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Simultaneous Removal of Nitrate and Natural Organic Matter from Drinking Water Using a Hybrid Heterotrophic/ Autotrophic/Biological Activated Carbon Bioreactor

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Abstract

Simultaneous removal of nitrate (NO_3^-) and natural organic matter (NOM) from drinking water using a hybrid heterotrophic/autotrophic/BAC bioreactor (HHABB) was studied in continuous mode. The HHABB consisted of three compartments: ethanol heterotrophic part, sulfur autotrophic part, and biological activated carbon (BAC)-part (including anoxic and aerobic sections). Experiments were performed with NO_3^- concentration 30 mg N/L, NO_3^- loading rate 0.72 kg N/m^3/d, C : N ratio 0.53, and three concentrations of NOM (0.6, 2.6, and 5.7 mg C/L). Overall denitrification rate and efficiency of the HHABB were not affected by NOM concentration and were in the suitable ranges of 0.69–0.70 kg N/m^3/d and 96.0%–97.7%, respectively. NOM removal at concentration 0.6 mg C/L was not efficient because of organic carbon replacement as soluble microbial products. At higher NOM concentrations, total NOM removal efficiencies were 55%–65%, 55%–70%, and 55%–65% for dissolved organic carbon, trihalomethane formation potential, and UV absorbance at 254 nm (UV_{254}), respectively. The more efficient compartments of the HHABB for the removal of NOM were the ethanol heterotrophic phase and aerobic BAC-phase. The efficiency of the HHABB in the removal of NOM was considerable, and the effluent dissolved organic carbon and trihalomethane formation potential concentrations were relatively low. This study indicated that the HHABB without the anoxic BAC-phase could be a feasible alternative for simultaneous removal of NO_3^- and NOM from drinking water at full scale.

***Key words*:** NO_3^-; NOM; drinking water; simultaneous removal; HHABB

Introduction

In recent years, treatment of drinking water by biological processes has been taken under more consideration, especially in North America and Europe. A wide range of organic and inorganic drinking water pollutants such as natural organic matter (NOM), 2-methyl-isoborneol, geosmin, algal toxins, pesticides, methyl tertiary-butyl ether, perchloroethylene, trichloroethylene, nitrate (NO_3^-), nitrite (NO_2^-), bromate, perchlorate, ammonia nitrogen, iron(II), manganese(II), and so on are potentially treatable by biological processes (Bouwer and Crowe, 1988; Herman and Frankenberger, 1999; Rittmann and McCarty, 2001; Brown *et al.*, 2005; Brown, 2006).

Contamination of water resources used for community water supply by NO_3^- is a worldwide public health problem. The health risk regarding the presence of NO_3^- and NO_2^- in drinking water at high concentrations is related to the occurrence of methaemoglobinaemia, so-called "blue-baby syndrome," in infants that causes cyanosis and at higher concentrations, asphyxia. Based on this health effect, WHO recommended the guideline values 11.3 mg NO_3^--N/L and 0.9 mg NO_2^--N/L for drinking water (Wang and Qu, 2003; Boumediene and Achour, 2004; WHO, 1996, 2006). The conventional technologies for NO_3^- removal from drinking water are ion exchange, reverse osmosis, and electrodialysis that require high capital, operation, and maintenance costs. The other disadvantage of these methods is the production of a large amount of concentrated brine (Ergas and Rheinheimer, 2004; McAdam and Judd, 2006). Therefore, there is an urgent need for development of cost-effective processes for NO_3^- removal from drinking water. Biological denitrification has promising potential to be the most attractive alternative for the conventional technologies of NO_3^- removal. Both

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heterotrophic and autotrophic organisms are capable of denitrification (Feleke and Sakakibara, 2002; Kim *et al.*, 2004; McAdam and Judd, 2006; Sierra-Alvarez *et al.*, 2007; Ghafari *et al.*, 2008). Heterotrophic denitrification (HD) process that requires an organic carbon source such as glucose, methanol, ethanol, and so on as a terminal electron donor or substrate has rapid kinetics. Among the organic substrates used for the HD process, ethanol was determined to be one of the most suitable options considering the high values of its kinetic parameters, cheapness, readily availability, and lack of toxicity (dos Santos *et al.*, 2004). The overall reaction of HD process using ethanol can be summarized in the following equation (Matějů *et al.*, 1992):

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

Autotrophic denitrification process can be conducted by utilizing hydrogen gas or reduced sulfur compounds as terminal electron donor. The overall reaction of sulfur autotrophic denitrification (SAD) process can be summarized in the following stoichiometric equation (Soares, 2002):

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

In comparison with the HD process, the advantages of the SAD process are less sludge production (less cell yield), no need to organic substrate, low cost of elemental sulfur, and fewer release of soluble microbial products (SMPs), which result in easier post-treatment (Sierra-Alvarez *et al.*, 2007; Ghafari *et al.*, 2008). The HD process has also some advantages over SAD process such as rapid kinetics and alkalinity production (Matějů *et al.*, 1992; dos Santos *et al.*, 2004).

NOM comprising a complex mixture of compounds (such as humic substances, hydrophilic acids, carbohydrates, amino acids, carboxylic acids, etc.) is observed in all the water resources, but its presence at elevated level in raw water is one of the major concerns of water supply utilities. Some components of NOM can react with disinfectants to form disinfection byproducts such as trihalomethanes (THMs), which have health hazards and drinking water guideline values. The other important problem related to NOM is microbial regrowth in water distribution systems that has adverse effects on treated water quality (Xie, 2004; Matilainen and Sillanpää, 2010). The recommended treatment processes for NOM removal from drinking water are enhanced coagulation, granular activated carbon (GAC) adsorption, and membrane filtration that require high capital and operation costs and produce a large amount of waste byproducts (Marhaba and Pipada, 2000; Jiang and Wang, 2003; Murray and Parsons, 2004; Xie, 2004). Removal of NOM from drinking water using biological processes or combined chemical/biological processes was investigated in several research projects (Seredyńska-Sobecka *et al.*, 2006; Buchanan *et al.*, 2008); however, no study on the simultaneous removal of NO_3^- and NOM using biological processes has been conducted until now. In the previous studies, biological activated carbon (BAC) was frequently used as the biological process for NOM removal. The BAC utilizes GAC as the media for biofilm growth and can remove NOM through both adsorption and biodegradation processes (Li *et al.*, 2004; Toor and Mohseni, 2007; Buchanan *et al.*, 2008).

The objective of this research was to study the simultaneous removal of NO_3^- and NOM from drinking water using a hybrid heterotrophic/autotrophic/BAC bioreactor (HHABB). The HHABB was run at optimum NO_3^- loading rate 0.72 kg $N/m^3/d$ obtained at previous work by authors and three NOM concentrations. The performance of the HHABB was comprehensively investigated by measurement of NO_3^-, NO_2^-, dissolved organic carbon (DOC), trihalomethane formation potential (THMFP), UV absorbance at 254 (UV_{254}), pH, and alkalinity and SO_4^{2-} at influent and effluent of different parts of the bioreactor.

Materials and Methods

Experimental set-up

The experimental set-up used in this study is schematically shown in Fig. 1. As illustrated in Fig. 1, the HHABB 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 including two sections: anoxic BAC-part and aerobic BAC-part. The aerobic BAC-part was aerated using an aquarium blower and an air diffuser. All parts of the HHABB were constructed from plexiglas tubes. 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). In the SA-part, sulfur particles with irregular shape were used as both substrate and media for autotrophic biofilm growth. The media of BAC-part was GAC (AquaSorb® 2000; Jacobi Carbons), which can also act as an adsorbent. 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 equal (1.3 L); therefore, the hydraulic retention time (HRT) value of the EH-part was equal to the value of the SA-part. Also, the effective volume of each section of the BAC-part

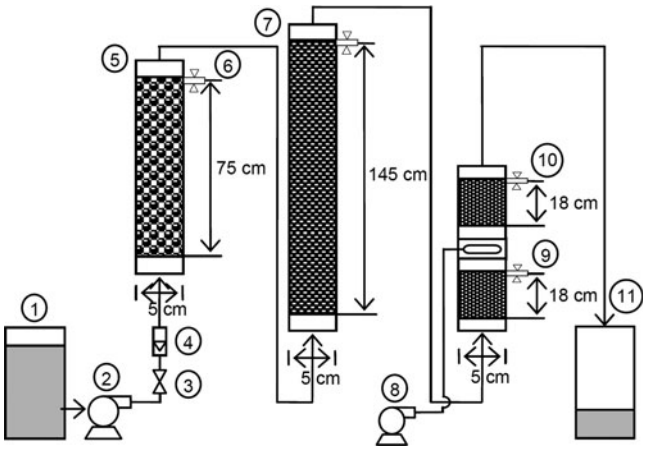

FIG. 1. Experimental set-up used in this study: 1, feed reservoir; 2, peristaltic pump; 3, cutoff valve; 4, flowmeter; 5, EH-part; 6, sampling port; 7, SA-part; 8, blower; 9, anoxic BAC-part; 10, aerobic BAC-part; 11, effluent reservoir. EH-part, ethanol heterotrophic part; SA-part, sulfur autotrophic part; BAC, biological activated carbon.

Table 1. Overall Specifications of Hybrid Heterotrophic/Autotrophic/Biological Activated Carbon Bioreactor Parts

		Value			
Parameter	*Unit*	*H-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

BAC, biological activated carbon.

(anoxic or aerobic) was 0.22 L; therefore, the HRT values of these parts were about one-sixth of the EH-part HRT.

Feed water quality

The synthetic feed water was prepared using tap water, KNO_3, NOM as humic acid (50%–60%), NH_4Cl, NaH_2PO_4, trace element solution, and ethanol (C_2H_6O) as a heterotrophic electron donor. All of the experiments (excluding start-up stage) were conducted in approximately constant concentrations of NO_3^-, ammonia nitrogen, and phosphate (as nutrients) at the values 30 mg NO_3^--N/L, 0.5 mg NH_4^+-N/L, and 0.3 mg PO_4^{3-}-P/L, respectively. The quality characteristics of the tap water are presented in Table 2. The ingredients of the trace element solution and their concentrations were $ZnSO_4\cdot7H_2O$ at 800 mg/L, $MnCl_2$ at 600 mg/L, $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ at 200 mg/L, $CuSO_4\cdot5H_2O$ at 400 mg/L, and $CoCl_2\cdot6H_2O$ at 400 mg/L. The trace element solution was used at 1.0 mL per 10 L of feed water (0.01% v/v). The ethanol concentration in the influent water was adjusted to 15.8 mg C/L based on applied C : N ratio 0.53. All chemicals used in this study for preparation of influent water and quality analysis were of analytical grade.

Microbial inoculation and start-up of bioreactor

The HHABB was inoculated using some sludge collected from a full-scale wastewater treatment plant with activated sludge process (Sahrak-e Ghodss). The EH-part and the BAC-part were seeded by return activated sludge, and the SA-part

Table 2. Quality Characteristics of Tap Water Used in Influent Water Preparation

Quality parameter	*Unit*	*No. of measurement*	*Average*	*Standard deviation*
pH	–	24	7.9	0.2
EC	μmohs/cm	24	382	19
Turbidity	NTU	24	0.4	0.1
Dissolved oxygen (DO)	mg/L	24	6.2	0.3
HPC	CFU/mL	12	94.9	58.5
Hardness	mg $CaCO_3$/L	12	166.1	12.7
Alkalinity	mg $CaCO_3$/L	12	114.8	5.5
Ca^{2+}	mg/L	12	52.6	3.9
Mg^{2+}	mg/L	12	8.4	4.1
Na^+	mg/L	12	22.7	3.3
K^+	mg/L	12	1.0	0.1
HCO_3^-	mg/L	12	140.1	6.8
SO_4^{2-}	mg/L	12	65.1	4.8
Cl^-	mg/L	12	18.4	2.1
NO_2^-	mgN/L	12	0.00	0.00
NO_3^-	mgN/L	40	1.7	0.4
TOC	mg/L	12	0.53	0.06
THMs	μg/L	12	26.2	9.1
Chloroform	μg/L	12	21.9	7.7
Bromoform	μg/L	12	0.4	0.8
Bromodichloromethane	μg/L	12	2.3	2.0
Dibromochloromethane	μg/L	12	1.6	1.4

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 days to enrich heterotrophic denitrifying mixed culture, acclimatize the bacteria by the feed water (containing NO_3^-, NOM, and ethanol), and accelerate biofilm development on the media. Similarly, the SA-part was also operated in batch and recirculation mode for 45 days separately, but its feed water contained $NaHCO_3$ instead of ethanol. After this period, the EH-part, the SA-part, and the BAC-part were rearranged in series as indicated in Fig. 1 and operated in continuous mode for 2 weeks with a gradually increasing flow rate in the range of 0.5–2.6 L/h to complete start-up stage. In the start-up stage, the influent concentration of NO_3^- was set in the range of 50–200 mg NO_3^--N/L, and the performance of the system was monitored by measurement of NO_3^-, NO_2^-, UV_{254}, DOC, pH, alkalinity, and SO_4^{2-} in the influent and effluent of different parts of the bioreactor.

Experimental runs

The experiments were conducted at three runs by continuous pumping the feed water in upflow mode through the packed bed columns with a peristaltic pump. The previous study by the authors indicated that the optimum NO_3^- loading rate of the HHABB regarding denitrification rate, efficiency, and effluent quality was 0.72 kg/m^3/d; therefore, in this study, the simultaneous removal of NO_3^- and NOM was investigated at the optimum NO_3^- loading rate and three NOM concentrations 0.6, 2.6, and 5.7 mg C/L. At the NO_3^- loading rate, the HRT values of the EH-part (or SA-part), each section of BAC-part, and HHABB were 30, 5, and 70 min, respectively, and the flow rate was 2.6 L/h. In the first experimental run (Run I), NOM at the concentration 0.6 mg C/L was originated from tap water, whereas in the second and third experimental runs (Run II and Run III), NOM as humic acid (50%–60%) was added in the feed water to increase the NOM concentrations to 2.6 and 5.7 mg/L, respectively. In each experiment, the bioreactor was run until steady-state condition was observed. Steady-state condition was assumed to exist when variation of sample data of three sequential sampling was <5%. Hence, each experimental run lasted about one month to obtain steady-state operation. All of the experiments were performed at room temperature (20°C ± 2°C).

To prevent the bioreactor bed clogging 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 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 this study, the parameters DOC, UV_{254}, and THMFP were used as the NOM indicators. To investigate the HHABB performance, including denitrification rate and efficiency, NOM removal efficiency, and influence on physical and chemical quality of influent water, the parameters NO_3^-, NO_2^-, DOC, THMFP, UV_{254}, pH, alkalinity, and SO_4^{2-} were measured in the influent and effluent samples from desired sampling ports at predetermined time intervals.

Analytical methods

All of the quality parameters NO_3^-, NO_2^-, DOC, THMFP, UV_{254}, pH, alkalinity, and SO_4^{2-} were measured according to the instructions of Standard Methods (APAH/AWWA/WEF, 1998). For analysis of the parameters NO_3^-, NO_2^-, DOC, THMFP, UV_{254}, and SO_4^{2-}, samples were passed through 0.45 μm membrane filters to remove turbidity of samples. 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 days reaction of each sample with free chlorine residual in the concentration ranging 3–5 mg/L at temperature of 25 ± 2°C and controlled pH at 7.0 ± 0.2 with phosphate buffer. The parameter UV_{254} was measured by reading the light absorbance at 254 nm using a UV-visible spectrophotometer (Lambda 25; PerkinElmer Inc.).

Results and Discussion

Denitrification rate and efficiency: influence of NOM concentration

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 ratio less than the stoichiometric value, NO_2^- is accumulated in considerable amounts. In the previous studies, calculation of denitrification rate and efficiency was frequently interfered by NO_2^- accumulation (Mohensi-Bandpi and Elliott, 1998; dos Santos *et al.*, 2004). To solve the problem, in this research, the parameter "total concentration of NO_3^- and NO_2^- as NO_3^- concentration" was defined based on nitrogen oxidation state in these anions as shown below and used in 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 concentration 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.

Figure 2 shows profiles of $C_{(NO_3^- + NO_2^-)\text{ as }NO_3^-}$ values in the influent and effluents of EH-part and SA-part during experimental runs. Based on the stoichiometric value of C:N

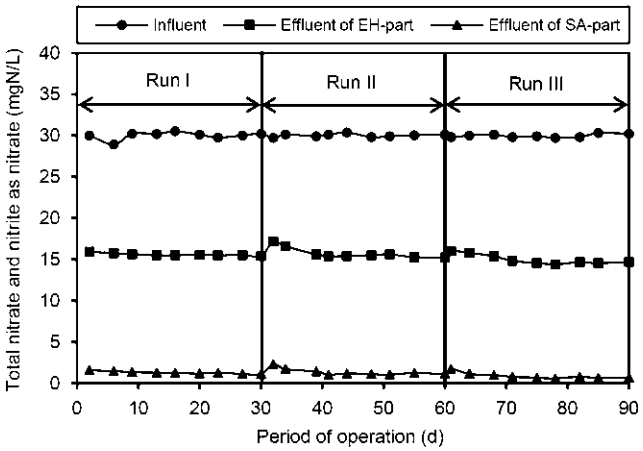

FIG. 2. Profiles of $C_{(NO_3^- + NO_2^-)\text{ as }NO_3^-}$ values in influent and effluents of EH-part and SA-part during experimental runs.

ratio for HD process using ethanol (1.05), the maximum possible denitrification efficiency in the EH-part was 50% for applied C : N ratio 0.53. Corresponding values for $C_{(NO_3^- + NO_2^-)\text{ as }NO_3^-}$ of EH-part effluent was 15 mg N/L. According to Fig. 2, average $C_{(NO_3^- + NO_2^-)\text{ as }NO_3^-}$ of EH-part effluent at NOM concentrations 0.6, 2.6, and 5.7 mg C/L (Run I, Run II, and Run III, respectively) obtained were 15.5, 15.4, and 14.7 mg N/L, respectively; therefore, in these cases, denitrification efficiencies of EH-part were 48.5%, 48.6%, and 51.1%, respectively. At NOM concentration 5.7 mg C/L, in addition to ethanol, a considerable portion of NOM was applied as electron donor of HD process, which resulted in a denitrification efficiency higher than the maximum possible one using just ethanol, but in other experimental runs, the concentration of NOM was low (0.6 and 2.6 mg C/L) and did not have any significant effect on EH-part denitrification efficiency. At Run I, Run II, and Run III, average denitrification efficiencies of the SA-part were 92.2%, 92.7%, and 95.3%, respectively, resulting in suitable total denitrification efficiencies of 96.0%, 96.2%, and 97.7% for the HHABB. As shown in Fig. 2, in these cases, the NO_3^- loading rate was 0.72, and the denitrification rates were 0.69, 0.69, and 0.70 kgN/m^3/d, respectively. The denitrification rates and efficiencies achieved in the HHABB were relatively high in comparison with those of other systems for drinking water treatment reported in the literature (Soares, 2002; Wan *et al.*, 2009; Zhang *et al.*, 2009).

Figure 3 represents variations of NO_2^- concentration in the effluent of EH-part and SA-part at different experimental runs. The influent NO_2^- concentration was very low in most of the cases (0.03 mg N/L, averagely). As shown in Fig. 3, NO_2^- accumulation in the effluent of EH-part increased by increasing NOM concentration, so the highest average NO_2^- concentration (10.1 mg N/L) was observed in Run III. At all of the runs, the main portion of the accumulated NO_2^- was removed in the SA-part by conversion to N_2 gas; as in the effluent of SA-part, NO_2^- concentration decreased significantly to 0.12, 0.25, and 0.29 mg N/L at Run I, Run II, and Run III, respectively. At higher NOM concentration, some of the influent NOM was adsorbed on biofilm surface and this phenomenon increased the amount of biofilm mass, age, and depth in the EH-part. With increasing biofilm depth, the main portion of organic electron donor was consumed at the surface of biofilm and C : N ratio at deeper layers of biofilm decreased; therefore, the higher NO_2^- accumulation at greater NOM concentration could result from the lower C : N ratio at the deeper layers of biofilm (Mohensi-Bandpi and Elliott, 1998; dos Santos *et al.*, 2004).

The anoxic BAC-part did not have any effect on the denitrification process, and its effluent data are not given here. The effect of aerobic BAC-part on the NO_2^- and NO_3^- concentrations of final effluent is presented in Fig. 4. The ion NO_2^- is toxic and biologically instable and causes microbial regrowth in water distribution network; therefore, this ion should be completely removed from treated water. The ion can be chemically or biologically oxidized to NO_3^-. The stoichiometric chlorine demand of NO_2^- oxidation is 5.1 mg Cl_2/mg NO_2^--N (WHO, 2006; McAdam and Judd, 2007). As illustrated in Fig. 4, a considerable portion of NO_2^- in the effluent of SA-part was oxidized to NO_3^- in the aerobic BAC-part through nitrification process (86%–94%); so, the average concentrations of NO_2^- in the final effluent at Run I, Run II, and Run III were determined to be 0.02, 0.03, and 0.02 mg N/L, respectively. These NO_2^- concentrations were very low and did not require any further treatment.

NOM removal efficiency

In the biological processes, effluent DOC is derived from SMPs and organic matter existing in the influent water (McAdam and Judd, 2007). Figure 5 shows the concentration of NOM indicators (DOC, THMFP, and UV_{254}) in the influent and EH-part, SA-part, and aerobic BAC-part effluents at different experimental runs. The anoxic BAC-part did not have any effect on these parameters; therefore, its effluent data are not shown here. The total efficiency of the HHABB in the removal of NOM is presented in Fig. 6.

The results of this study indicated that the main component of THMPF was chloroform and formed over the 76% of THMPF concentration in all of the experiments (data not shown). Measurement of the parameter THMFP indicated that the influent THMs (THM_0) with an average concentration

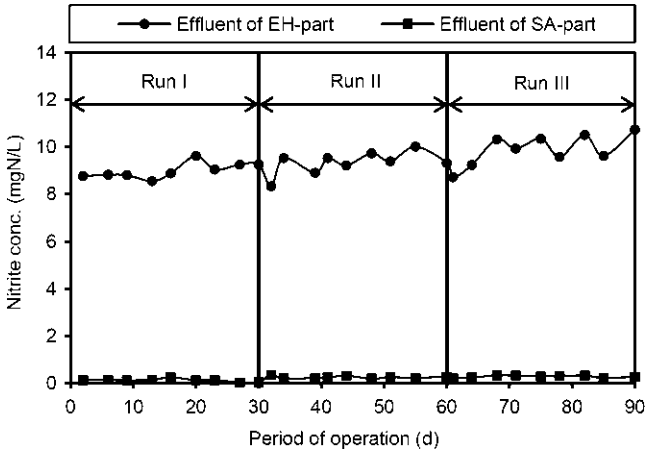

FIG. 3. Variations of NO_2^- concentration in effluent of EH-part and SA-part at different experimental runs.

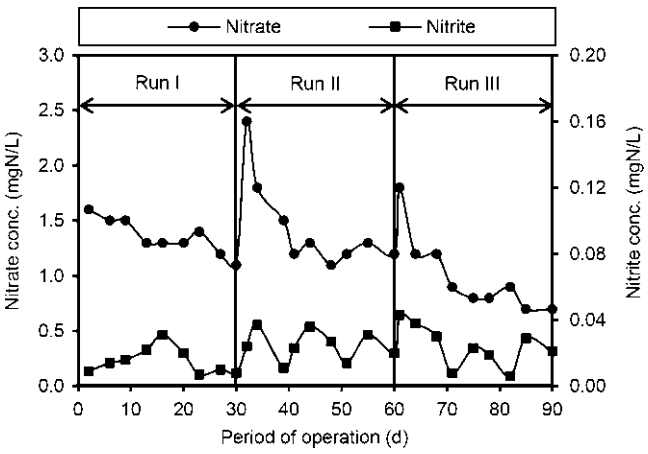

FIG. 4. Effect of aerobic BAC-part on the NO_2^- and NO_3^- concentrations of final effluent.

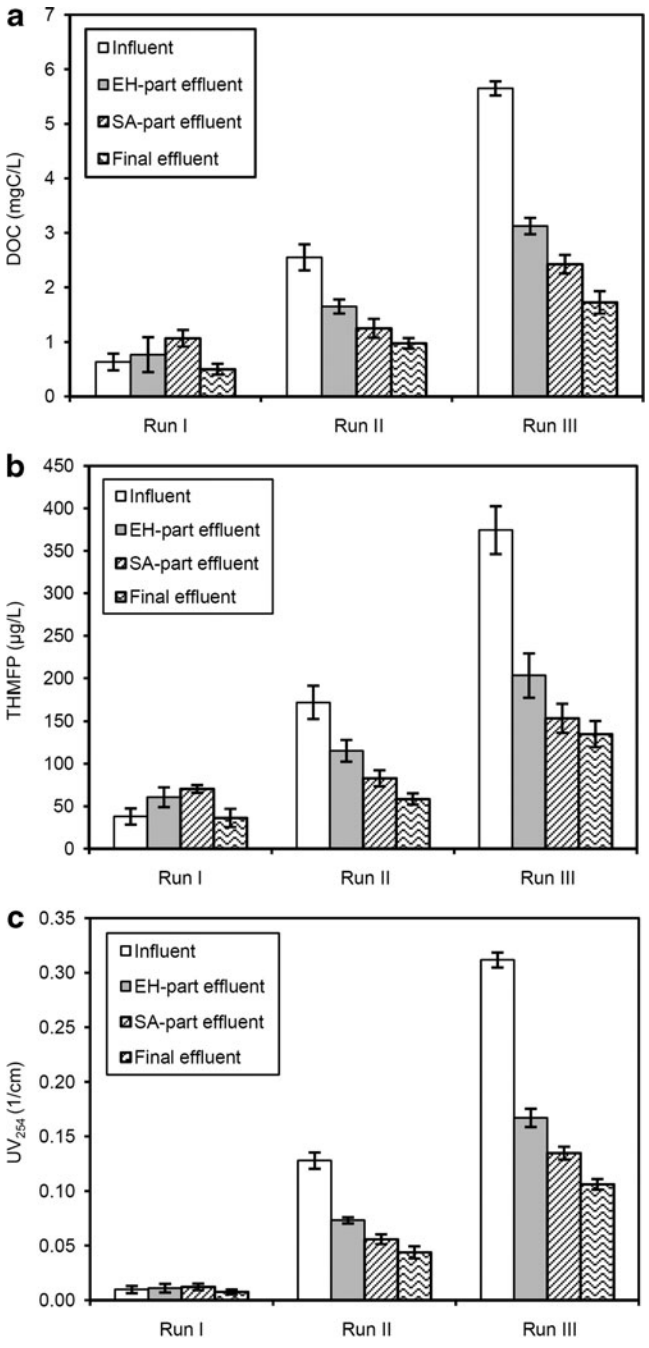

FIG. 5. Concentration of natural organic matter indicators in influent and EH-part, SA-part, and aerobic BAC-part effluents (average ± SD): **(a)** DOC, **(b)** THMFP, and **(c)** UV_{254}. DOC, dissolved organic carbon; THMFP, trihalomethane formation potential.

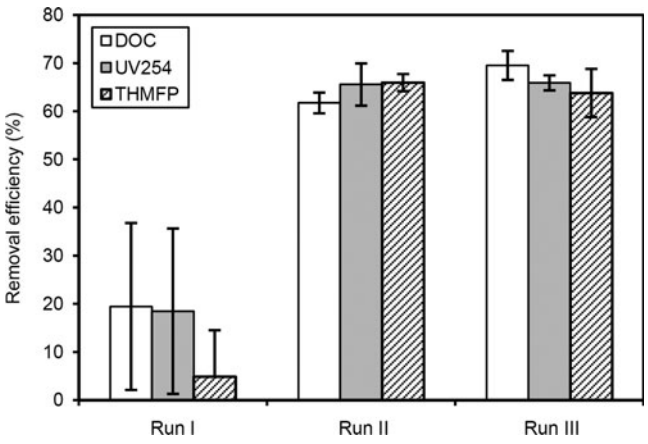

FIG. 6. Total efficiency of the hybrid heterotrophic/autotrophic/BAC bioreactor in the removal of natural organic matter indicators (average ± SD).

26 ± 9 µg/L (± standard deviation) were completely removed at the EH-part in all of the cases. At lowest NOM concentration (Run I), the total efficiency of the HHABB in the removal of NOM indicators was relatively low (ranged 5%–19%), because the main portion of removed NOM was compensated by SMPs liberation by microorganisms. In contrast, at Run II and Run III, the HHABB had excellent performance in the removal of NOM ranging 59%–73%, 61%–72%, and 58%–70% for DOC, UV_{254}, and THMFP, respectively (Fig. 6). According to Fig. 5, the EH-part was the most efficient compartment of the HHABB for NOM removal; where at Run II and Run III, the NOM indicators were reduced by 33%–43% and 45%–46%, respectively. The denitrification efficiency of EH-part indicated that some part of NOM was removed through biodegradation. The non-biodegradable part of NOM could be also removed by adsorption onto the biofilm. At Run II and Run III, color of the biofilm was changed to brown, and the thickness of biofilm increased. These observations confirmed that the adsorption onto the biofilm was one of the NOM removal mechanisms. After the EH-part, the aerobic BAC part had also suitable performance in the removal of NOM through biodegradation and adsorption.

The removal efficiencies of the HHABB for DOC, UV_{254}, and THMFP were approximately equal; this observation indicated that UV_{254} with easy measurement could be used for routine monitoring of the bioreactor effectiveness. The influent concentrations of the parameter THMFP at Run I, Run II, and Run III were 38, 172, and 375 µg/L and at the final effluent decreased to 36, 59, and 135 µg/L, respectively; therefore, the HHABB efficiently removed the THMFP in a manner that did not require further treatment. In previous studies, to achieve similar removal efficiency for NOM, BAC reactor was combined with a chemical oxidation process. Seredyńska-Sobecka *et al.* (2006) observed that ozonation increased the NOM (as DOC and UV_{254}) removal efficiency of BAC reactor. Buchanan *et al.* (2008) observed that pretreatment of raw water by vacuum ultraviolet reactor promoted the effectiveness of BAC for NOM (as DOC) removal from 10%–29% to 44%–54%. Other oxidative pretreatment processes followed by BAC were $TiO_2/UV/O_3$-BAC, UV/O_3-BAC, and UV/H_2O_2-BAC, whose removal efficiencies for NOM (as DOC) were obtained to be 52%, 46%, and 52%, respectively (Li *et al.*, 2004; Toor and Mohseni, 2007).

Effect on other quality parameters

Figure 7 shows the rate of sulfate production in the SA-part at different experimental runs. According to Equation (2), the stoichiometric ratio of SO_4^{2-}:NO_3^--N is 7.54, but in this

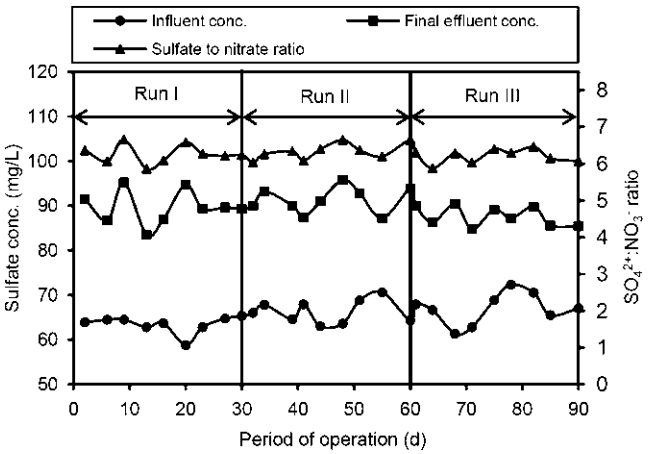

FIG. 7. Rate of sulfate production in SA-part at different experimental runs.

study, the ratio was determined to be 6.21, 6.39, and 6.23 at Run I, Run II and Run III, respectively. This observation confirmed that in the SA-part a portion of denitification was conducted heterotrophically using influent organic matter (SMPs, NOM, and ethanol) as substrate, which is in accordance with reduction of DOC in the SA-part. With assumption the stoichiometric value of 7.54 for SO_4^{2-}:NO_3^--N ratio in the SAD process, the portion of SAD process ranged from 82% to 85% at different runs. The maximum concentration of SO_4^{2-} in the final effluent during the whole operation time was determined to be 161.6 mg/L, which was far lower than 400 mg/L, the Iranian drinking water standard for SO_4^{2-} (ISIRI, 1992).

The optimum pH for heterotrophic and autotrophic denitrifying bacteria has been reported to be in the ranges of 7–8 and 6–9, respectively (Oh *et al.*, 2001). Figure 8 shows pH and alkalinity variations at different parts of the HHABB during the experiments. It can be seen from Fig. 8 that pH and alkalinity increased in the effluent of the EH-part and subsequently decreased along the SA-part. These parameters were not changed at the anoxic BAC-part, but in the aerobic BAC-part pH increased due to exhaustion of excess CO_2 by aeration. As shown in Fig. 8, consecutive arrangement of the HD and SAD processes in the HHABB decreased the fluctuations of pH and alkalinity at the EH-part and SA-part. Also, the final effluent pH and alkalinity were maintained at moderate ranges of 7.9–8.0 and 115.4–121.3 mg $CaCO_3$/L, respectively, during the experimental runs. However, in previous studies, for inorganic carbon supply and adjustment of pH at SAD reactor, limestone was usually used along with elemental sulfur. Application of limestone lowered the SAD reactor performance by increasing treated water hardness and decreasing sulfur surface area as the effective growth media per unit volume of the reactor (Flere and Zhang, 1998; Soares, 2002; Zeng and Zhang, 2005; Wan *et al.*, 2009).

Conclusions

In this study, performance of the HHABB in the simultaneous removal of NO_3^- and NOM from drinking water was investigated in continuous mode. At different experimental runs with variable concentration of NOM (0.6, 2.6, and 5.7 mg C/L) and constant NO_3^- loading rate (0.72 kg N/m^3/d), the denitrification rate and efficiency of the HHABB were determined to be in the suitable ranges of 0.69–0.70 kg N/m^3/d and 96.0%–97.7%, respectively. At NOM concentration 0.6 mg C/L, NOM removal efficiency of the HHABB was relatively low, because most of the removed NOM was replaced by SMPs. In contrast, at higher NOM concentrations, performance of the HHABB in NOM removal was promising as the removal efficiencies of DOC, THMFP, and UV_{254} were obtained to be 55%–65%, 55%–70%, and 55%–65%, respectively. This study indicated that the HHABB without the anoxic BAC-part could be a feasible alternative for simultaneous removal of NO_3^- and NOM from drinking water at full scale.

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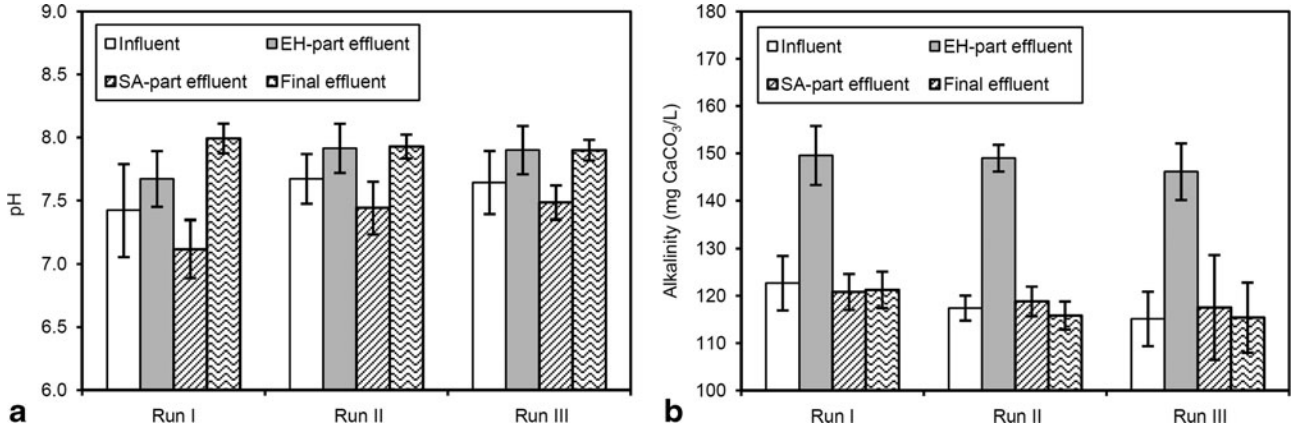

FIG. 8. Variations of pH and alkalinity at different phases of hybrid heterotrophic/autotrophic/BAC bioreactor (average ± SD).

Author Disclosure Statement

No competing financial interests exist.

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