Simultaneous removal of nitrate and pesticide endosulfan in groundwater using membrane biofilm reactor

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Abstract

Aim: In this study, a hydrogen-based membrane biofilm reactor (H₂-MBfR) was operated to investigate the simultaneous removal of endosulfan and nitrate.

Methodology: The MBfR was fed with synthetic groundwater prepared and operated at constant pH (7.2) and temperature (30 °C). The membrane bundle consisted of 40 hollow fiber membranes with an active length of 10 cm and surface area of 0.0078 m². The H₂-MBfR was operated for 237 days with varying influent nitrate concentrations (2.25-10 mg N l⁻¹), hydraulic retention times (HRT, 0.5-12hr), hydrogen pressures (2-6psi), and endosulfan concentrations (0.1-10 µg l⁻¹).

Results: The study results showed that complete denitrification and endosulfan removal above 99% could be achieved when influent endosulfan concentration was 1 µg l⁻¹ with an HRT of 1 hr, nitrate concentration of 10 mg N l⁻¹, and H₂ pressure of 6psi. Increasing endosulfan concentration to 10 µg l⁻¹ decreased denitrification rate from 99 to 93%.

Interpretation: The H₂-MBfR presented here has proved to be efficient for depuration of water contaminated with nitrate and pesticide endosulfan.

Key words: Drinking water, Endosulfan, H₂-MBfR, Nitrate

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Introduction

Contamination of groundwaters; which are the major source of drinking water; is mainly contaminated with nitrogen and pesticide originating from the use of chemical fertilizers is a matter of concern. Nitrogen is mainly found in groundwaters in the form of nitrate and nitrite nitrogen. High nitrate level in water can cause methemoglobinemia or blue baby disease in humans, especially in infants under six months (Westerman and Bicudo, 2005; Mirvish, 2013; Ozturk *et al.*, 2013; Hakeem *et al.*, 2011, 2017). EPA's maximum contaminant level for nitrate set to 10 mg/L, whereas the drinking water Directive (98/83/EC) sets a maximum allowable concentration for nitrate of 50 mg l⁻¹. Besides, pesticides such as endosulfan are highly toxic chlorinated organic compounds even if in micro levels, and due to long half-lives, they are highly persistent in the environment (Nerenberg and Rittmann, 2004). Endosulfan concentration is often low compared to surface waters which ranges between (0.21 – 54 ng l⁻¹) (ATSDR, 2015). These contaminants adversely affect ecological system and threaten human health through drinking water (Ozturk *et al.*, 2012; Feng *et al.*, 2015), therefore, increasing chemical pressure in drinking water supplies. Therefore, there is need to take these into account.

Removal of nitrogen has become one of the most important concerns in water pollution control (Rittmann and Asce, 2009). Biological nitrogen (N) removal is widely performed by autotrophic nitrification coupled to heterotrophic denitrification. In general, nitrification requires anaerobic environment for oxidation of ammonium to nitrite (phase I) and then to nitrate (phase II) whereas heterotrophic denitrification occurs by utilizing organic electron donors under anoxic condition. However, groundwaters contaminated with nitrate have almost no organic carbon, the heterotrophic denitrification process remains inoperative. The autotrophic denitrification which uses inorganic electron source makes it a sustainable solution (Shin *et al.*, 2015; Ergas and Reuss, 2001; Lee and Rittmann, 2002).

Autotrophic denitrification can be achieved by so many inorganic electron donors such as hydrogen (Puig *et al.*, 2012), sulfur compounds (Zang *et al.*, 2018) and ferrous iron (Di Capua *et al.*, 2015). The suspended and attached growth profiles have often been applied. The attached growth provides conditions favoring efficient autotrophic denitrification process. At this point, membrane biofilm reactor (MBfR) would be ideal for the reduction of oxidized contaminants (Martin and Nerenberg, 2012; Ontiveros-Valencia *et al.*, 2012; Zhou *et al.*, 2017; M. Ziv-El *et al.*,). When hydrogen gas is supplied from the interior of membrane, an autotrophic biofilm layer forms on the membrane surface and suitable environmental conditions for denitrification are provided. This H₂-based MBfR has advantage of high gas utilization efficiency, low energy consumption and small reactor volumes (Martin *et al.*, 2012).

Studies related to simultaneous removal of nitrate and pesticides are scanty. To our knowledge, no study on the removal of endosulfan from ground water is available by MBfR. Most studies in this connection have been carried out involving the simultaneous removal of nitrate and pesticides in wastewater treatment system with external organic carbon sources (Rittmann, 2006, Choi *et al.*, 2006; Ginige *et al.*, 2004). However, we have focused on the evaluation of MBfR performance in terms of its potential for simultaneous removal of nitrate and endosulfan from groundwater. MBfR was operated under varying operational conditions for maximum removals from groundwaters.

Materials and Methods

Membrane biofilm reactor (MBfR) set-up and operational conditions : Fig.1 shows a schematic diagram of MBfR used in this study. Hollow-fiber membranes (P5S polypropylene) with inner diameter of 0.24 mm, outer diameter of 0.31 mm, and pore size 0.1 µm was supplied from Zena Membranes Company (The Czech Republic). Membrane bundle was placed centrally within glass reactor (Fig.1). The membrane bundle consisted of 40 hollow fiber membranes with an active length of 10 cm and surface area of 0.0078 m². Reactor was connected to H₂ tank with pressure ranging from 2 to 6 Psi. The active working volume of MBfR was determined as 0.5 l. MBfR was operated at constant pH of 7.2 and temperature 30°C, respectively. Additionally, MBfR was operated at continuous mode and influent flow rate was adjusted by a Masterflex peristaltic pump (Cole-Parmer Instrument Co., Chicago, IL) to perform varying HRTs, according to the experimental plan (Table1). A magnetic stirrer was used to mix the liquid in the reactor at 500 rpm. Influent dissolved oxygen was kept below 0.1 mg l⁻¹ by continuously purging nitrogen gas. pH, ORP and DO changes during the reaction were monitored continuously using a pH electrode (Mettler Toledo, Switzerland), ORP meter (Mettler Toledo, Greifensee, Switzerland) and DO electrode (Hamilton, Switzerland), respectively.

The performance of MBfR was evaluated for 237 days (Table1). Denitrification process in MBfR was optimized in Period I (days 0-25) and II (days 26-73) at varying H₂ pressures (2-6) and HRT (0.5-6). NO₃-N concentration and HRT in period I was kept constant at 2.25 mg l⁻¹ and 12 hr, respectively. In period II, H₂ pressure was adjusted to 6 psi and the effect of HRT was tested. In period III (days 74-133), MBfR was operated at 6 psi H₂ pressure and 1 hr HRT; the effect of NO₃-N concentration in the range of 2.25-10 mg l⁻¹ was tested. Afterwards, the effect of endosulfan concentration (0.1-15 ng l⁻¹) on denitrification process was carried out. During the study, the temperature and pH were kept constant at 7.2 and 30°C, respectively. H₂ pressure was continuously monitored during the whole study period. Sampling was performed in MBfR effluent for measuring dissolved oxygen, pH, NO₃, NO₂, endosulfan to determine the system performance in the bulk liquid. All data were processed in duplicate and mean values were taken.

Fig. 1 : Schematic diagram of MBfR designed.

Table 1 : Experimental plan

Parameters	Periods			
	I	II	III	IV
Days	0–25	26–73	74–133	134–237
HRT (hr)	12	6-0.5	1	1
NO ₃ -N concentration(mg l ⁻¹)	2.25	2.25	2.25-10	10
Nitrate flux (mgNO ₃ ⁻ -N cm ⁻² .d)	0.029	0.116-0.69	0.346-1.54	1.54
H ₂ pressure (psi)	2-5	5	5-6	6
Endosulfan concentration (ng l ⁻¹)	-	-	-	0.1-15

Simulated groundwater and culture : MBfR was fed with synthetic ground water prepared daily. Synthetic feeding water consisted of macro and micro nutrients necessary for microorganism's growth. Trace element stock solution consisted of ZnSO₄.7H₂O 100 mg l⁻¹, MnCl₂.4H₂O 30 mg l⁻¹, H₃BO₃ 300 mg l⁻¹, CuCl₂.2H₂O 10 mg l⁻¹, Na₂SeO₃ 30 mg l⁻¹, NiCl₂.6H₂O 10 mg l⁻¹ and CoCl₂.6H₂O 200 mg l⁻¹ chemicals. Synthetic ground water was prepared by adding 1 ml of trace element stock solution to synthetic feeding water containing 252 mg l⁻¹ NaHCO₃, 33 mg l⁻¹ KH₂PO₄, 50 mg l⁻¹ MgSO₄.7H₂O and 10 mg l⁻¹ NO₃.

Bacteria culture responsible for denitrification was originally enriched with activated sludge sample taken from domestic treatment plant located at Kayseri, Turkey. Additionally, MBfR was inoculated with sludge sample taken from denitrification tank in Seyhan Wastewater Treatment Plant Adana, Turkey. H₂ gas as electron donor and nitrate as electron acceptor source were used for bacterial population. Endosulfan was procured from Sigma Aldrich Chemical Company (USA) and was 98% pure.

Analyses : 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 8 mM sodium carbonate (Na₂CO₃) and 1.5 mM sodium hydroxide (NaOH) was prepared and used for nitrate and nitrite ion analyses at a flow rate of 1 ml min⁻¹.

Endosulfan was measured following liquid-liquid extraction. Solvent used for extraction was cyclohexane. Extracted endosulfan was estimated with Shimadzu 2010 (GC-MS, Shimadzu, Kyoto, Japan) gas chromatograph equipped with a split-splitless auto-injector model AOC-20i. A silica capillary column (TRB5MS), (30mx0.32mmi.d) with a 0.25 µm thickness was used for GC separation. Helium was used as carrier gas at a constant flow of 1.21 ml min⁻¹. The temperature of injection port was 240°C and 1 µl volume was injected in splitless mode. Initial temperature was 60°C and increased to 180°C at the rate of 40°C min⁻¹, this temperature was maintained for 2 min. Afterwards, temperature was increased to 280°C at the rate of 5°C min⁻¹. During electron impact, ionization mode an ionizing energy of 63

eV, and ion source temperature of 200°C was used. The accuracy of determination was routinely checked by using standard samples containing known amount of endosulfan. The limit of detection for endosulfan ranged from 0.001–0.1 ng ml⁻¹ and the precisions ranged from 2.5–5.9%.

Results and Discussion

Effect of HRT on nitrate removal performance : The effect of HRT on nitrate removal was investigated in H₂ based MBfR (periods I, and II). The reactor was operated at 12 hr HRT with

various H₂ pressure (2–5 psi) between 0 and 25 days (Period I), (Fig. 2). In this period, nitrate removal efficiency was relatively low (23%) and increasing H₂ pressure to 3 psi had no effect on MBfR performance corresponding to 0.029 mg NO₃⁻N cm⁻².d nitrate removal fluxes. After day 21, H₂ pressure was increased to 5 psi (Fig. 2). According to these results, increase in H₂ pressure enhanced the respiratory activity of microorganism, which was correlated with the increased nitrate removal fluxes. The obtained results showed that the number of electrons was greater than the number of unoccupied electron levels of nitrate, thereby the

Fig. 2 : Effect of HRT on nitrate removal performance.

Fig. 3 : Effect of nitrate concentration on H₂-based MBfR performance.

higher unoccupied electron level was filled up resulting in higher nitrate reduction. After day 25, HRT decreased step wise from 6-0.5 hr corresponding to 0.116-0.69 mg $\text{NO}_3^- \text{N cm}^{-2} \cdot \text{d}$ nitrate removal fluxes (period II). Nitrate removal efficiency reached to about 99% and H_2 based MBfR was adapted well to the nitrate degrading conditions. Van Ginker *et al.* (2011) have obtained the results similar to ours. They concluded that increase in denitrification resulted from decrease in hydraulic retention time. They also observed an increase in nitrate removal by raising in fluent flow rate from 0.016 ml min^{-1} to 0.037 ml min^{-1} , and reducing hydraulic retention time. However, in the last period, when HRT decreased from 1 hr to 0.5 hr, the nitrate removal performance of the reactor decreased suddenly corresponding to 1.54 mg $\text{NO}_3^- \text{N cm}^{-2} \cdot \text{d}$ nitrate removal flux (Fig.2). The nitrate reduction efficiency dropped to 5.51%, which should be due to insufficient reaction time for H_2 oxidation and nitrate reduction. No nitrite accumulation was observed during operational conditions.

Effect of nitrate concentration : The effect of nitrate concentration was investigated in H_2 based MBfR in Period III (days 74-133). Reactor was operated at 1 hr HRT at various nitrate concentrations (2-10 mg $\text{NO}_3^- \text{N}$) (Fig. 3). Days 74-85 nitrate removal efficiency was relatively low (23%) and increasing nitrate concentration to 5 mg l^{-1} at 5 psi pressure had no effect on nitrate removal performance, corresponding to 0.77 mg $\text{NO}_3^- \text{N cm}^{-2} \cdot \text{d}$ nitrate removal flux. Hasar (2009) studied nitrate flux in the MBfR in the range of 4–8 g $\text{N m}^{-2} \cdot \text{d}$ and achieved almost complete denitrification. Nitrate removal improved later, when H_2 pressure increased to 6 psi, corresponding to 99% nitrate removal efficiency (Xia *et al.*, 2010). Similarly, Lee and Rittmann (2002)

and Schnobrich *et al.* (2007) had achieved complete denitrification by increasing hydrogen pressure. Nerenberg *et al.* (2002) achieved maximum nitrate removal of 99% at 2.5 psi H_2 pressure and reported that higher hydrogen pressures did not increase nitrate removal. However, when nitrate concentration increased to 10 mg l^{-1} , flocculations were observed initially and nitrite was observed in effluent. After day 125, the reactor was almost stable and over 99% nitrate removal was observed without nitrite accumulation.

Effect of endosulfan concentration on denitrification : The effect of endosulfan concentration on nitrate removal was investigated during the days 134-237 (period IV, Table. 1). Fig. 4 shows nitrate removal profile at various endosulfan

Fig. 4 : Effect of endosulfan on nitrate removal.

Fig. 5 : Endosulfan removal.

concentrations, while Fig. 5 shows endosulfan removal profile. The results revealed that nitrate removal was not adversely affected by endosulfan, and endosulfan removal was over 99% in H₂-based MBfR. Only small increase in effluent endosulfan and nitrate was observed when endosulfan concentration was 10 ng l⁻¹. Additionally, endosulfan had a tendency to accumulate in the reactor when influent concentration was set to above 1 ng l⁻¹ (Fig. 5), which was confirmed by increase in influent endosulfan values. Aslan and Turkman (2004) had achieved complete nitrate removal below 1000 µg l⁻¹ endosulfan (α+β) concentration and they stated that above this concentration value microbial activity was inhibited.

In this study, nitrate reduction by H₂ based MBfR was investigated under endosulfan availability. Our results showed that nitrate removal decreased remarkably as HRT was decreased and increased directly proportional to increase in H₂ pressure. Simultaneous endosulfan (15 ng l⁻¹) and nitrate (10 mg l⁻¹ NO₃-N) removal was achieved with high efficiencies (over 99%). The results of this study clearly demonstrated that H₂ based MBfR was effective for removing simultaneous endosulfan and nitrate from the contaminated ground waters. Therefore, the MBfR proposed could help in reducing the pesticide contamination in ground water and will be useful to meet drinking water standards where ground water is used as drinking water source. Additionally, high removal rates obtained from this reactor operation showed that additional treatment unit is not needed. However, pretreatment should be taken into account to remove suspended solids before MBfR operation along with disinfection after treatment.

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