Using the combined bioelectrochemical and sulfur autotrophic denitrification system for groundwater denitrification

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ABSTRACT

A combined bioelectrochemical and sulfur autotrophic denitrification system (CBSAD) was evaluated to treat a groundwater with nitrate contamination (20.9–22.0 mg NO₃[−]-N/L). The reactor was operated continuously for several months with groundwater to maximize treatment efficiency under different hydraulic retention times (HRT) and electric currents. The denitrification rate of sulfur autotrophic part followed a half-order kinetics model. Moreover, the removal efficiency of bioelectrochemical part depended on the electric current. The reactor could be operated efficiently at the HRT ranged from 4.2 to 2.1 h (corresponding nitrogen volume-loading rates varied from 0.12 to 0.24 kg N/m³ d; and optimum current ranged from 30 to 1000 mA), and the NO₃[−]-N removal rate ranged from 95% to 100% without NO₃[−]-N accumulation. The pH of effluent was satisfactorily adjusted by bioelectrochemical part, and the sulfate concentration of effluent was lower than 250 mg/L, meeting the drinking water standard of China EPA.

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1. Introduction

Nitrate as a kind of common contaminates in groundwater aquifers has steadily been increasing in recent years mainly due to the extensive use of nitrogen fertilizers and improper treatment of waste water from the industrial sites. It was discovered that for ground water from 10% to 25% of the water-supply wells in large region of the US exceeded the maximum contaminant level for nitrate (10 mg NO₃[−]-N/L) (Nolan et al., 1997). In China, the pollution of nitrate in ground water was even more severe, nitrate concentration of groundwater in some rural area even exceeded 130 mg NO₃[−]-N/L. Ground water is a universal, and in some cases exclusive, drinking-water source used for both humans and livestock in rural and suburban areas. Because of its health risks, removing nitrate from groundwater has gained great attention in recent years (Kleinjans et al., 1991). The methods that can remove nitrate from groundwater mainly include ion exchange (IE) (Chen et al., 2002; Samatya et al., 2006), reverse osmosis (RO), catalytical (Prüsse et al., 2000) and biological process. However, IE and RO processes can not transfer nitrate into harmless compounds but only concentrate nitrate from water to brine and need afterwards treatment; catalytical process may generate more toxic byproduct (such as NO₂ and NH₄⁺) and it is still in the experimental test stage (Prüsse

et al., 2000). Only biological denitrification is the most favorable way to remove nitrate and it is successfully used for nitrate contaminated groundwater treatment.

Heterotrophic biological denitrification of drinking water has been widely applied because of its high efficiency and low cost, but residual carbon sources (such as methanol, ethanol or acetic acid, etc.) may cause many problems in drinking water treatment. Since groundwater always has a very low concentration of biodegradable organic materials, autotrophic denitrification which utilizes CO₂ as their carbon source from water requires addition of an electron donor substrate. Elemental sulfur (Batchelor and Lawrence, 1978; Claus and Kutzner, 1985; Wang, 1998; Koenig and Liu, 2001; Liu and Koenig, 2002; Kimura et al., 2002; Moon et al., 2004; Zeng and Zhang, 2005; Sierra-Alvarez et al., 2007) and H₂ (Mansell and Schroeder, 2002; Rezanian et al., 2007) as electron donor for autotrophic denitrification systems has been studied extensively.

The sulfur-limestone autotrophic denitrification (SLAD) process for treatment of nitrate contaminated water has been studied and applied for decades in Europe and USA. Element sulfur is used as electron donor and limestone is used to adjust the pH, but the increase of sulfate concentration and hardness limits its application. Hydrogen gas is an ideal electron donor for biological autotrophic denitrification that it is completely harmless to drinking water, and no further steps are needed to remove either excess substrate or its derivatives. However, it has a poor solubility in water (1.6 mg/L at 20 °C) and dangerous to control. To overcome the above mentioned problems, development of a new appropriate

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treatment method is required. Biofilm-electrode reactor as an electrochemical and biological reactor was firstly developed by Sakakibara et al. in 1993 (Sakakibara and Kuroda, 1993). In this system, autotrophic denitrifying microorganisms was immobilized on the surface of the cathode, hydrogen gas as an electron donor was produced of by electrolysis of water. Considerable efforts had been taken to improve designs for the efficient and economical removal of nitrate from water by bioelectrochemical denitrification recently (Sakakibara et al., 1994; Feleke et al., 1998; Sakakibara and Nakayama, 2001; Szekeres et al., 2001; Feleke and Sakakibara, 2002; Prosnansky et al., 2002).

Combined bioelectrochemical and sulfur autotrophic denitrification system (CBSAD) for drinking water denitrification was firstly proposed in our previous study (Wang and Qu, 2003). In such process, sulfur autotrophic and hydrogen autotrophic were integrated for the following reasons: the H^+ generated in sulfur denitrification could be consumed by the bioelectrochemical hydrogen denitrification to achieve neutralization, thus the limestone added in SLAD system could be cancelled and the hardness increase could be avoided in this process; the sulfate concentration of effluent could be controlled by the nitrogen load of sulfur autotrophic denitrification part, and would be lower than SLAD process. In this study, the CBSAD system amplified with 33.47 L effective volume was established and evaluated for groundwater denitrification. The system was operated at various water effluent flux (or nitrogen volume-loading rates) and current intensities for 105 days. Its optimum operation conditions were also determined in this study.

2. Methods

2.1. Experimental apparatus

The experimental apparatus used in this study is shown schematically in Fig. 1. The reactor consisted of two parts: sulfur autotrophic denitrification part (mentioned as S-part) and bioelectrochemical

hydrogen autotrophic denitrification part (mentioned as E-part). The groundwater from feed tank was pumped to the S-part first and then to the E-part, the inflow flux was controlled by influent pump, ranged from 7.97 L/h to 15.93 L/h. The total effective liquid volume of the reactor was 33.47 L.

The S-part was a stainless steel cylindrical with 17.5 cm diameter and 2.2 m length. 1.5 m of sulfur part was packed with sulfur and anthracite granules (1:1 v/v, 3–4 mm diameter YanShanpc Co., Ltd., Beijing, China). The porosity of the medium column is 40%, thus the effective pore water volume of sulfur part was 14.43 L. Three sample ports were fixed at different height of S-part for kinetic study. E-part was made of stainless steel column with 17.5 cm diameter and 1.1 m length, and its effective liquid volume was 19.04 L. The anode was carbon rod of 10.2 cm diameter, and the cathode was the cylindrical stainless steel wall with 6594 cm² surface area. The distance between the electrodes was 3.65 cm. The reactor was operated under room temperature ($21 \pm 2^\circ\text{C}$). The water flow was upward and isolated from the air to preserve an anaerobic environment within the column. Direct current was supplied by Silicon Rectifier (Model DH1718E-4, Beijing Dahua Electronic Instruments Group, Beijing, China).

The influent water in this study was a groundwater with nitrate contamination in Fengtai district, Beijing. The details of the influent water and the experimental conditions in this study were: well depth 37 m, pH 7.10–7.34, NO_3^- -N 20.9–22.0 mg/L, NO_2^- -N Not detected, DO 3.5–4.9 mg/L, Alkalinity (CaCO_3) 420.11 mg/L, Conductivity 1210 μS , IC 93 mg/L, TOC 2 mg/L, COD 8 mg/L, SO_4^{2-} 101.86 mg/L and Cl^- 105.61 mg/L.

2.2. Bacterial inoculation and acclimation

The bioreactor was inoculated and acclimated according to the method described in detail in our previous publication (Wang and Qu, 2003). Under continuous-flow, with the applied electric current of 80 mA, biofilm was formed on the cathode and sulfur granule surface in about 25 days.

2.3. Experimental design

During the whole operating time of 105 days, the hydraulic retention time (HRT) was maintained at 4.2, 3.6, 3.0, 2.4 and 2.1 h for 21 days each to investigate the effect of HRT. Correspondingly, the nitrogen volume-loading rate was maintained at 0.12, 0.14, 0.17, 0.20, 0.24 kg N/m³ d. Direct current were applied to the reactor sequentially, 30–400 mA for HRT of 4.2, 3.6, 3.0 h; and 180–1200 mA for HRT of 2.4 h and 2.1 h.

Since the groundwater contained a trace amount of phosphate (6 mg/L), no phosphates added to the influent as nutrition during the whole operating time. As DO of this groundwater (3.5–4.9 mg/L) was much lower than surface water, no method was used to remove DO and the water flow was upward and isolated from the air to keep an anaerobic environment within the column.

During electrical process, it was necessary to prevent O_2 generated on anode. For carbon rod anode reaction, CO_2 is formed prior to O_2 for their electrode potential at low applied voltage (Wang and Qu, 2003), so it was essential to operate the reactor under 30–1200 mA (corresponding voltage was 0.5–5.5 V) to test its electrical chemical changes and find maximum applied current. The results showed that ORP decreased slowly from -20 mV to -50 mV when applied current increased from 30 to 1000 mA; and increased sharply to $+20$ mV under 1200 mA applied current. Therefore, the maximum applied current was fixed at 1000 mA (corresponding voltage was 5.0 V) in order to prevent O_2 generated at anode.

Under different HRT and different currents, the system run and stabilized 3.5 days and steady-state condition was achieved when

Fig. 1. Schematic drawing of continuous-flow reactor.

variation of sample data of three sequential retention times was less than 5%. Optimum operation conditions was determined at different HRT with minimum applied current to achieve more than 95% nitrate removal efficiency and without accumulation of nitrate.

2.4. Analytical methods

The NO_3^- -N, NO_2^- -N, SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, pH, TOC and turbidity of the influent, effluent from S-part and E-part was measured at each steady-state condition. Samples were passed through 0.45 μm membrane for NO_3^- -N, NO_2^- -N, SO_4^{2-} and $\text{S}_2\text{O}_3^{2-}$ measurement. The concentrations of NO_3^- -N, NO_2^- -N, SO_4^{2-} and $\text{S}_2\text{O}_3^{2-}$ were determined by ion chromatograph (Metrohm 861, Switzerland). TOC was measured by a TOC analyzer (Jena multi N/C 3000, Germany). COD was measured by a COD analyzer (HACH DRB200 and DR/2800, USA). VSS was determined according to Standard Methods (APHA et al., 1992). The DO, pH, ORP and Conductivity were measured by multi parameters portable instruments (HACH Sension, USA). Turbidity was determined with a turbidity meter (HACH 2100N, USA).

3. Results and discussion

3.1. Principle of the CBSAD system

In the CBSAD process, nitrate is firstly reduced to nitrogen gas by the biofilm on sulfur granule surface in S-part, and H^+ is generated meanwhile (Koenig and Liu, 2001):

Similarly, based on the basic equation of E-part (Wang and Qu, 2003):

Assuming that the bacterial yield coefficient of E-part was the same as S-part (0.057), Eq. (2) could be express as:

H^+ produced in the S-part can be used for further hydrogen denitrification in the E-part. According to the calculation of H^+ balance (Eqs. (1) and (3)), when the nitrate removal ratio of E-part to S-part was ≥ 1.09 , the whole reactor effluent will kept neutral; otherwise the whole reactor effluent pH will be lower than influent as a result of redundant H^+ formed by S-part that can not be completely consumed by E-part.

For anode reaction, CO_2 is formed prior to O_2 for their electrode potential. Thus a favorable anoxic condition is provided and dissolved CO_2 is also as an IC source. Besides, CO_2 can adjust pH as well.

3.2. Kinetics study of the S-part

The nitrate and nitrite concentration of effluent from S-part under different nitrogen volume-loading rates during the whole operation period is shown in Fig. 2a. It could be seen that by the decrease of HRT, nitrogen volume-loading rate became larger; the concentration of effluent nitrate increased steadily, and the same phenomena appeared as nitrites. The removal efficiency decreased from 98.3% to 66.8% when nitrogen volume-loading rate increased from 0.12 to 0.24 $\text{kg N/m}^3\text{d}$.

Kinetics of biological denitrification is usually assumed to be described by Monod expressions (Zeng and Zhang, 2005). Since

Fig. 2. (a) NO_3^- -N and NO_2^- -N in the effluent from S-part as a function of nitrogen volume-loading rate and (b) two kinetics models fitted for sulfur autotrophic denitrification.

the Monod saturation constant K_s of autotrophic denitrification is very low (e.g. Batchelor and Lawrence reported a K_s value of 0.03 mg/L as NO_3^- (Batchelor and Lawrence, 1978); Claus and Kutzner reported a K_s value of 0.2 mg/L as NO_3^- (Claus and Kutzner, 1985)), the intrinsic kinetics of the biofilm can be taken as a zero-order reaction. And the following two equations for substrate removal can be obtained using a simplified pore diffusion model based on the assumptions of steady-state condition and substrate transport in the biofilm according to Fick's diffusion law (Harremoes, 1976; Jasen and Harremoes, 1985).

Zero-order bulk reaction: Based on the assumption that the kinetics at conditions that sulfur as substrate was sufficient and there was no mass-transfer limitation into the biofilm (Wang, 1998; Liu and Koenig, 2002; Moon et al., 2004). It can be expressed as:

$$r_v = K_{\text{ov}} \quad \text{valid when} \quad \beta = \sqrt{\frac{2D_i C_i}{K_{\text{ov}} \delta}} \geq 1 \quad (4)$$

where r_v is the removal rate per unit biofilm area ($\text{mg/dm}^2\text{h}$); C_i is the bulk concentration of substrate at the surface of the biofilm (mg/L); D_i is the diffusion coefficient of substrate (dm^2/h); K_{ov} is the zero-order reaction rate constant per unit biofilm area ($\text{mg/dm}^2\text{h}$); β is the penetration ratio, and δ is the thickness of the biofilm (dm).

Half-order bulk reaction: Based on the hypotheses that the kinetics at conditions that the nitrate concentration was not so high that it can not penetrate the whole biofilm; and development of this

model had been applied in a number of studies (Wang, 1998; Koenig and Liu, 2001; Moon et al., 2004). It can be expressed in integrated form:

$$r_v = K_{1/2} C_i^{1/2} \quad \text{valid when } \beta < 1 \quad (5)$$

where $K_{1/2}$ is the half-order reaction rate constant per unit biofilm area ($\text{mg}^{1/2}/\text{dm}^{1/2} \text{ h}$).

In this reactor, the upward flow of groundwater through the sulfur and anthracite granules medium layer for autotrophic denitrification can be considered as the flow pattern of a plug flow reactor. The effluent concentration of a plug flow reactor can be calculated by the following equation:

Zero-order bulk reaction:

$$C = C_0 - K_{0v} T \quad (6)$$

Half-order bulk reaction:

$$C = (C_0^{1/2} - \frac{1}{2} K_{1/2} T)^2 \quad (7)$$

where C_0 (mg-N/L) is the initial concentration of nitrate; T (h) is the reaction time which can be calculated by flux and relevant effective liquid volume of S-part; C (mg-N/L) is the concentration of effluent nitrate at reaction time T (h).

In the above two kinetics models, Eqs. (6) and (7) give methods to calculate kinetics parameters and coefficients. These can be used to calculate sulfur autotrophic denitrification rate, the very important parameter to describe sulfur autotrophic denitrification of fixed system. Fig. 2b shows the nitrate concentration in the S-part as a function of reaction time, and also gives the results of experimental data fitted to the two kinetics models. Table 1 lists the calculated parameters and correlation coefficients. It can be seen from Table 1 that the experimental data is in better agreement with half-order kinetics model on the basis of correlation coefficients (R^2).

Since the proportion of effective liquid volume of S-part volume to total effective liquid volume was 0.431, the relationship between nitrate concentration of S-part effluent and HRT can be expressed as:

$$C = (4.55 - 0.431 \cdot \text{HRT} \cdot \frac{1}{2} K_{1/2})^2 \quad (8)$$

and when $\frac{1}{2} K_{1/2} = 2.09$ ($\text{mg}^{1/2}/\text{dm}^{1/2} \text{ h}$), that becomes:

$$C = (4.55 - 0.90 \cdot \text{HRT})^2 \quad (9)$$

If $\text{HRT} \geq 5.05$ h, nitrate could be completely decreased by S-part, and there was no need for E-part to reduce nitrate, so the maximum HRT and the minimum flux of this system were 5.05 h, 6.62 L/h, respectively. And, the minimum nitrogen volume-loading rate was 0.10 $\text{kg N/m}^3 \text{ d}$.

It was also indicated that the biofilm was thick enough and the nitrates diffusion in the biofilm was the limitation step in the S-part. Sulfur autotrophic denitrification rate first achieved the maximum at bottom of the S-part, and then became lower as the nitrate decreased; it lowered to the minimum value at the top of the S-part.

Table 1
Kinetics parameters and correlation coefficients (R^2) for the two kinetic models

Kinetics model	Kinetics coefficients		
	$C_{0\text{cal}}(\text{NO}_3^- \text{ -N mg/L})$	K_{0v} or $\frac{1}{2} K_{1/2}$	R^2
$C = C_0 - K_{0v} T$	19.37	11.62	0.9500
$C = (C_0^{1/2} - \frac{1}{2} K_{1/2} T)^2$	20.72	2.09	0.9790

3.3. Sulfate in the effluent

In this study, sulfate was the only product of sulfur oxidation detected in the effluent, and thiosulfate was under detection limit (0.1 mg/L) due to its low concentration. From Fig. 3a it could be founded that sulfate concentration was largely affected by nitrogen volume-loading rate. With the increase of nitrogen volume-loading rate, the removal efficiency of S-part decreased. And the sulfate concentration appeared a decreasing tendency. The sulfate concentration decreased from 243 mg/L to 200 mg/L when nitrogen volume-loading rate increased from 0.12 to 0.24 $\text{kg N/m}^3 \text{ d}$. It can also be seen from Fig. 3b that the removed nitrate is well linearly fitted with the formed sulfate with high correlation coefficients ($R^2 = 0.9836$). The average concentration ratio of formed sulfate concentration to removed $\text{NO}_3^- \text{ -N}$ was 7.14, which was very near to the stoichiometric value of 7.18. Fig. 3a also shows that the sulfate concentration of effluent during the whole operation time was lower than 250 mg/L , the drinking water standard of sulfate from China EPA.

In this combined process, the sulfate concentration of the effluent was linearly fitted with removed nitrate of S-part, and it could be controlled by the nitrogen volume-loading rate. Therefore, the effluent sulfate concentration of this system would be much lower than SLAD system by increasing the nitrogen volume-loading rate.

Fig. 3. (a) Sulfate concentration of effluent as a function of nitrogen volume-loading rate and (b) removed nitrate as a function of formed sulfate in the S-part.

3.4. Optimum current applied at different nitrogen volume-loading rate

Fig. 4 shows performance of reactor under different currents and nitrogen volume-loading rates. In this reactor, nitrate was firstly denitrified in S-part, and then the residual nitrate and formed nitrite from S-part were both further reduced by hydrogen denitrification in E-part. It could be concluded from kinetics study of the S-part that with the increase of nitrogen volume-loading

rate, the concentration of effluent nitrate increased and nitrite formed as well, so higher applied current was in need. From Fig. 4a and b it can be seen that low current (≤ 400 mA) was suitable for E-part when nitrogen volume-loading rate ranged from 0.12 to 0.17 kg N/m³ d. Residual nitrate and nitrite in effluent from the S-part can be well hydrogen denitrified in the E-part. The optimum currents applied at nitrogen volume-loading rates of 0.12, 0.14, 0.17 kg N/m³ d were 30, 150, 400 mA, respectively; and corresponding nitrate removal efficiency were up to 98% without nitrite accumulation. Furthermore, both the nitrate and nitrite removal were increased steadily with the increase of applied currents. It can also be concluded that the applied current was the key influencing factor in the CBSAD process under the voltage from 0.5–5.0 V with the HRT ranged from 4.2 to 2.4 h. But when HRT was shortened from 2.4 h to 2.1 h, and nitrogen volume-loading rate increased from 0.20 to 0.24 kg N/m³ d, higher current (1200 mA) applied did not bring out an increase in nitrate and nitrite removal, which was caused by O₂ forming on anode at voltage of 5.5 V. The corresponding DO was 8.3 mg/L at 1200 mA, thus the activity of hydrogenotrophic denitrifiers was reduced in such aerobic condition. The suitable applied current at HRT of 2.4 h and 2.1 h were 900 mA and 1000 mA, respectively. The maximum volume-loading rate of the system and the maximum surface loading rate of the cathode were 0.24 kg NO₃⁻ N/m³ d, 0.33 mg NO₃⁻ N/cm² d, respectively. And, the maximum flux and the minimum HRT of this system were 15.93 L/h, 2.1 h, respectively.

The effective current (I_E) of bioelectrochemical part, which can indicate efficiency of applied current, was defined as:

$$I_E = \left[(C_{\text{NO}_3^-, \text{in}} - C_{\text{NO}_3^-, \text{eff}}) \cdot 5 + (C_{\text{NO}_2^-, \text{in}} - C_{\text{NO}_2^-, \text{eff}}) \cdot 3 \right] \cdot F \cdot Q \quad (10)$$

where unit of C is nitrate or nitrite concentration (mol-N/L), F is Faraday constant (26.8 C/mol), Q is the flux (L/h). The electric current efficiency can be calculated as: $E_i = I_E / I$. It can be seen from Fig. 4c that efficiency of optimum current at different nitrogen volume-loading rates ranges from 76% to 90%. It can be concluded that the majority of hydrogen generated by anode was utilized for autotrophic denitrification.

3.5. pH in the effluent

The pH decrease of S-part and E-part effluent at different nitrogen volume-loading rates is shown in Fig. 5. It could be seen that the pH decrease of S-part exhibited a decreasing tendency by

Fig. 4. (a and b) NO₃⁻-N and NO₂⁻-N in the effluent as a function of applied current and nitrogen volume-loading rate (L₁ = 0.12 kg N/m³ d; L₂ = 0.14 kg N/m³ d; L₃ = 0.17 kg N/m³ d; L₄ = 0.20 kg N/m³ d; L₅ = 0.24 kg N/m³ d) and (c) efficiency of optimum current at different nitrogen volume-loading rates.

Fig. 5. pH decreases of S-part effluent and E-part effluent at different applied currents and nitrogen volume-loading rates (L₁ = 0.12 kg N/m³ d; L₂ = 0.14 kg N/m³ d; L₃ = 0.17 kg N/m³ d; L₄ = 0.20 kg N/m³ d and L₅ = 0.24 kg N/m³ d).

increasing nitrogen volume-loading rate: pH decreased 0.51–0.52 for $L_1 = 0.12 \text{ kg N/m}^3 \text{ d}$; while 0.23–0.25 for $L_5 = 0.24 \text{ kg N/m}^3 \text{ d}$.

The pH decrease of E-part was lower than S-part, and the pH decrease of E-part reduced slightly with the increase of current when the current $\leq 1000 \text{ mA}$. The result indicated that the H^+ generated by S-part was consumed well by E-part. With the adjustment of E-part, neutralization could be maintained. And for the nitrate removal ratio of E-part to S-part was < 1.09 , the effluent pH of E-part was slightly lower than influent. It should be noticed that when higher current (1200 mA) applied, the pH of E-part effluent was lower than S-part. This was because alkalinity of water could be consumed by the generation of O_2 at anode.

3.6. Turbidity in the effluent

Multiplication of biomass was very low and did not change obviously during the whole operation time. COD in the effluent of both parts was lower than 10 mg/L . In this study, turbidity was used to indicate total count of bacteria of effluent from both parts. It can be seen from Fig. 6 that the turbidity of both parts was lower than 1 NTU during the whole operation time; and turbidity of E-part effluent was slightly higher than S-part effluent.

Fig. 6. Turbidity variations of influent, S-part effluent and E-part effluent at different operate stages.

In addition, cell assimilation could be estimated by VSS variation. In this study, the average VSS of effluent minus influent was 8.5 mg/L . Assuming that biomass of reactor was not change obviously under the steady-state condition; 8.5 mg/L VSS increase was attributed to $\text{C}_5\text{H}_7\text{O}_2\text{N}$ (final product of cell assimilation) generation; influent $\text{NO}_3^- \text{-N}$ was 21 mg/L ; and removal efficiency was 100%; therefore the bacteria yield coefficient could be calculated as 0.050, and the inaccuracy was understandable for approximate calculation.

3.7. Comparison with other denitrification systems

To compare with other heterotrophic biological denitrification systems (including bio-electrochemical reactors, hydrogen dependent reactor and sulfur packed-bed reactor), the main operation parameters for the best removal capacity of each reactor are summarized in Table 2:

It can be seen from Table 2 that the CBSAD system has advantages of shorter HRT, larger treatment capacity and higher removal efficiency. Compared with previous CBSAD reactor (Wang and Qu, 2003), the reactor was amplified for about 28 times in this study, and some regularity including kinetics study of S-part, sulfate concentration and pH variation as a function of nitrogen volume-loading rate was obtained this time. And it was also approved that the CBSAD system was possible for groundwater denitrification.

4. Conclusions

The CBSAD process was possible for groundwater denitrification. The two denitrification processes could realize and be integrated in this system.

In such process: The H^+ generated in the S-part could be consumed by the E-part to achieve neutralization; the effluent sulfate concentration could be controlled by the nitrogen volume-loading rate.

The denitrification rate of the S-part followed a half-order kinetics model. And the removal rate of E-part depended on the electric current.

The reactor could be operated efficiently at the nitrogen volume-loading rate ranging from 0.12 to $0.24 \text{ kg N/m}^3 \text{ d}$ (corresponding HRT varied from 4.2 to 2.1 h; optimum current varied from 30 to 1000 mA; efficiency of optimum current ranged from 76% to 90%), and the $\text{NO}_3^- \text{-N}$ removal rate in the range of 95–100% without nitrite accumulation.

Table 2
Comparison with other denitrification systems

Reactor	Effective volume (L)	Influent	Initial ($\text{NO}_3^- \text{-N}$) (mg/L)	Current (mA)	HRT(h)	Removal efficiency	Reference
BER* coupled with adsorber	0.205	Synthetic water	24	5	10	>95 %	Feleke and Sakaibara (2002)
Multi-electrode system	36	Synthetic water	20	960	6	80 %	Sakakibara and Nakayama (2001)
BER* combined with microfiltration	0.6	Synthetic water	25	60	2.88	80 %	Prosnansky et al. (2002)
BER* with a two-reactor system	0.27	Synthetic water	25	70	3.3	92 %	Szekeres et al. (2001)
Anaerobic MBR with a novel hydrogen delivery system	5.6	Synthetic water	25	–	3	>98 %	Rezania et al. (2007)
Elemental sulfur packed bed reactor	–	Synthetic water	60	–	4	96 %	Koenig and Liu (2001)
The CBSAD system of previous Study	1.23	Synthetic water	30	16	1.9	90%	Wang and Qu (2003)
The CBSAD system in this study	33.47	Ground water	20.9–22.0	1000	2.1	95%	This study

* Bio-electrochemical reactor.

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