR was fed with synthetic groundwater prepared daily. Synthetic feeding water that has been used consists of the macro and micro nutrients necessary for microorganism's growth. Trace element stock solution consists of $ZnSO_4.7H_2O$ 100 mg L^{-1}, $MnCl_2.4H_2O$ 30 mg L^{-1}, H_3BO_3 300 mg L^{-1}, $CuCl_2.2H_2O$ 10 mg L^{-1}, Na_2SeO_3 30 mg L^{-1}, $NiCl_2.6H_2O$ 10 mg L^{-1} and $CoCl_2.6H_2O$ 200mg L^{-1} chemicals. Synthetic ground water prepared by adding 1 mL of trace element stock solution to synthetic feeding water containing $NaHCO_3$ 252 mg L^{-1}, KH_2PO_4 33 mg L^{-1}, $MgSO_4.7H_2O$ 50 mg L^{-1}, NO_3 10 mg L^{-1}. Nitrate in synthetic ground water was kept constant at 10 mg L^{-1} throughout the study of HRT investigation.

Analyses

An ion chromatography (Dionex ICS-3000) was used to measure the concentrations of nitrate (Dionex, Sunnyvale, CA, USA) with Ion Pac AG19 guard and AS19 analytical columns. Eluent containing 8mM sodium carbonate (Na_2CO_3) and 1.5mM sodium hydroxide (NaOH) was prepared and used for the nitrate and nitrite ion analyses with a flow rate of 1 mL min^{-1}.

RESULTS AND DISCUSSION

H_2 pressure is known to be an important parameter for nitrate removal by MBfR. Autotrophic denitrification using hydrogen as the supplemental donor has been extensively investigated to remove nitrate from polluted drinking water. Additionally, hydrogen is cheaper, nontoxic and lower biomass yield without a residual (Lee and Ritmann 2002; Haugen *et al.* 2002). Autotrophic denitrification of energy equations in hydrogen based membrane biofilm reactor is shown below (Lee and Ritmann 2002) (Eq. 1-8)

Nitrate reduction reaction: $NO^-_{3\,+}H_2 \rightarrow NO^-_{2+}H_2O$ (1)

Nitrite reduction reaction: $NO^-_{2\,+}\ 0{,}5H_2O \rightarrow NO^{(g)} + H_2O$ (2)

Reduction of nitrite oxide: $2NO^{(g)} + H_2 \rightarrow N_2O^{(g)} + H_2O$ (3)

Nitrous oxide reaction: $N_2O^{(g)} + H_2O \rightarrow N_2{}^{(g)} + H_2O + \frac{1}{2}O_2$ (4)

Denitrification reaction: $2NO^-_{3\,+}2H^+ + 5H_2 \rightarrow N_{2+}6H_2O$ (5)

Oxidation of hydrogen gas : $H_2 \rightarrow 2e^- + 2H^+$ (6)

Reduction of nitrate: $NO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}N_2 + 3H_2O$ (7)

Overall denitrification reaction: $NO_3^- + 2.5\ H_2 \rightarrow \frac{1}{2}N_2 + 2H_2O + OH^-$ (8)

For this reason, the objective of this part of this study was to evaluate the influence of H_2 pressure on reactor performance. The MBfR was operated over 81 days to investigate effect of H_2 pressure and HRT on nitrate removal in H_2-based MBfR and results were shown in Figure 2.

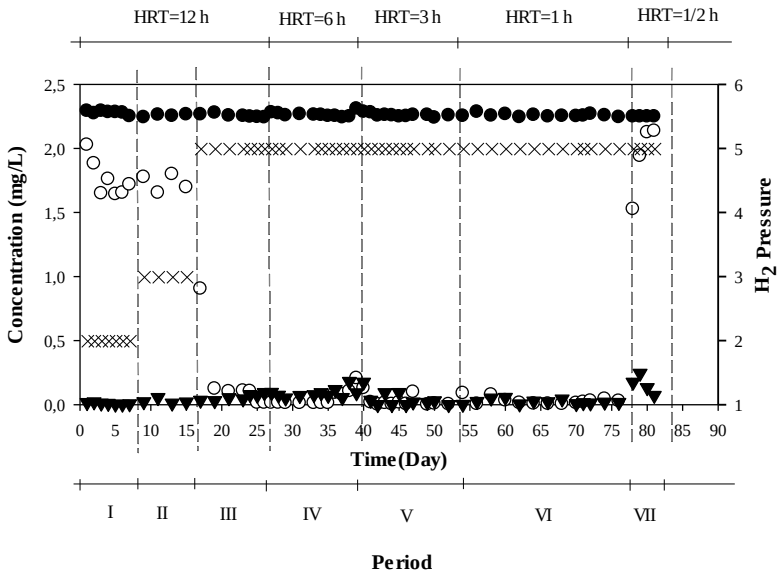

Figure 2. Effect of HRT on nitrate removal (●: Influent NO_3-N, ○: Effluent NO_3-N, ▼: Effluent NO_2-N, ×: H_2 Pressure).

In the first period, nitrate concentration was kept constant at 2.25mg N L^{-1}. Initial H_2 pressure was 2 psi, however, after 7 d of this stage H_2 pressure was increased from 2 to 3 psi to enhance nitrate reduction performance. Nitrate reduction efficiency remained similar in both periods being 25.99%. This should be due to insufficient electrons released from oxidation of the electron donating primary substrate (H_2 gas) to remove nitrate which acts as electron acceptor.

To increase the available electron donor source for the nitrate reduction, H_2 pressure was increased to 5 psi after day 17 (Period III) (Table 2). As a result, the nitrate removal efficiency of the reactor increased gradually and reached to 99% (Fig. 1). Therefore; increasing H_2 pressure had a positive effect on nitrate reduction efficiency. In the literature review, 2-3 psi H_2 pressure was mentioned to be sufficient for denitrification. The denitrification has been conducted by using gas permeable membrane. In the research, 98% of nitrate removal efficiency was obtained at 25 minutes HRT and 2.94 psi H_2 pressure (Hasar 2009b).

In period III, H_2 pressure was adjusted to 5psi. In this period the nitrate removal performances of the reactor increased gradually and reached to 99%. In the second part of the study (periods IV, V, VI, and VII) the effect of HRT on nitrate removal was investigated in H_2 based MBfR. Between days 26 and 39 (Period IV), HRT was decreased and reactor was operated at 6h HRT with unchanged H_2 pressure (5psi). In this period, nitrate removal efficiency was similar to previous period in which 12h HRT was applied. The decrease in HRT did not adversely affect nitrate removal performance, which was still above 99%. In the following two periods (Periods V and VI), HRT was decreased to 3 and 1 h, respectively. The results were similar to previous periods, and H_2 based MBfR was adapted well to the nitrate degrading conditions. In following stage, the HRT was decreased from 1 h to 0.5 h. In this stage (Period VII), the nitrate removal performance of the reactor decreased suddenly (Fig. 2). The nitrate reduction efficiency was dropped to 14%, which should be due to insufficient reaction time for H_2 oxidation and nitrate reduction. No nitrite accumulation was observed during operational conditions.

Nitrate removal flux was also used as an indicator of denitrification capacity. The application of H_2 pressure and HRT to the H_2 based MBfR showed important effects on the rate of nitrate reduction especially. For these reason, another parameter used for evaluating denitrificaton performance within the system was nitrate removal flux. The results were shown in Fig. 3.

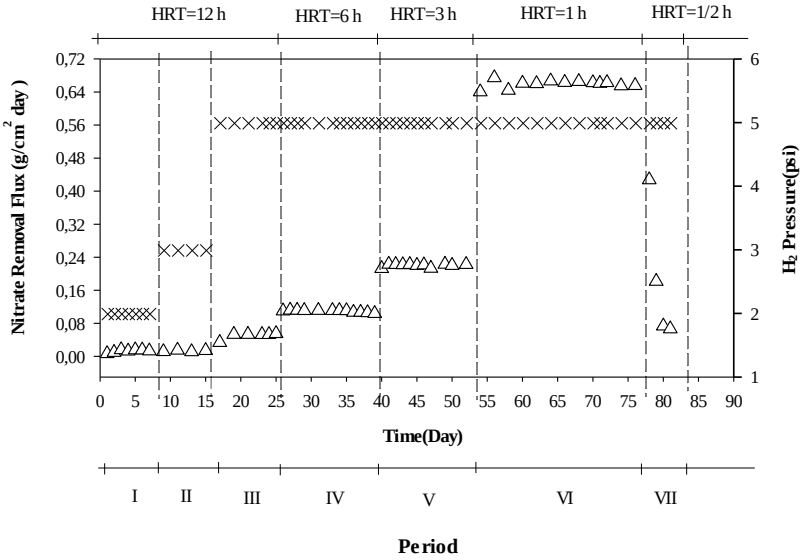

Figure 3. Nitrate removal flux in different hydraulic retention and hydrogen pressure (Δ: Nitrate removal flux, ×: H_2 Pressure).

Figure 3 illustrates the nitrate removal flux under each of the study periods. The nitrate removal flux showed similar profile to that of nitrate removals in Fig.2. During period I and II, the similar values were observed at H_2 pressure of 2 and 3 psi corresponding to 0.012 $N0^-_3/cm^2$.d nitrate removal fluxes. After day 17 H_2 pressure was increased to 5 psi (period IV). According to these results increase in H_2 pressure has enhanced the respiratory activity of the microorganism, which was correlated with the increased nitrate removal fluxes observed during period III. In this period nitrate removal flux approached to 0.05 $N0^-_3/cm^2$.d. The obtained results showed that the number of electrons was greater than the number of unoccupied electron levels of nitrate, thereby the higher unoccupied electron level was filled up resulted in higher nitrate reduction. Afterwards, the HRT was decreased from 12 h to 6 h in period IV and similar nitrate removal flux of 0.109 $N0^-_3/cm^2$.d was attained. However when HRT was dropped to 3h in period V, nitrate removal flux was increased to 0.22 $N0^-_3/cm^2$.d. It was due to increase in denitrification performance of the system. Similar to our result Rittmann *et al.* (2011), conducted that increase in denitrification was resulted from decrease in HRT. They observed an increase in nitrate removal flux by raising influent flow rate from 0,016 mL min^{-1} to 0,037 mL min^{-1}, and reducing HRT. After day 52, HRT was decreased from 3h to 1h (period VI). As expected, nitrate removal flux was relatively increased and approached to 0,659 g $N0^-_3$- N/cm^2.d (3.01 g $N0^-_3/cm^2$.d).

However, nitrate removal flux during period VII decreased as the HRT of the reactor was decreased to 0.5 h. The nitrate removal flux of 0,659 g $N0^-_3$- N/cm^2.d was decreased gradually and approached to 0.19 g $N0^-_3$- N/cm^2.d. Because the H_2 pressure of the MBfR was held constant at 5psi, this suggests that nitrate removal flux decreased as HRT was decreased. According to our results, HRT of 1 h and H_2 pressure of 5 psi was optimum for nitrate removal in H_2 based MBfR. In recent years, Chen *et al.* (2017), Zhou *et al.* (2018), Wu *et al.* (2018) and Chen *et al.* (2019) were studied on hydrogen-based membrane biofilm reactors as similar to our study.

CONCLUSIONS

In this study, nitrate reduction by H_2 based MBfR was investigated. Nitrate removal was enhanced as the H_2 pressure was increased from 2 to 5 psi at constant HRT of 12 h. The maximum nitrate removal was observed under H_2 pressure of 5psi. Afterwards, effect of HRT was investigated in the range of 12 h to 0.5 h at 5psi H_2 pressure. Nitrate removal was stable until HRT was being 0.5 h. Our results show that nitrate removal decreased remarkable as HRT was decreased to 0.5 h which was quite low. Additionally, nitrate removal flux is a good indicator of denitrification capacity that takes place on membrane surface. Denitrification capacity increased directly proportional to increased H_2 pressure. This research showed that H_2 based MBfR is effective for removing nitrate from the contaminated groundwater.

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