Desalination and Water Treatment
www.deswater.com
1944-3994/1944-3986 © 2012 Desalination Publications. All rights reserved
doi: 10/5004/dwt.2012.3147

Taylor & Francis
Taylor & Francis Group

45 (2012) 1–10
July

Denitrification of drinking water using a hybrid heterotrophic/autotrophic/BAC bioreactor

Reza Saeedi[a], Kazem Naddafi[b,*], Ramin Nabizadeh[b], Alireza Mesdaghinia[b], Simin Nasseri[b], Mahmood Alimohammadi[b], Shahrokh Nazmara[b]

[a]*Department of Public Health, Faculty of Health, Safety and Environment, Shahid Beheshti University of Medical Sciences, Tehran, Iran*
[b]*Department of Environmental Health Engineering, School of Public Health and Center for Environmental Research, Tehran University of Medical Sciences, P.O. BOX 14155-6446, Tehran, Iran*
Tel. +98 21 88954914; Fax: +98 21 88950188; email: knadafi@tums.ac.ir

Received 25 July 2011; Accepted 15 September 2011

ABSTRACT

The performance of a hybrid heterotrophic/autotrophic/BAC bioreactor (HHABB) for denitrification of drinking water was studied in continuous mode for several months to determine the optimal conditions. The HHABB was consisted of three compartments: ethanol heterotrophic part (EH-part), sulfur autotrophic part (SA-part) and BAC-part (including anoxic and aerobic sections). The experiments were conducted at six runs with NO_3^- loading rates ranged from 0.36 to 1.45 kgN $m^{-3}\,d^{-1}$, C:N ratios 0.53 and 0.70 and approximately constant NO_3^- concentration of 30 mgN l^{-1}. At lower NO_3^- loading rates (0.36 and 0.72 kgN $m^{-3}\,d^{-1}$), the C:N ratio 0.53 provided high denitrification efficiencies (96–99%) with very low effluent DOC and trihalomethane formation potential (THMFP) concentrations of 0.33–0.50 mgC l^{-1} and 26–41 μg l^{-1}, respectively. In contrast, at NO_3^- loading rate 1.07 kgN $m^{-3}\,d^{-1}$, an increase in C:N ratio to 0.70 was required to achieve suitable results. The aerobic BAC-part showed suitable efficiency in the oxidation of NO_2^- and removal of DOC and THMFP. This study predicted that the HHABB without the anoxic BAC-part could be as a feasible alternative for NO_3^- removal from drinking water at full-scale.

Keywords: Heterotrophic denitrification; Autotrophic denitrification; BAC; Drinking water NO_3^- loading rate; C:N ratio

1. Introduction

Contamination of groundwater resources considered as a major source of drinking water by nitrate (NO_3^-) is a worldwide public health problem. The health risk associated with the presence of NO_3^- and nitrite (NO_2^-) in drinking water at high concentrations is mainly related to the occurrence of methaemoglobinaemia, so-called "blue-baby syndrome" in infants [1–4]. The main sources of NO_3^- contamination of groundwater include fertilization in agriculture, landfill leachate, leaking septic tanks, municipal runoff and disposal of industrial and municipal raw or insufficiently treated wastewater [5–8]. In Iran, NO_3^- level in groundwater resources has been increased in recent years, so presently in some circumstances NO_3^- concentration of groundwater has been observed to be higher than the Iranian drinking water standard of 11.3 mg NO_3^- l^{-1} – N [9–11].

The conventional technologies for NO_3^- removal from drinking water are ion exchange, reverse osmosis

*Corresponding author.

and electrodialysis that require high capital and operation costs. The other disadvantage of these methods is the production of a large amount of concentrated brine as a waste by-product [12,13]. Therefore, there is an urgent need for development of cost-effective processes for NO_3^- removal from drinking water. Biological denitrification is one of the best potential alternatives for the conventional technologies. Biological denitrification is complete reduction of NO_3^- to nitrogen gas (N_2) in which NO_3^- is used as a terminal electron acceptor by denitrifying microorganisms in anoxic environment [13–15].

Biological denitrification is feasible by both heterotrophic and autotrophic organisms. Heterotrophic denitrification (HD) process that requires an organic carbon source such as glucose, methanol, ethanol, etc. as a terminal electron donor or substrate has rapid kinetics. Among the substrates used for HD process, ethanol was found to be one of the most appropriate options considering the high values of its kinetic parameters, cheapness, readily availability and lack of toxicity [16–18]. The following equation presents the overall reaction of HD process using ethanol [19].

$$0.613\ C_2H_6O + NO_3^- \rightarrow 0.102C_5H_7O_2N + 0.714CO_2 + 0.98H_2O + 0.286OH^- + 0.449N_2 \quad (1)$$

According to the above equation, in the HD process stoichiometric ratio of utilized ethanol as organic carbon to removed NO_3^- – N (C:N ratio) is 1.05. Autotrophic denitrification process can be accomplished by utilizing hydrogen gas or reduced sulfur compounds as terminal electron donor [20,21]. The overall reaction of sulfur autotrophic denitrification (SAD) process can be summarized in the following simplified stoichiometric equation [22].

$$55S^0 + 50NO_3^- + 38H_2O + 20CO_2 + 4NH_4^+ \rightarrow 4C_5H_7O_2N + 55SO_4^{2-} + 25N_2 + 64H^+ \quad (2)$$

The advantages of SAD in comparison with HD are less sludge production (lower cell yield), no need to organic substrate, low cost of elemental sulfur and fewer release of soluble microbial organic products which result in easier post-treatment [6,23,24]. HD process has also some advantages over SAD process such as rapid kinetics and alkalinity production [17].

Therefore in this study, in order to benefit from advantages of both SAD and HD processes, a hybrid heterotrophic/autotrophic denitrification process was developed and studied at four nitrate loading rates (as kgN $m^{-3}d^{-1}$) and two C:N ratios to optimize nitrate removal from drinking water. A biological activated carbon (BAC) reactor composed of anoxic and aerobic sections was used as a post treatment of the denitrification process. The anoxic BAC part expected to participate in completion of denitrification process and removal of organic matter. The aerobic BAC part also seemed to be efficient especially in removal of NO_2^- (by oxidation to NO_3^-) and organic matter from final effluent. Aside from NO_3^- removal efficiency, performance of the hybrid heterotrophic/autotrophic/BAC bioreactor (HHABB) was comprehensively investigated by measurement of turbidity, pH, alkalinity, NO_2^-, SO_4^{2-}, SO_3^{2-}, S^{2-}, ammonia nitrogen, heterotrophic plate count (HPC), dissolved organic carbon (DOC) and trihalomethane formation potential (THMFP) at influent and effluent of different parts of the bioreactor.

2. Materials and methods

2.1. Experimental set-up

The experimental set-up used in this study is schematically shown in Fig. 1. As presented in Fig. 1, the HHABB was consisted of three compartments; the first compartment is the ethanol heterotrophic reactor or "EH-part", the second compartment is the sulfur autotrophic reactor or "SA-part" and the last compartment is the BAC-part containing two sections; the anoxic BAC-part and the aerobic BAC-part. The aerobic BAC-part was aerated using an aquarium blower and an air diffuser. All part of the HHABB was constructed from plexiglas tubes. In order to study the performance of

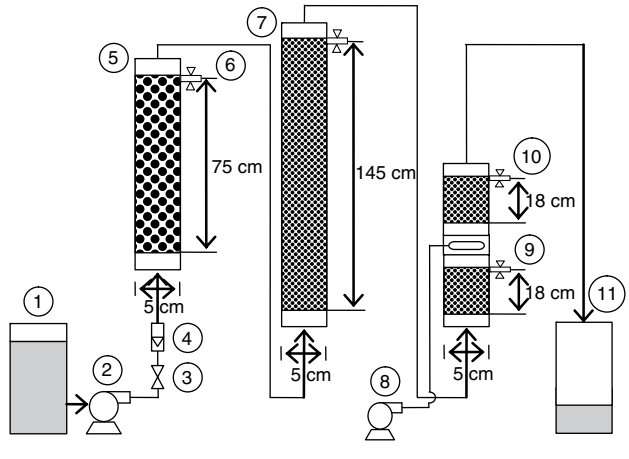

Fig. 1. The experimental set-up used in this study.

the HHABB in different parts, four sampling ports were installed on it (Fig. 1). As a fixed film bioreactor, all parts of the HHABB were packed by media for biofilm formation. The EH-part was filled with an inert packing material (Bee-Cell 2000, DANAQ, Denmark). In the SA-part, sulfur particles with irregular shape were used as both substrate and media for autotrophic biofilm growth. The growth media of BAC-part was GAC (AquaSorb® 2000, Jacobi Carbons, Sweden) which can also act as an adsorbent. According to the results of tracer tests conducted at the flow rate range applied in the denitrification experiments, the EH-part and SA-part were considered to be plug flow reactors with low dispersion (data not shown). The overall specifications of the HHABB parts are summarized in Table 1. As observed in Table 1, the effective or void volumes of the EH-part and SA-part were the same (1.3 l); therefore throughout the experiments the hydraulic retention time (HRT) values of the EH-part were equal to the values of the SA-part. Also the effective volume of each section of the BAC-part (anoxic or aerobic) was 0.22 l; therefore the HRT values of these parts were about one-sixth of the EH-part HRT.

2.2. Feed water quality

The synthetic feed solution was prepared using tap water, KNO_3, NH_4Cl, NaH_2PO_4, trace element solution and ethanol as a heterotrophic electron donor. All of the experiments were performed in approximately constant concentrations of NO_3^-, ammonia nitrogen and phosphate (as nutrients) at the values 30 mg NO_3^- – N l^{-1}, 0.5 mg NH_4^+ – N l^{-1} and 0.3 mg PO_4^{3-} – P l^{-1}, respectively. The quality characteristics of the tap water are presented in Table 2. The ingredients of the trace element solution and their concentrations were $ZnSO_4.7H_2O$ at 800 mg l^{-1}, $MnCl_2$ at 600 mg l^{-1}, $(NH_4)_6Mo_7O_{24}.4H_2O$ at 200 mg l^{-1}, $CuSO_4.5H_2O$ at 400 mg l^{-1} and $CoCl_2.6H_2O$ at 400 mg l^{-1}. The trace element solution was used at 1.0 ml per 10 l of influent water (0.01% v/v). The denitrification experiments were performed at two C:N ratios 0.53 and 0.70; based on these C:N ratios the ethanol concentrations in the influent were adjusted to 15.8 or 21.0 mgC l^{-1} at different experiments. All chemicals used in this study for preparation of influent water and quality measurement were of analytical grade.

2.3. Microbial inoculation and start-up of bioreactor

The HHABB was inoculated by some sludge collected from a full-scale wastewater treatment plant with activated sludge process. The EH-part and the BAC-part were seeded with return activated sludge and the SA-part was seeded with digested sludge. After microbial seeding, the EH-part and BAC-part in series were run in batch and recirculation mode for 45 d to enrich heterotrophic denitrifying mixed culture, to acclimatize the bacteria by the feed water (containing NO_3^- and ethanol) and to accelerate biofilm development on the media. Similarly, the SA-part was also operated in batch and recirculation mode for 45 d separately, but its feed water contained $NaHCO_3$ instead of ethanol. Following this period, the EH-part, the SA-part and the BAC-part were rearranged in series as illustrated in Fig. 1 and operated in continuous mode for 2 wk at a gradually increasing flow rate from 0.5 to 1.3 l h^{-1} to complete start-up stage.

Table 1
Overall specifications of the HHABB parts

Parameter	Unit	Value			
		EH- part	SA- part	Anoxic BAC-part	Aerobic BAC-part
Inner diameter	cm	5.0	5.0	5.0	5.0
Bed depth	cm	75	145	17	17
Bed volume	l	1.47	2.85	0.35	0.35
Void volume	l	1.3	1.3	0.22	0.22
Packing material properties					
Type	–	Polystyrene (Bee-Cell 2000)	Sulfur granule	GAC (AquaSorb® 2000)	GAC (AquaSorb® 2000)
Specific surface area	$m^2\ m^{-3}$	650	536	5.0×10^8 (very high)	5.0×10^8 (very high)
Porosity	%	87	45	65	65
Size	cm	About 1.0	0.5–1.0	0.2–0.3	0.2–0.3

Table 2
Quality characteristics of the tap water used in the influent water preparation

Quality parameter	Unit	No. of measurements	Average	Standard deviation: SD
pH	–	24	7.9	0.2
EC	µmohs cm^{-1}	24	382	19
Turbidity	NTU	24	0.4	0.1
Dissolved oxygen (DO)	mg l^{-1}	24	6.2	0.3
HPC	CFU ml^{-1}	12	94.9	58.5
Hardness	mg $CaCO_3$ l^{-1}	12	166.1	12.7
Alkalinity	mg $CaCO_3$ l^{-1}	12	114.8	5.5
Ca^{2+}	mg l^{-1}	12	52.6	3.9
Mg^{2+}	mg l^{-1}	12	8.4	4.1
Na^{+}	mg l^{-1}	12	22.7	3.3
K^{+}	mg l^{-1}	12	1.0	0.1
HCO_3^-	mg l^{-1}	12	140.1	6.8
SO_4^{2-}	mg l^{-1}	12	65.1	4.8
Cl^-	mg l^{-1}	12	18.4	2.1
NO_2^-	mgN l^{-1}	12	0.00	0.00
NO_3^-	mgN l^{-1}	40	1.7	0.4
TOC	mg l^{-1}	12	0.53	0.06
THMs	µg l^{-1}	12	20.4	2.1
Chloroform	µg l^{-1}	12	14.0	1.4
Bromoform	µg l^{-1}	12	0.7	0.3
Bromodichloromethane	µg l^{-1}	12	2.7	1.4
Dibromochloromethane	µg l^{-1}	12	2.9	0.4

2.4. Denitrification experiments

The denitrification experiments were conducted by continuous pumping the feed solution in upflow mode through the packed bed columns with a peristaltic pump. The denitrification experiments were performed at four HRT values of the EH-part (or SA-part) to be 15, 20, 30 and 60 min and approximately constant NO_3^- concentration of 30 mgN l^{-1}. The corresponding values of NO_3^- loading rates were 0.36, 0.72, 1.09 and 1.44 kgN m^{-3} d^{-1}, respectively. The related values of flow rates were also 1.3, 2.6, 3.9 and 5.2 l h^{-1}. At HRT values 30 and 60 min for the EH-part, the C:N ratio was 0.53, which is just one half of the stoichiometric value, whereas at HRT values 15 and 20 min for the EH-part, the experiments were conducted at two C:N ratios 0.53 and 0.70 (one-half and two-thirds of the stoichiometric value). The experimental runs were called as follows: the runs with flow rates 1.3, 2.6, 3.9 and 5.2 l h^{-1} and C:N ratio 0.53 to Run I, Run II, Run III, Run V and the runs with flow rates 3.9 and 5.2 l h^{-1} and C:N ratio 0.70 to Run IV and Run VI, respectively. At each experiment, the bioreactor run until steady-state condition was observed. Steady-state condition was assumed to exist when variation of sample data of three sequential sampling was less than 5%. Hence each experimental run lasted about 1 mo to obtain steady state operation. All of the experiments were conducted at room temperature (20 ± 2°C).

In order to prevent clogging of the bioreactor bed, channelization of flow in the bioreactor and short circuiting as a result of biomass accumulation and to remove entrapped gases, the HHABB was backwashed within a period of 5 min using water at a flow rate of 2–3 l min^{-1} once a week. Also after each experimental run, the packing materials were discharged from the columns, washed with de-ionized water to remove excess biomass and then reloaded in the columns.

In each experimental run, samples were collected from influent and four sampling ports located in different parts of the HHABB. To investigate the performance of the HHABB, including rate and efficiency of denitrification and its effect on physical, chemical and microbial quality of influent water, the parameters NO_3^-,

NO_2^-, pH, alkalinity, SO_4^{2-}, SO_3^{2-}, S^{2-}, ammonia nitrogen, HPC, DOC and THMFP were measured in the influent and effluent samples from desired sampling ports at predetermined time intervals.

2.5. Analytical methods

All of the quality parameters NO_3^-, NO_2^-, pH, EC, alkalinity, SO_4^{2-}, SO_3^{2-}, S^{2-}, ammonia nitrogen, HPC, DOC and THMFP were measured according to the instructions of Standard Methods [25]. For analysis of the parameters NO_3^-, NO_2^-, SO_4^{2-}, ammonia nitrogen, DOC and THMFP, samples were passed through 0.45 μm membrane filters to remove turbidity of samples. Heterotrophic bacteria were counted using pour plate method on R2A agar with incubation at 35°C for 2 d expressed as HPC in term of colony forming units per ml (CFU ml^{-1}). The parameter THMFP is the difference between the total THM_7 concentration and the initial total THM concentration (THM_0). The total THM_7 concentration was determined by 7 d reaction of each sample with free chlorine residual in the concentration ranged 3–5 mg l^{-1} at temperature of 25 ± 2°C and controlled pH at 7.0 ± 0.2 with phosphate buffer.

3. Results and discussion

3.1. Denitrification rate and efficiency: influence of nitrate loading rate and C:N ratio

Since NO_2^- is one of the intermittent products in the metabolic route of biological denitrification, in many cases, especially HD process with C:N ratios lower than the stoichiometric value, NO_2^- is accumulated in considerable amounts [17,26]. In the previous studies, NO_2^- accumulation was found as the major source of difficulty for calculation of denitrification rate and efficiency. However to solve this problem, in this study the parameter "total concentrations of NO_3^- and NO_2^- as NO_3^- concentration" was defined based on nitrogen oxidation state in these anions as below and used for calculation of denitrification rate and efficiency:

$$C_{(NO_3^-+NO_2^-)\text{ as }NO_3^-} = C_{NO_3^-} + \frac{3}{5} C_{NO_2^-} \quad (3)$$

where $C_{(NO_3^- + NO_2^-)\text{ as }NO_3^-}$ is total concentrations of NO_3^- and NO_2^- as NO_3^- concentration, $C_{NO_3^-}$ is NO_3^- concentration and $C_{NO_2^-}$ is NO_2^- concentration.

Fig. 2 shows profiles of $C_{(NO_3^-+NO_2^-)\text{ as }NO_3^-}$ values in the influent water and effluents of the EH-part and SA-part during different experimental runs. Denitrification efficiencies of the EH-part, SA-part and HHABB as a function of NO_3^- loading rate at different experimental runs are illustrated in Fig. 3. Based on the stoichiometric value

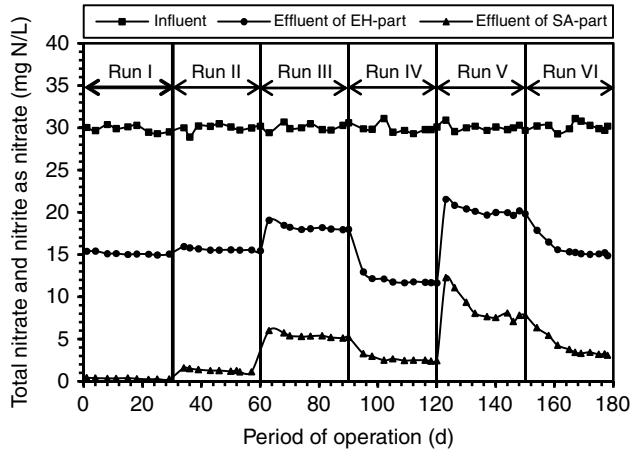

Fig. 2. Profiles of $C_{(NO_3^- + NO_2^-)\text{ as }NO_3^-}$ values in the influent water and effluents of the EH-part and SA-part during experimental runs.

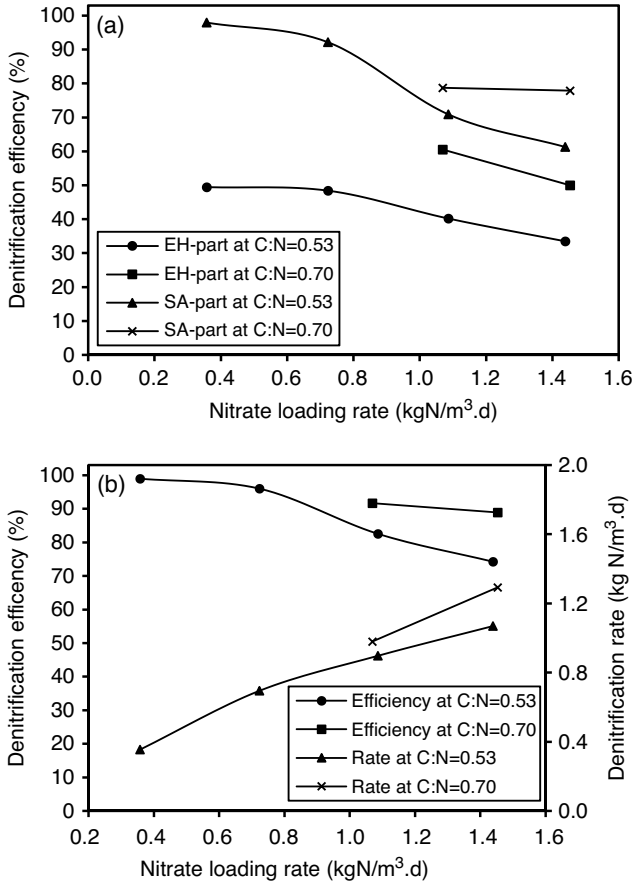

Fig. 3. Denitrification efficiencies as a function of NO_3^- loading rate at different experimental runs: (a) EH-part and SA-part and (b) HHABB.

of C:N ratio for HD process using ethanol (1.05), the maximum possible denitrification efficiencies in the EH-part were 50 and 67% for applied C:N ratios 0.53 and 0.70, respectively. Corresponding values for $C_{(NO_3^- + NO_2) \text{ as } NO_3^-}$ of EH-part effluent were 15 and 10 mgN l^{-1}, respectively. According to Fig. 2, average $C_{(NO_3^- + NO_2) \text{ as } NO_3^-}$ of EH-part effluent at HRT values 60 and 30 min (Run I and Run II) were determined to be 15.0 and 15.4 mgN l^{-1}, respectively; therefore in these cases denitrification efficiencies were 49.5 and 48.5%, respectively and approximately equal to the maximum possible ones. In these HRT values, denitrification efficiencies of the SA-part were 98.0 and 92.2% resulting in suitable total denitrification efficiencies of 99.0 and 96.0% for the HHABB with total HRT values 120 and 60 min, respectively. As shown in Fig. 3, in these cases the NO_3^- loading rates were 0.36 and 0.72 kgN /m^{-3}.d and the denitrification rates were 0.35 and 0.69 kgN $m^{-3}\,d^{-1}$, respectively.

Decreasing EH-part HRT values to 20 and 15 min at C:N ratio 0.53 (Run III and Run V) caused the overall denitrification efficiencies of the HHABB decreased to 82.6 and 74.3%, respectively (Figs. 2 and 3). A change in C:N ratio from 0.53 to 0.70 at EH-part HRT value 20 min (Run IV) improved the denitrification efficiencies of the EH-part, SA-part and HHABB to 60.6, 77.9 and 91.6%, respectively. Corresponding values of improved denitrification efficiencies due to increasing C:N ratio at EH-part HRT value 15 min (Run VI) were 50.0, 77.9 and 89.0%, respectively. Among the last four experimental runs, the best result was related to Run IV, where the total denitrification rate and efficiency of the HHABB were determined 0.98 kgN $m^{-3}\,d^{-1}$ and 91.6% (Fig. 3), respectively. The denitrification rates and efficiencies achieved in the HHABB exceeded those of the other systems for drinking water treatment reported in the literature [22,27,28]. Wang and Qu [2] reported maximum denitrification rate of a combined bioelectrochemical and SAD system to be 0.34 kgN $m^{-3}\,d^{-1}$ with a NO_3^- removal efficiency of about 90%. According to Rocca et al. [18], denitrification rate of a heterotrophic/autotrophic denitrification process was in the range of 0.19–0.28 kgN $m^{-3}\,d^{-1}$.

Fig. 4 represents variations of NO_2^- concentration at different experimental runs in the effluent of EH-part and SA-part. As shown in Fig. 4, NO_2^- accumulation in the effluent of EH-part decreased through increasing HRT and C:N ratio, so the highest NO_2^- concentration was 15.1 mgN l^{-1} which observed at NO_3^- loading rate 1.44 kgN $m^{-3}\,d^{-1}$ and C:N ratio 0.53 (Run V). In this NO_3^- loading rate an increase in C:N ratio to 0.70 (Run VI) decreased NO_2^- concentration of EH-part effluent to 11.2 mgN l^{-1}. At all of the runs, a portion of accumulated NO_2^- was removed in the SA-part by conversion to N_2 gas.

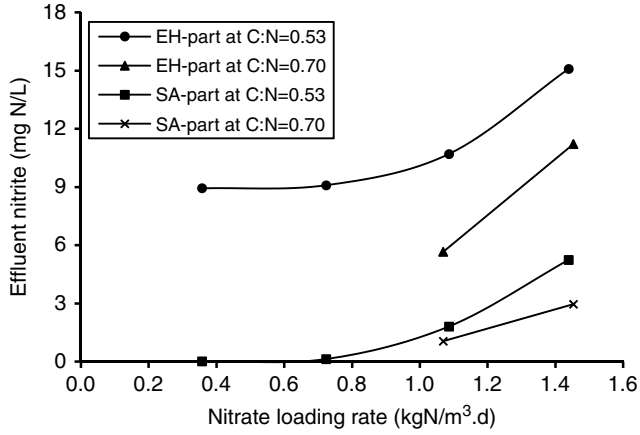

Fig. 4. Variations of NO_2^- concentration at different experimental runs in the effluent of EH-part and SA-part.

The anoxic BAC-part had not any effect on the denitrification process; therefore its effluent data is not presented here. The effect of aerobic BAC-part on the NO_2^- and NO_3^- concentrations of final effluent is presented in Fig. 5. As indicated in Fig. 5, a considerable amount of remained NO_2^- in the effluent of SA-part was oxidized to NO_3^- in the aerobic BAC-part through nitrification process. NO_2^- is known as a toxic and biologically instable compound that causes microbial regrowth in water distribution network. NO_2^- can be chemically oxidized to NO_3^- using chlorine gas (Cl_2) and other chemical oxidizing agents. McAdam and Judd [29] utilized chlorine gas for removal of NO_2^- in effluent of a membrane bioreactor. In this investigation, the chlorine demand of NO_2^- oxidation was determined to be 5.0 mgCl_2 mg^{-1} NO_2^- – N. According to Figs. 4 and 5, at NO_3^- loading rate

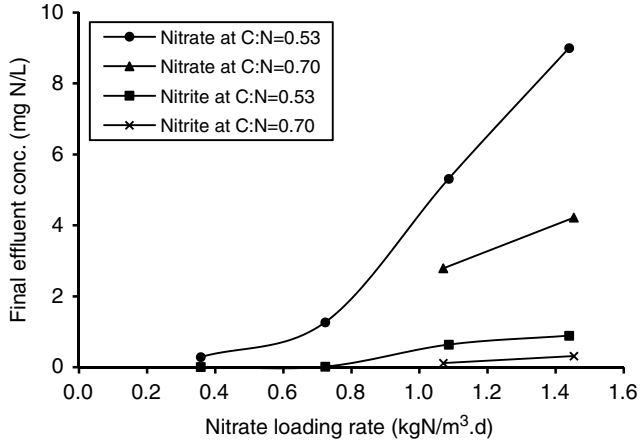

Fig. 5. The effect of aerobic BAC-part on the NO_2^- and NO_3^- concentrations of final effluent.

0.36 kgN m^{-3} d^{-1} the NO_2^- concentration in the effluent of SA-part is very low (<0.01 mgN l^{-1}) and further reduction was not observed in the aerobic BAC-part, but at other runs the aerobic BAC-part decreased the NO_2^- concentrations from 0.12–5.23 to 0.02–0.88 mgN l^{-1}. Although the guideline value of NO_2^- is 0.9 mgN l^{-1} and in all of the scenarios final effluent concentration of NO_2^- was lower than the guideline, but due to the problems occur in the water distribution system, complete removal of NO_2^- is recommended by increasing HRT in the aerobic BAC-part or use of chemical oxidizing agents.

3.2. Effect on DOC and THMFP

One of the most important concerns associated with the use of biological processes for treatment of drinking water is liberation of DOC in the effluent water which acts as a precursor of disinfection by-products (DBPs). In the biological processes, effluent DOC is derived from soluble microbial products (SMPs) and organic substrate added into the influent water [29]. Fig. 6 shows the average concentration of DOC and THMFP in the influent, effluent of EH-part, SA-part and BAC-part (final effluent) at different runs. The anoxic BAC-part had not any effect on the concentration of these parameters; therefore its effluent data is not presented. The main component of THMFP was chloroform which formed over the 84% of THMFP concentration in all of the experiments (data not shown). Measurement of the parameter THMFP indicated that the influent THMs (THM_0) in concentration 20 ± 2 μg l^{-1} was completely removed within the EH-part in all of the cases.

As observed in Fig. 6, DOC concentration in the effluent of EH-part at Run I and Run II was very low (lower than 1.0 mgC l^{-1}). This parameter increased considerably at flow rates 3.9 and 5.2 l h^{-1}. These results were confirmed by denitrification data obtained in these cases. According to the DOC and denitrification data, at Run I and Run II all of the DOC concentration in the EH-part effluent was related to SMPs whereas at Run III to Run VI, both SMPs and ethanol formed the effluent DOC concentration. In the SA-part at Run I and Run II, the effluent DOC and THMFP were slightly higher than their influent values (effluent DOC and THMFP of EH-part) as a result of SMPs release in SAD process. In contrast, at Run III to Run VI DOC and THMFP were removed in the SA-part efficiently (Fig. 6). This result indicated that HD process was continued in the SA-part when the SA-part influent water contained biodegradable organic matter.

In all of the experiments, aerobic BAC-part had an important role in the reduction of DOC and THMFP; so its efficiency in the removal of these parameters were in the ranges of 23–66% and 29–65%, respectively. The final effluent concentrations of THMFP at Run I and Run II were 22 and 42 μg l^{-1}, respectively. These THMFP concentrations were approximately equal to the ones in the influent water (34 μg l^{-1}). But at other experimental runs, DOC and THMFP values of final effluent exceeded over the influent values; so the maximum DOC and THMFP concentrations of final effluent were 2.7 mgC l^{-1} and 213 μg l^{-1}, respectively which related to Run VI. At three experimental runs (Run I, Run II and Run IV) out of six ones, the final effluent concentration of THMFP and DOC were relatively low and did not required any further treatment. Soares [22] reported DOC concentration in the effluent of a SAD reactor increased about 3 mg l^{-1} higher than those in the influent. In contrast, McAdam and Judd [29] by using a membrane bioreactor under carbon limited condition (C:N ratios ranged 0.7–1.5 with ethanol as substrate) controlled DOC concentration of the effluent and achieved to 0.4 mgC l^{-1} as effluent DOC concentration.

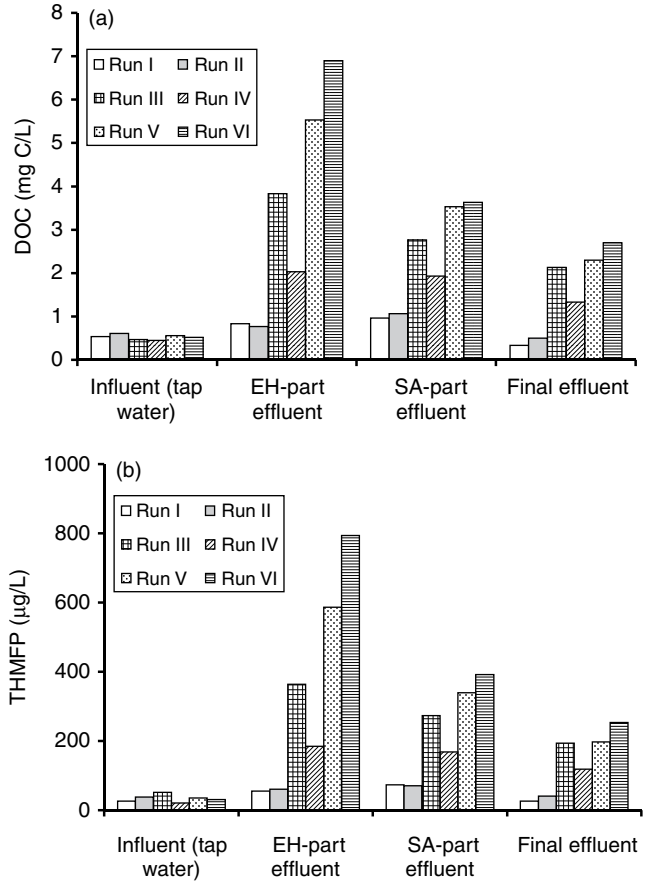

Fig. 6. The concentrations of DOC and THMFP in the influent, effluent of EH-part, SA-part and BAC-part (final effluent) at different runs: (a) DOC and (b) THMFP.

3.3. Rate of sulfate production

Fig. 7 shows the rate of sulfate production per mg NO_3^- – N removed expressed as mgSO_4^{2-} : mgNO_3^- – N in the SA-part at various experimental runs. As given in Eq. (2), the stoichiometric ratio of SO_4^{2-} : NO_3^- – N is 7.54, but in this study SO_4^{2-} : NO_3^- – N ratio was obtained to be in the range of 3.87–6.50. According to Fig. 7, with the increase of NO_3^- loading rate and C:N ratio, the SO_4^{2-} : NO_3^- – N ratio decreased. This observation confirmed that in the SA-part a portion of denitification was conducted heterotrophically using influent organic matter (SMPs and ethanol) as substrate which was in accordance with denitrification results and reduction of DOC in this part. Assuming the stoichiometric value of 7.54 for SO_4^{2-} : NO_3^- – N ratio in the SAD process, the portion of this process is presented in Fig. 7. The portion of SAD process in the SA-part was calculated to be from 51.4% (at Run VI) to 86.2% (at Run I). The maximum production of SO_4^{2-} in the SA-part during the whole operation time was 95.9 mg l^{-1} that with regard to influent concentration of SO_4^{2-} was resulted in a final effluent concentration of 157.8 mg l^{-1}, far lower than 400 mg l^{-1} (the Iranian drinking water standard for SO_4^{2-}) [10]. Soares [22] reported sulfate production rate of 7.5 with a maximum effluent concentration of 320 mg l^{-1}.

3.4. Effect on other quality parameters

The optimum pH for heterotrophic and autotrophic denitrifying bacteria has been reported to be in the ranges of 7–8 and 6–9, respectively [30]. Fig. 8 shows the pH and alkalinity variations in different parts of the HHABB at various experimental runs. As indicated in Fig. 8, pH and alkalinity increased in the effluent of the EH-part from 7.4–7.8 and 109.8–122.7 mg $CaCO_3$ l^{-1} to 7.7–7.9 and 134.4–162.7 mg $CaCO_3$ l^{-1} and subsequently decreased along the SA-part to 7.1–7.9 and 120.9–155.7 mg $CaCO_3$ l^{-1}, respectively. These parameters were not changed in the anoxic BAC-part, but in the aerobic BAC-part, pH increased slightly due to exhaustion of excess CO_2 by aeration. It can also be seen from Fig. 8 that the final effluent pH and alkalinity were maintained at moderate ranges of 7.9–8.0 and 120.6–161.6 mg $CaCO_3$ l^{-1}, respectively throughout the experimental runs which resulted from consecutive arrangement of the HD and SAD processes in the HHABB. However in previous studies, limestone was usually used along with elemental sulfur for inorganic carbon and alkalinity supply and pH adjustment in SAD reactor. Application of limestone lowered performance of the SAD reactor owing to the increase of treated water hardness and decrease of sulfur surface area as the effective growth media per unit volume of the reactor [22,28,31,32].

During the experimental periods, SO_3^{2-}, S^{2-} and ammonia nitrogen were not detected in the final effluent

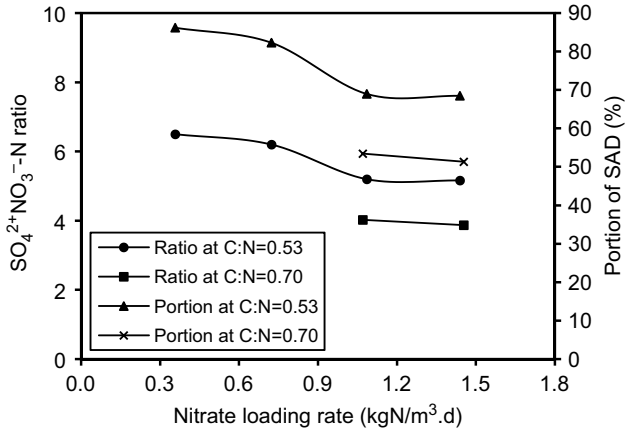

Fig. 7. The rate of sulfate production per mg NO_3^- – N removed in the SA-part at various experimental runs.

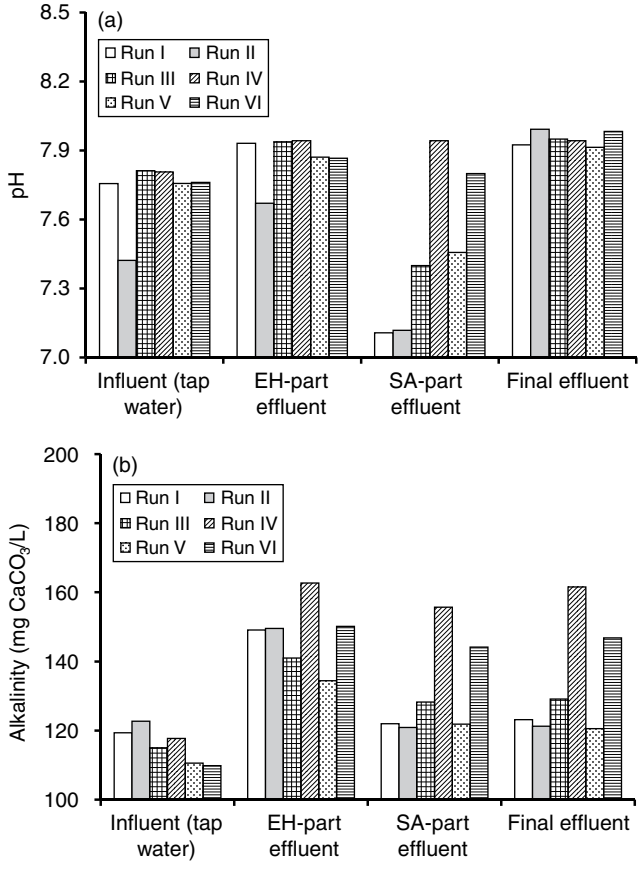

Fig. 8. Variations of pH and alkalinity in different part of the HHABB during various experimental runs: (a) pH and (b) alkalinity.

of the HHABB. The HPC in the influent and final effluent of the HHABB were in the ranges of 3–120 and 1.5×10^4–6.7×10^5 CFU ml^{-1}. Turbidity was lower than one NTU in all of the final effluent samples during the experiment periods.

4. Conclusions

In this research, in order to benefit from the advantages of both autotrophic and HD, the HHABB was developed and studied for denitrification of drinking water. Despite of most of the conducted investigations, in addition to maximizing denitrification efficiency, effluent quality regarding DOC, THMFP, sulfate, etc. was also taken into consideration. At NO_3^- loading rates 0.36–0.72 kgN $m^{-3}\,d^{-1}$, the C:N ratio 0.53 provided high denitrification efficiencies of 96–99%. In contrast at NO_3^- loading rate 1.07 kgN $m^{-3}\,d^{-1}$, an increase in C:N ratio to 0.70 was required to achieve suitable results and at NO_3^- loading rate 1.45 kgN $m^{-3}\,d^{-1}$, performance of the HHABB was not acceptable. According to the results, the disadvantages of HD and SAD processes could be overcome through the hybrid arrangement. The application of anoxic BAC-part had no positive effect on the improvement of effluent quality. In contrast, the aerobic BAC-part represented a suitable effectiveness in the oxidation of effluent NO_2^- and removal of DOC and THMFP. This study indicated that the HHABB without anoxic BAC-part optimized denitrification of drinking water, so that the rate and efficiency of denitrification were suitable and final effluent quality was acceptable.

Acknowledgements

This research has been supported by Tehran University of Medical Sciences grant No. 9679. The authors are most grateful to the laboratory staff of the Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Iran, for their collaboration in this research.

References

[1] M. Boumediene and D. Achour, Denitrification of the underground waters by specific resin exchange of ion, Desalination, 168 (2004) 187–194.
[2] H. Wang and J. Qu, Combined bioelectrochemical and sulfur autotrophic denitrification for drinking water treatment, Water Res., 37 (2003) 3767–3775.
[3] WHO, Guidelines for Drinking-Water Quality, 2nd ed., Volume 2, Health Criteria and Other Supporting Information, WHO, Geneva, 1996.
[4] WHO, Guidelines for Drinking-Water Quality, Incorporating First and Second Addenda, 3rd ed., Volume 1, Recommendations, World Health Organization, Geneva, 2008.
[5] O.O. Nalcaci, N. Boeke and B. Ovez, Potential of the bacterial strain Acidovorax avenae subsp avenae LMG 17238 and macro algae Gracilaria verrucosa for denitrification, Desalination, 274 (2011) 44–53.
[6] S. Ghafari, M. Hasan and M.K. Aroua, Bio-electrochemical removal of nitrate from water and wastewater–a review, Bioresour. Technol., 99 (2008) 3965–3974.
[7] K.S. Haugen, M.J. Semmens and P.J. Novak, A novel in situ technology for the treatment of nitrate contaminated groundwater, Water Res., 36 (2002) 3497–3506.
[8] A.H. Mahvi, J. Nouri, A.A. Babaei and R. Nabizadeh, Agricultural activities impact on groundwater nitrate pollution, Int. J. Environ. Sci. Technol., 2 (2005) 41–47.
[9] M.M. Gheysari, M. Houdaji, P. Najafi and A. Abdollahi, Assessment of nitrate pollution of groundwater in South-East of Isfahan region, J. Environ. Stud., 33 (2007) 43–50 (in Persian).
[10] ISIRI, Chemical specifications of drinking water, ISIRI No. 1053, 4th ed., Institute of Standards and Industrial Research of Iran, 1992, http://www.isiri.org/std/1053.htm. Accessed 20 August 2009 (in Persian).
[11] A. Khosravi Dehkordi, M. Afyouni and S.F. Mousavi, Nitrate concentration in groundwater in the Zayanderoud river basin, J. Environ. Stud., 32 (2006) 33–40 (in Persian).
[12] C. Malika, A. Kenza, A.O. Yasmine, A. Abdeltif and B. Aicha, Removal of nitrate from drinking water by adsorption using ion exchange resin, Desalin. Water Treat., 24 (2010) 109–116.
[13] E.J. McAdam and S.J. Judd, A review of membrane bioreactor potential for nitrate removal from drinking water, Desalination, 196 (2006) 135–148.
[14] Metcalf & Eddy, Inc., Wastewater Engineering: Treatment and Reuse, 4th ed., McGraw-Hill, Inc., New York, 2003.
[15] Z. Feleke and Y. Sakakibara, A bio-electrochemical reactor coupled with adsorber for the removal of nitrate and inhibitory pesticide, Water Res., 36 (2002) 3092–3102.
[16] G. Bitton, Wastewater Microbiology, 3rd ed., John Wiley & Sons, Inc., Hoboken, NJ, 2005.
[17] S.G. dos Santos, M.B.A. Varesche, M. Zaiat and E. Foresti, Comparison of methanol, ethanol, and methane as electron donors for denitrification, Environ. Eng. Sci., 21 (2004) 313–320.
[18] C.D. Rocca, V. Belgiorno and S. Meriç, An heterotrophic/autotrophic denitrification (HAD) approach for nitrate removal from drinking water. Process Biochem., 41 (2006) 1022–1028.
[19] V. Matějů, S. Čižinská, J. Krejčí and T. Janoch, Biological water denitrification–a review, Enzyme Microb. Technol., 14 (1992) 170–183.
[20] J.L. Campos, S. Carvalho, R. Portela, A. Mosquera-Corral and R. Méndez, Kinetics of denitrification using sulphur compounds: effects of S/N ratio, endogenous and exogenous compounds, Bioresour. Technol., 99 (2008) 1293–1299.
[21] M. Shrimali and K.P. Singh, New methods of nitrate removal from water, Environ. Pollut., 112 (2001) 351–359.
[22] M.I.M. Soares, Denitrification of groundwater with elemental sulfur, Water Res., 36 (2002) 1392–1395.
[23] R. Sierra-Alvarez, R. Beristain-Cardoso, M. Salazar, J. Gómez, E. Razo-Floresc and J.A. Field, Chemolithotrophic denitrification with elemental sulfur for groundwater treatment, Water Res., 41 (2007) 1253–1262.
[24] H. Wang and J. Qu, Combined bioelectrochemical and sulfur autotrophic denitrification for drinking water treatment, Water Res., 37 (2003) 3767–3775.
[25] APHA, AWWA and WEF, Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association, Washington, DC, 2005.
[26] A. Mohseni-Bandpi and D.J. Elliott, Groundwater denitrification with alternative carbon source, Water Sci. Technol., 38 (1998) 237–243.
[27] M.M. Emamjomeh and M. Sivakumar, Denitrification using a monopolar electrocoagulation/flotation (ECF) process. J. Environ. Manage., 91 (2009) 516–522.

[28] D. Wan, H. Liu, J. Qu, P. Lei, S. Xiao and Y. Hou, Using the combined bioelectrochemical and sulfur autotrophic denitrification system for groundwater denitrification, Bioresour. Technol., 100 (2009) 142–148.
[29] E.J. McAdam and S.J. Judd, Denitrification from drinking water using a membrane bioreactor: Chemical and biochemical feasibility, Water Res., 41 (2007) 4242–4250.
[30] S.E. Oh, Y.B. Yoo, J.C. Young and I.S. Kim, Effect of organics on sulfur-utilizing autotrophic denitrification under mixotrophic conditions, J. Biotechnol., 92 (2001) 1–8.
[31] H. Zeng and T.C. Zhang, Evaluation of kinetic parameters of a sulfur–limestone autotrophic denitrification biofilm process, Water Res., 39 (2005) 4941–4952.
[32] J.M. Flere and T.C. Zhang, Sulfur-based autotrophic denitrification pond systems for in-situ remediation of nitrate-contaminated surface water. Water Sci. Technol., 38 (1998) 15–22.