

Full Paper

## Groundwater Denitrification by Using MBBR With KMT Packing

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### ABSTRACT

Many communities in the world use groundwater as a source of potable water. The high nitrate concentration is a serious problem in groundwater usage. This study utilizes a biological denitrification method to investigate a moving bed biofilm reactor (MBBR) for the case of Tehran's groundwater. One pilot-scale MBBR with a 3 liter volume was designed and used in this research. The denitrification reactor operates under anoxic conditions. Methanol was used as a carbon source in the reactor throughout the study, and fifty percent of the reactor volume was occupied with KMT packing ( $k_1$ ). To determine the optimum nitrate loading rate, the concentration of nitrate changed from 100 to 400 mg N/l. It was concluded that heterotrophic denitrifying bacteria converted nitrate to nitrogen. According to obtained results, the removal efficiency and optimum loading rate were estimated during the experiments in different concentrations and different HRTs for this type of reactor. Sodium nitrate was in the feed source in the anoxic reactor. The maximum removal rate of nitrate was measured to be 2.8 g of  $\text{NO}_3\text{-N m}^{-2}$  carrier  $\text{d}^{-1}$ . Therefore, it was shown that the optimum loading rate of nitrate and the optimum COD/N were equal to 3.2 g of  $\text{NO}_3\text{-N m}^{-2}$  carrier  $\text{d}^{-1}$  and 6 g of COD/g N respectively.

### 1. Introduction

Groundwater safety is a notable concern because many people consume more than 50 % of their potable water from groundwater [1]. In many agricultural states, this percentage even goes beyond 50 %. About 50 million people rely on groundwater in the areas identified as vulnerable to agriculturally polluted groundwater. The nitrate contamination of groundwater sources is one of the consequences of anthropogenic

activities associated with agriculture and farming. The nitrate concentration was observed as more than 40 mg of N/l in some areas while the WHO guideline value is 10 mg of N/l [2]. There are many wells in Tehran, of which the nitrate content is more than standard values and their concentrations reach 100 mg of  $\text{NO}_3\text{/l}$ . Therefore, they remain unused.

Methemoglobinemia is a health condition induced by the nitrate contamination, and that is when nitrate is ingested by infants and

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carcinoma also can be a potential disease when nitrate is transformed into nitrosamines [3]. Some physical and chemical processes such as reverse osmosis (RO), ion exchange (IE), and electrodialysis (ED) are applied to denitrificate groundwater; however, biological processes are replacements as economical operations.

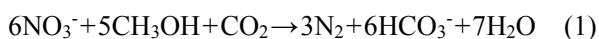
The biological denitrification can use autotrophic bacteria or heterotrophic Bacteria and hydrocarbons to consume nitrate and convert it to nitrogen gas [3]. The biological denitrification can be performed in attached or suspended growth processes. For water treatment many different biofilm systems can be used. The fixed bed bioreactor (FBBR), membrane bioreactor (MBR), Upflow anaerobic sludge blanket (UASB) and fluidized bed reactors (FBR) are some examples of the biological reactors. The advantages can be compared. The fixed bed bioreactor is not effective in the mass transfer. It is even difficult to distribute the biomass on the whole carrier inside and outside of the surface in them. RBCs are often prone to mechanical failures. The UASB with recycle due to the need for difficult maintenance, and many of the fluidized bed reactors are not stable hydraulically. The most efficient type of biofilm reactors is the fluidized bed type due to their high solid retention time (SRT) and also the high removal rate of nitrate. The fluid bed reactor may have uncertain control of stable fluidization, high need of energy for recirculation, and problematic particle/biomass separation [4].

MBBR can be a replaced technology without the disadvantages of the fluidized bed bioreactor. The carriers are continuously in motion in a MBBR [5]. The MBBR process was developed for the first time in Norway between the years of 1980 and 1990 [6]. The company manufactured the Kaldnes media

with the specific Surface Area (SSA) of 500  $\text{m}^2/\text{m}^3$  and cylindrical shape to supply the appropriate surface with high roughness for the bacterial attach growth [6].

The MBBR are commercially successful in the process of wastewater treatment and reuse. There are presently many large-scale MBBRs in the operation in the world. Besides, there are several pilot scale MBBRs -most of which are located in Germany. The MBBR is an alternative reactor, which is the combination of the CAS process and the fluidized-bed reactor. It is a continuous stirred-tank reactor (CSTR) with continuous operation, where the small carrier grows biomass on its surface with a slightly lower density than that of water, and these carriers are in circulation inside the reactor. Gas bubbling in an aerobic reactor and, also, a mechanical stirrer in anaerobic or anoxic one can produce agitation inside a MBBR. The MBBR has been successfully applied to industrial wastewater treatments such as pulp and paper industry [7], poultry wastewater [8], dairy wastes [9], oil and gas processes and slaughterhouse waste [10], and phenolic wastewater [11]. Also, it has been applied to remove phosphor from wastewater [12]. Recently, the MBBR has been used for nitrification and the COD removal from landfill Leachate [13] and fish farming which may be suitable for the polluted water treatment [5]. Scientists demonstrated that MBBR can have many advantages such as the thick biomass growth, efficient COD removal, high resistance for fluctuations in the overloading rate and no sludge bulking problem while it can also occupy a smaller physical area for treatment [5]. Denitrification process is defined as a reduction in the nitrate content and converting it to nitrogen by denitrifying micro-organisms. Under an anoxic condition and in the presence of a

carbon source, denitrifiers use nitrate instead of oxygen as an electron acceptor. For example methanol can be used as a carbon source and energy supplier. The denitrification reaction is shown in following chemical reaction:



According to this reaction, the denitrifying bacteria can use methanol and nitrate as an electron donor and an electron acceptor respectively. Nitrate and methanol are substrates for the biomass growth.

Biofilm reactors are quite suitable for denitrification since they can be compactable and flexible. Many researchers have studied nitrification and denitrification in MBBRs. The MBBR can be applied with an MBR to improve its efficiency [14]. It also has been used for the sea-water denitrification and nitrification [15] and denitrification at low temperatures [16]. In this study, the potential of an MBBR for groundwater nitrate reduction has been investigated. For this purpose an anoxic MBBR in the pilot scale was designed and operated in different nitrate concentrations and organic loading rates (OLR).

## 2. Materials and methods

### 2.1. Characteristics of groundwater

In this study, reactors have been fed with the artificial groundwater. Tehran's potable water was used as feed in reactors and  $\text{NaNO}_3$  was applied as a source of nitrate. The concentration of  $\text{NO}_3^-$  increased from 100 mg of  $\text{NO}_3^-$ -N to 400 mg of  $\text{NO}_3^-$ -N to study its removal rate. The carbon source of the biomass growth was methanol, where the ratio of C/N was 2:1 (wt/wt). Some trace elements such as  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Cu}^{2+}$  ions were also added to the feed as micronutrients.  $\text{KH}_2\text{PO}_4$  was added to the feed as a phosphorous source with an N/P ratio of 5:1 (wt/wt).

### 2.2. Experimental set-up

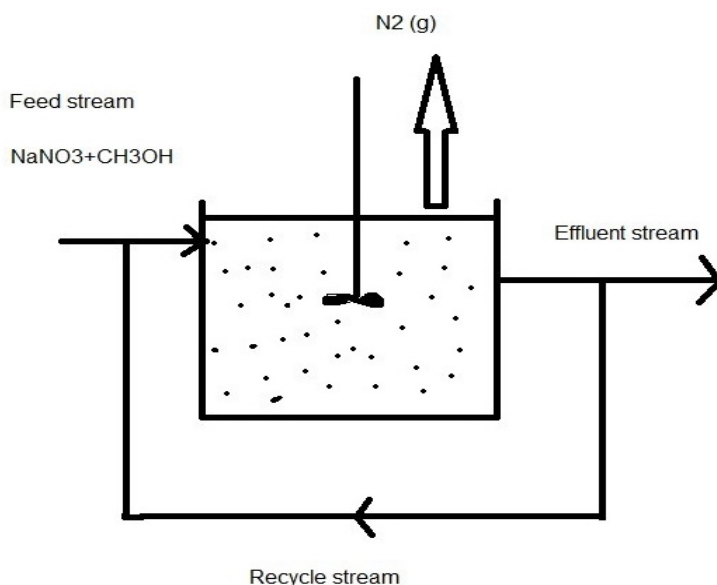
The experimental setup consists of an MBBR with the working volume of 3 L and with 50 % (v/v) packing ratio of KMT carriers (Kaldnes K1). The corrugated carrier was made of cylindrically shaped polyethylene with an active surface area of  $500 \text{ m}^2/\text{m}^3$ . The carriers can have a good circulation inside the reactor by a magnetic stirrer at 30 rpm speed and be retained in the reactor by a sieve at the outlet. The reactor was made of plexiglass in a cylindrical shape with an inside diameter of 145 mm and 185 mm length. The schematic diagram of the pilot plant is shown in Figure 1. A recycle stream returns a portion of the outlet to the reactor as a recycle flow of which the recycle ratio is 4. A Watson-Marlow pump (MHRE 200 type) is used to create this recycle ratio; however, the feed is added to the reactor by elevation.

### 2.3. Analytical Methods

The analytical tests are carried out based on the standard methods [17]. The  $\text{NO}_3^-$ -N concentration was measured by a spectrophotometer through reading the absorbance at 220 nm and 275 nm and calculated by eliminating the effect of the COD in absorption. Nitrite was also measured by the same method at 540 nm. The biomass attached to the bio-carrier was first desquamated by vibrating in a 2 glass tube, the mixed liquid was filtered through Whatman 42 filter and then dried at  $105^\circ\text{C}$  for 1 hour. The weight of the filter was measured before the filtration and after drying and decreasing the temperature to ambient temperature in the desiccator. The pH of the mixed liquor was always kept between 7.8 and 8.2 to enhance the growth of denitrifying bacteria. The dissolved oxygen (DO) in the anoxic reactor was kept below 1 mg/l. The residual methanol was

measured by the COD method to calculate the percentage of the removal. The hydraulic

retention time (HRT) changed from 4 to 24 h during the experiments.



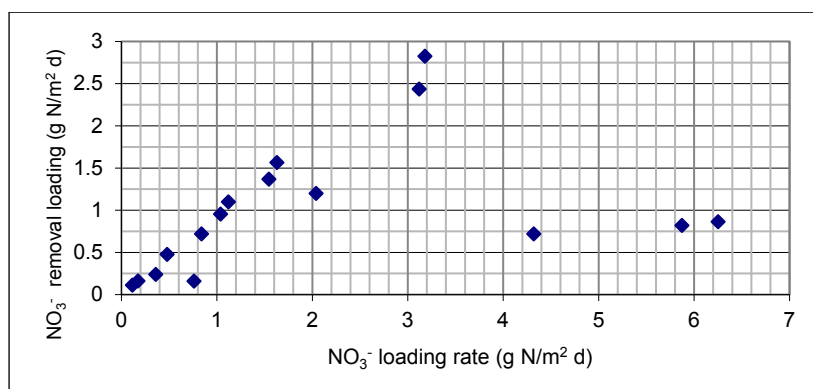
**Figure 1.** The anoxic reactor.

### 3. Results and discussion

#### 3.1. Nitrate removal

Experiments were designed to see how the changes in the over loading rate (OLR) would improve the denitrification in the MBBR and how much the optimum loading rate of the substrate in the reactor is. The anoxic reactor aims to remove nitrate from the simulated groundwater. The DO concentration reached 1 mg/l in the first few days of the batch experiment and didn't exceed that amount. The

results of batch experiments are not shown in this study. The denitrification rate was measured by increasing the volumetric loading rate from 0.11 to 6.2 g of N m<sup>-2</sup> carrier d<sup>-1</sup> during the experiment period. The results of continuous experiments after achieving steady-state conditions are shown in Figure 2. The COD and nitrate content in the output were measured at the maximum rates to determine the removal rate.



**Figure 2.** The removal rate of NO<sub>3</sub><sup>-</sup>.

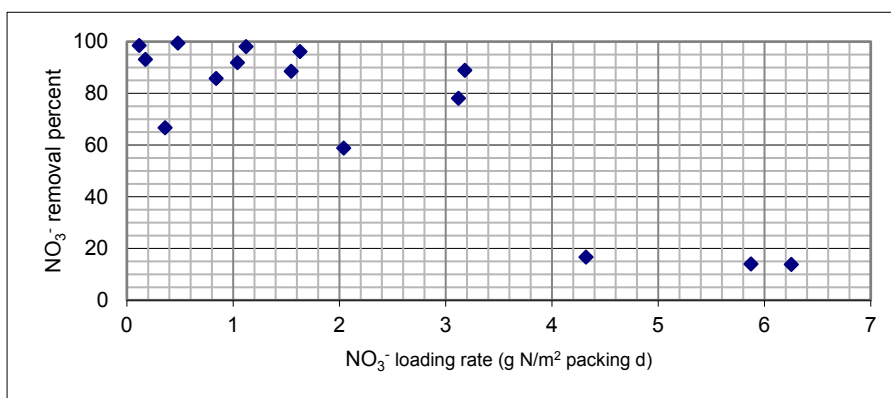
The denitrification rate has increased with increasing the load at lower rates. With a

loading rate of 3.2 g of N m<sup>-2</sup> carrier d<sup>-1</sup>, the denitrification rate reached beyond 2.8 g of

$\text{N m}^{-2} \text{ carrier d}^{-1}$ , showing the optimum loading rate of achieving the maximum removal rate of denitrification at this point. Under this optimum condition the nitrate concentration in feed was  $300 \text{ mg of NL}^{-1}$  and the HRT was 8 h. The nitrate was 80 % removed in this condition. At a lower loading rate, the substrate is not sufficient to supply food for microorganisms and, at a higher loading rate, the nitrate concentration is toxic for them. The  $\text{NO}_2^- \text{-N}$  concentration remained between 0.003 and  $5.68 \text{ mg l}^{-1}$  at the outlet.

When HRT was more than 8 h, the nitrate removal (NRP) reached beyond 60 %;

however, under this HRT, the removal suddenly got decreased to 20 %. This value was more than 80 % at a higher HRT of above 16 h. According to the experimental results, HRT play an important role in the nitrate removal from groundwater. As shown in Figure 3, NRP is expressed based on the rate of loading nitrate to the reactor. The percentage of the removal in the loading rates less than  $3 \text{ g of N m}^{-2} \text{ carrier d}^{-1}$  in the entire reactor runs was more than 60 %; however, that value suddenly decreased by 20 % in the reactor loading rate of higher than  $4 \text{ g of N m}^{-2} \text{ carrier d}^{-1}$ .

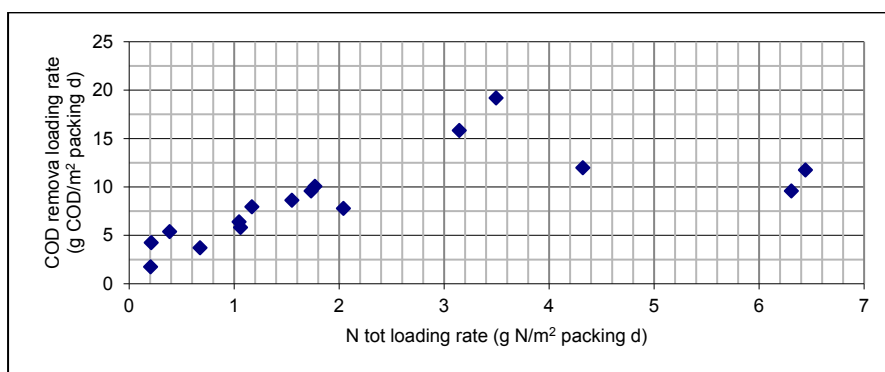


**Figure 3.** The percentage of the removal of  $\text{NO}_3^-$  versus the loading rate of  $\text{NO}_3^-$ .

### 3.2. COD removal

The COD concentration was changed from 500 to  $2400 \text{ mg l}^{-1}$  in the feed. At the outlet, the concentration varied between 80 and  $1000 \text{ mg l}^{-1}$ . The COD concentration at the outlet showed that the residual COD in the outlet was higher than that of the drinking water guideline

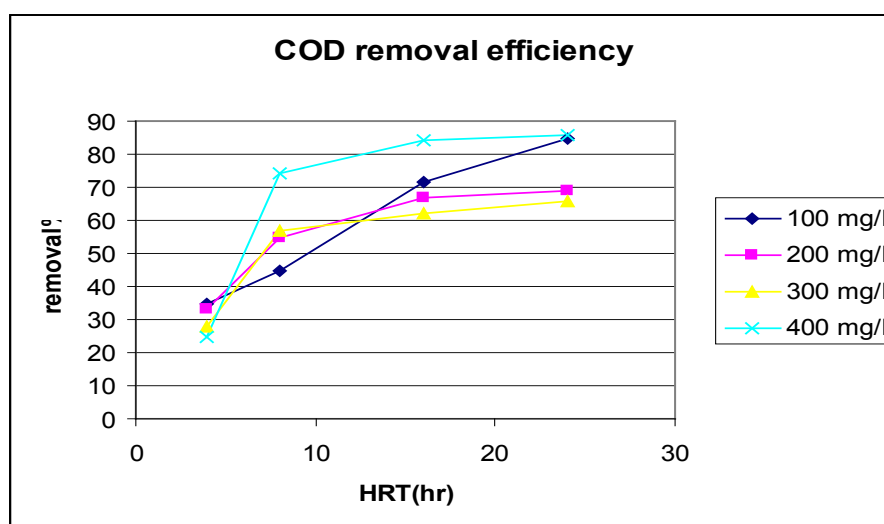
( $\text{COD} < 11 \text{ mg l}^{-1}$ ) at those loading rates when the carbon source in the influent was in excess. It is important to determine the optimum COD/N ratio because a higher-than-necessary COD/N ratio will cause a higher COD in the discharge line.



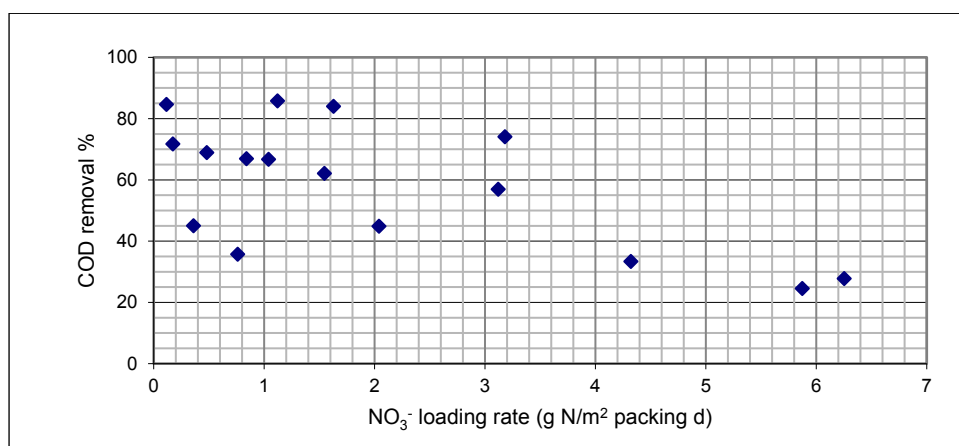
**Figure 4.** The removal rate of COD versus the loading rate of N.

The comparison between the percentage of the COD removal, HRT, and different concentrations of the nitrate in the feed during the process showed that percentage of the removal reached beyond 60 % while the HRT was more than 16 h in all the nitrate concentrations; however, it was reduced to less than 30 % when the HRT was set to 4 h. Figure 4 shows the COD removal rate at different loading rates of nitrogen. It was concluded that the maximum removal rate of COD appeared at 3.5 g of N m<sup>-2</sup> carrier d<sup>-1</sup>, which was approximately the same as the optimum loading rate of nitrate for the nitrate removal, and 0.3 g of N m<sup>-2</sup> carrier d<sup>-1</sup> was measured for other sources of nitrogen in the feed. Figure 5

also is the demonstration of the COD removal of the reactor versus the hydraulic retention time (HRT) according to the anoxic digestion by sludge. It is shown in Figure 6 that the percentage of the COD removal at different loading rates of nitrate. In loading rates lower than 5 g of N m<sup>-2</sup> carrier d<sup>-1</sup>, the percentage of removal was higher than 30 %. The anaerobic reactor showed an excellent performance in reducing COD concentrations in the groundwater. It can be the resultant of high percentage of the biodegradable carbon source and also the accumulation of the biomass on the surface of the carriers which shows high performance in the anoxic reactor.



**Figure 5.** The COD removal from the groundwater versus HRT at different nitrate concentrations.



**Figure 6.** The percentage of the COD removal versus the loading rate of nitrate.

In Figure 7, the removal rate of COD is plotted as a function of the loading rate of COD. In the loading rate ranging from 2 g of COD  $\text{m}^{-2}$  carrier  $\text{d}^{-1}$  to 25 g of COD  $\text{m}^{-2}$  carrier  $\text{d}^{-1}$ , the removal rate increased with an increase in the loading rate. The highest removal of COD

obtained in this study has been 19 g of COD  $\text{m}^{-2}$  carrier  $\text{d}^{-1}$ , which occurred at 25 g of N  $\text{m}^{-2}$  carrier  $\text{d}^{-1}$  in contrast to the highest rate of denitrification; the optimum COD/N ratio was estimated to be 6 g of COD/g N or 1.25 g C/g N.

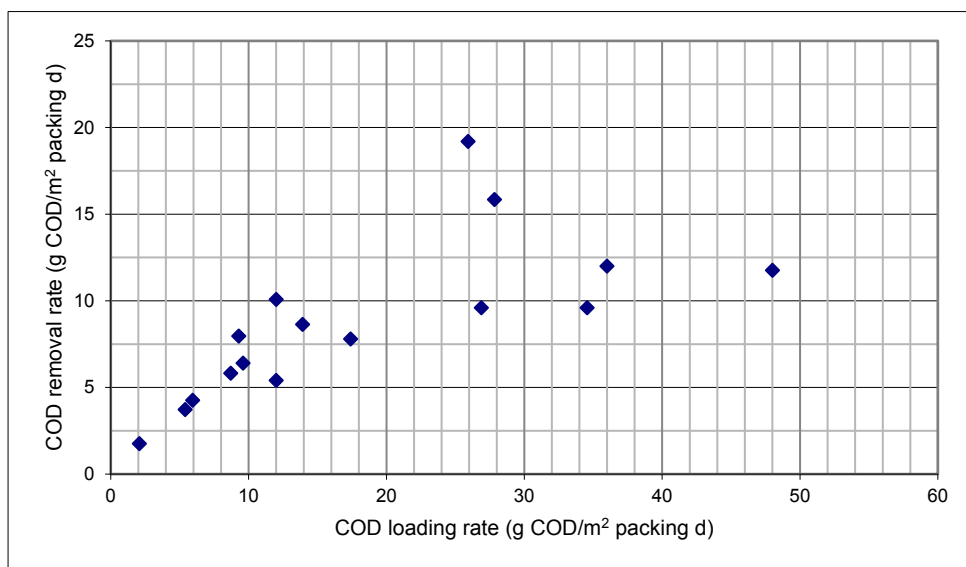


Figure 7. The rate of the COD removal.

### 3.3. Biofilm thickness

The system operated without backwashing or any clogging due to the excessive biomass. The biofilm thickness can maintain denitrifying bacteria in the reactor and can prevent the carrier from biofouling. The microscopic pictures of a carrier, taken during the experiments, were demonstrating that no fouling occurred during the experiments due to the effective biofilm growth on the surface of the carriers despite the lack of the biomass growth on the outer surfaces of the packings. In the batch experiments, the biofilm thickness was not visible; however, following the outset of the steady-state period, a thin, black and resistant layer of the biofilm was detected. Hydrodynamic shear stress by the agitation in the reactor could be in the optimum amount which could prevent biofouling during the six-month period of denitrification.

### 4. Conclusions

This study demonstrates the feasibility of a MBBR system with the KMT (Kaldnes k1) packing for Tehran groundwater treatment. The results proposed the MBBR process as a useful process for denitrification at an optimum input rate of 3.2 g of N  $\text{m}^{-2}$  carrier  $\text{d}^{-1}$ . The maximum rate of denitrification obtained under this condition has been measured as 2.8 g of N  $\text{m}^{-2}$  carrier  $\text{d}^{-1}$ , and the maximum rate of the COD removal was found to be 19 g of N  $\text{m}^{-2}$  carrier  $\text{d}^{-1}$  with an influent g C/g N ratio of 2 if methanol was used as a carbon source. The system is simple to use and can operate at high loading rates for the groundwater denitrification in areas where potable water is extracted from groundwater sources. The high cell retention time in the attached growth process can suggest high treatment efficiency

and a stable operation, making the MBBR process as an alternative for the groundwater denitrification. According to the results of this study it is recommended that, the biofilm process can be a good easy operating technology as an option to eliminate the high nitrate content of groundwater.

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