Nitrate removal from groundwater driven by electricity generation and heterotrophic denitrification in a bioelectrochemical system
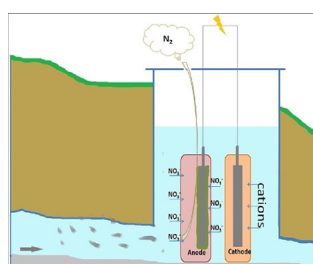
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HIGHLIGHTS

- A bioelectrochemical system is developed for nitrate removal from groundwater.
- Nitrate is moved from groundwater into an anode driven by an electric potential.
- Nitrate is reduced to nitrogen gas *via* heterotrophic denitrification.
- The present system remove nitrate from both synthetic and actual groundwater.

GRAPHICAL ABSTRACT

ABSTRACT

This research aims to develop a new approach for *in situ* nitrate removal from groundwater by using a bio-electrochemical system (BES). The BES employs bioelectricity generated from organic compounds to drive nitrate moving from groundwater into the anode and reduces nitrate to nitrogen gas by heterotrophic denitrification. This laboratory study of a bench-scale BES demonstrated effective nitrate removal from both synthetic and actual groundwater. It was found that applying an electrical potential improved the nitrate removal and the highest nitrate removal rate of 208.2 ± 13.3 g $NO_3{}^-$-N m^{-3} d^{-1} was achieved at 0.8 V. Although the open circuit condition (no electricity generation) still resulted in a nitrate removal rate of 158.5 ± 4.2 g m^{-3} d^{-1} due to ion exchange, electricity production could inhibit ion exchange and prevent introducing other undesired ions into groundwater. The nitrate removal rate exhibited a linear relationship with the initial nitrate concentration in groundwater. The BES produced a higher current density of 33.4 A m^{-3} and a higher total coulomb of 244.7 ± 9.1 C from the actual groundwater than the synthetic groundwater, likely because other ions in the actual groundwater promoted ion movement to assist electricity generation. Further development of this BES will need to address several key challenges in anode feeding solution, ion competition, and long-term stability.

1. Introduction

Human activity is extensively affecting global nitrogen circulation. Due to an increasing demand for more agricultural/industrial production and other resources because of a higher living standard and increased population, the discharge of nitrogen compounds such as inorganic nitrogen (*e.g.*, ammonia/ammonium, nitrogen oxide, and nitrate) and organic nitrogen (*e.g.*, urea, amines and protein) *via* water use also rises [1]. Excessive release of nitrogen and other nutrients into water bodies is responsible for eutrophication of aquatic systems, which deteriorates water quality [2]. High doses of nitrate, and nitrite, a reducing product of nitrate, also pose a potential risk to public health through human consumption of drinking water [3–6]. Because of its strong mobility, nitrate can move into groundwater with leachate or runoff. Groundwater plays

a critical role in the supply of drinking water: in the United States, groundwater is the primary source of drinking water for 44% of the population [7]. The United States government has established a strict standard for nitrate concentration in drinking water produced from groundwater (10 mg NO_3^--N L^{-1}) [8], and World Health Organization suggests a guideline value for nitrate of 11 mg NO_3^--N L^{-1} in drinking water [9]. Therefore, groundwater contaminated with nitrate must be properly remediated before use.

The removal of nitrate can be accomplished by using physical, chemical, and biological methods [10]. For example, ion exchange is commonly used in producing drinking water from groundwater [11], in which the cations in groundwater are exchanged with sodium ions and the anions are replaced by chloride ions when flowing through the packed ion exchange resin [12]. Reverse osmosis has not been particularly applied to remove nitrate, but its non-selective, semi-permeable membrane can stop many contaminants that may include nitrate. Biological nitrate removal is attractive because of its cost-effectiveness. Denitrification is commonly used to remove nitrate from sewage and natural water bodies including groundwater [13–15] and can be carried out by both heterotrophic and autotrophic bacteria [14,16]. Nitrate removal from groundwater is conducted by either *ex situ* or *in situ* approaches, and *in situ* treatment is preferred because it avoids the use of the energy-intensive pump-and-treat approach [17].

Bioelectrochemical systems (BES) are a relatively new concept for removing organic matters (including some hazardous materials [18–20]) from water and wastewater, while simultaneously producing electricity [21]. Prior laboratory studies have demonstrated that BES can also be applied for nitrate removal, mainly from wastewater through autotrophic or heterotrophic denitrification [22–25]; in such systems, electrons are produced from organic oxidation in the anode and transferred to a cathode electrode from which autotrophic denitrifying bacteria accept electrons for nitrate reduction.

A recent study applied the BES concept to nitrate removal from groundwater [26]. This submerged microbial desalination-denitrification cell takes advantage of the working principles of both microbial desalination cells (MDCs) and bioelectrochemical denitrification in microbial fuel cells (MFCs): nitrate ions migrate into an anode compartment driven by an electrical potential and then are transported into a cathode compartment for bioelectrochemical denitrification; an additional nitrifying bioreactor was added to the system to ensure that ammonium in the anode solution was converted to nitrate. The system achieved 90.5% removal of nitrate and exhibited a promising application of BES for *in situ* nitrate remediation in groundwater. However, the additional nitrifying bioreactor in this system could make the reactor construction and operation more complex and expensive; furthermore, since nitrate would first migrate into the anode compartment, it can be removed through heterotrophic denitrification. It was found that nitrate removal rate in a heterotrophic system was much higher than that in an autotrophic system with sulfide [27]; although there is no direct comparison between heterotrophic denitrification and autotrophic denitrification using a solid electron donor (cathode electrode), the latter could have a lower efficiency due to availability and accessibility of electron donors.

In this study, we have advanced the above system through simplifying the reactor structure and operation, accomplished nitrate removal in the anode of a BES, and improved the nitrate removal rate by applying external electric potentials. Nitrate was attracted from groundwater into an anode compartment by an electric force, and then heterotrophic denitrification occurred in the presence of organic compounds (Fig. 1). To examine its performance, we operated the present BES under several conditions with or without externally applied potential, and the effect of different applied potentials was studied. We investigated the role of ion exchange in
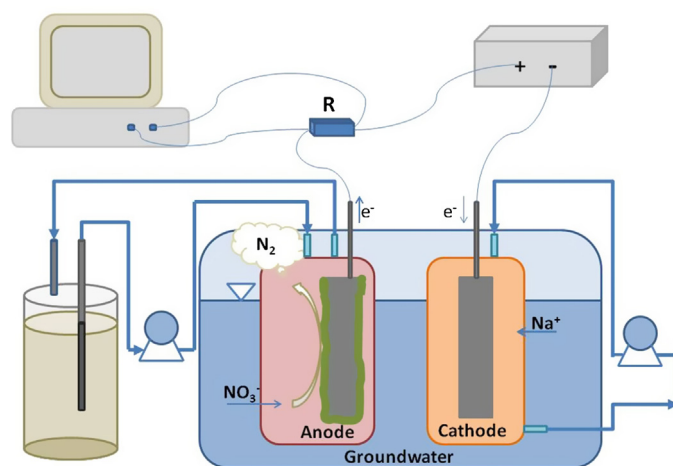

Fig. 1. Experimental setup of a bioelectrochemical system (BES) for nitrate removal from groundwater. The BES is controlled by a power supply and the data are collected by a computer.

nitrate removal and the influence of nitrate concentration on the BES performance. We also examined the nitrate removal in either a synthetic or an actual groundwater. The results are expected to provide a foundation for further development of a practical technology for *in situ* nitrate removal from groundwater.

2. Materials and methods

2.1. BES construction

The BES reactor consisted of two separated tubular compartments made of porous PVC tubes wrapped by exchange membranes and was submerged in a 2 L beaker containing 1 L of either synthetic or actual groundwater (Fig. 1). The anode compartment was created by a tube of an anion exchange membrane, and the cathode compartment was contained in a tube of a cation exchange membrane (Membrane International Inc., Ringwood, NJ, USA). The anode compartment contained a carbon brush as an anode electrode, resulting in an anode liquid volume of 90 mL while the cathode compartment had carbon cloth as a cathode electrode coated with 0.5 mg Pt cm^{-2} (prepared as previously described [28]), and a cathode liquid volume of 160 mL. The anode and the cathode electrodes were connected to an external circuit across a resistor of 10 Ω with or without being linked to a power supply.

2.2. BES operation

The BES was operated in a batch mode at a room temperature of ~20 °C. The feeding solution to the anode compartment was prepared as: 0.5 g L^{-1} CH_3COONa; phosphate buffer solution (diluted from 1 mol L^{-1} phosphate buffer solution containing 107 g L^{-1} K_2HPO_4 and 53 g L^{-1} KH_2PO_4); NH_4Cl, 75 mg L^{-1}; NaCl, 250 mg L^{-1}; $MgSO_4$, 7.5 mg L^{-1}; $CaCl_2$, 10 mg L^{-1}; $NaHCO_3$, 50 mg L^{-1}; trace mineral solution 0.1 mg L^{-1} [29]; and 1 g L^{-1} yeast extract. The conductivity of the fresh anode feeding solution was between 9 and 10 mS cm^{-1} and its pH was around 7. The anode feeding solution was purged with nitrogen gas before use. The catholyte was a 100 mmol L^{-1} phosphorus buffer solution and was purged with nitrogen gas when the BES was operated in an MEC (microbial electrolysis cell) mode. The anode compartment was connected to a reservoir containing 400 mL of the anolyte. Both the anolyte and the catholyte were recirculated at 100 mL min^{-1} by using a peristaltic pump. The synthetic groundwater was prepared by dissolving $NaNO_3$ in tap water. The actual groundwater

was collected from No.BQ185 well, Wisconsin, USA. The anode was inoculated with digested sludge (South Shore Water Reclamation Facility, WI, USA) at a volume ratio of 5%. The anode feeding solution and the groundwater were replaced with fresh solutions every 24 h.

The BES was operated under several different conditions: open circuit (OC), the MFC mode (without externally applied potential), and the MEC mode (with an externally applied potential). In the MEC mode, a power supply (3645 A, Circuit Specialist Inc., AZ, USA) was used to apply 0.5 V, 0.8 V or 1.0 V to the circuit, as previously described [28]. Those selected voltages are within the typical range of the applied voltage in an MEC (0.2–1.0 V) [30]. To maintain the conductivity and buffering capacity of the anolyte when using a low concentration of phosphate buffer solution (1 mmol L^{-1}), 3.3 g of NaHCO$_3$ was added into the 400 mL of the anolyte.

2.3. Measurement and analysis

The BES voltage was recorded every 5 min by a digital multimeter (2700, Keithley Instruments, Inc., Cleveland, OH, USA). The pHs of the anolyte and the catholyte were measured by a benchtop pH meter (Oakton Instruments, Vernon Hills, IL, USA). The conductivity was measured by a benchtop conductivity meter (Mettler–Toledo, Columbus, OH, USA). The concentrations of chemical oxygen demand (COD), nitrate-nitrogen (NO$_3^-$-N), nitrite-nitrogen (NO$_2^-$-N), and total phosphate were measured using a colorimeter following the manufacturer's instructions (Hach DR/890, Hach Company, Loveland, CO, USA). Nitrate removal rates were calculated based on the anode liquid volume, and comparison of nitrate removal rates between operating conditions was statistically analyzed by using two-sample t-test. Two types of Coulombic efficiencies, based on COD in the anode compartment or nitrate from groundwater, were calculated as the total coulomb output (integrating the production of time and current) divided by the total coulomb input (either the moles of COD removed assuming 4 mol of electrons/mol of COD, or the moles of nitrate removed from the system assuming 5 mol of electrons/mol of nitrate), according to the following equations:

$$CE_C = \frac{Q_{\text{output}}}{Q_{\text{input}}} = \frac{\Sigma It}{F \times COD_{\text{removed}} \times 4}$$

$$CE_N = \frac{Q_{\text{output}}}{Q_{\text{input}}} = \frac{\Sigma It}{F \times N_{\text{removed}} \times 5}$$

where CE_C is the Coulombic efficiency based on organic substrate, CE_N is the Coulombic efficiency based on nitrate, Q_{output} is the produced charge, Q_{input} is the total charge available in the substrate, F is the faraday constant (96,485 C/mol e$^-$), I is the electric current (A), and t is time (s). COD$_{\text{removed}}$ is the COD removed by the BES (mol) in the period of time t, and N_{removed} is the amount of nitrate removed (mol) within time t.

3. Results and discussion

3.1. Effects of operating conditions

The BES was started in an MFC mode (without applying an external potential) for two weeks and then switched to an MEC mode that applied 0.8 V to the electrical circuit. After a period of two months, the BES achieved an average current density of 28.2 A m^{-3} at 0.8 V and a relatively stable removal of nitrate from the synthetic groundwater. The current generation exhibited a typical batch profile with a peak current of 35–40 A m^{-3} upon replacement of the anode feeding solution, the cathode buffer and the synthetic groundwater, followed by a decrease to 24–25 A m^{-3} (Fig. 2A). With
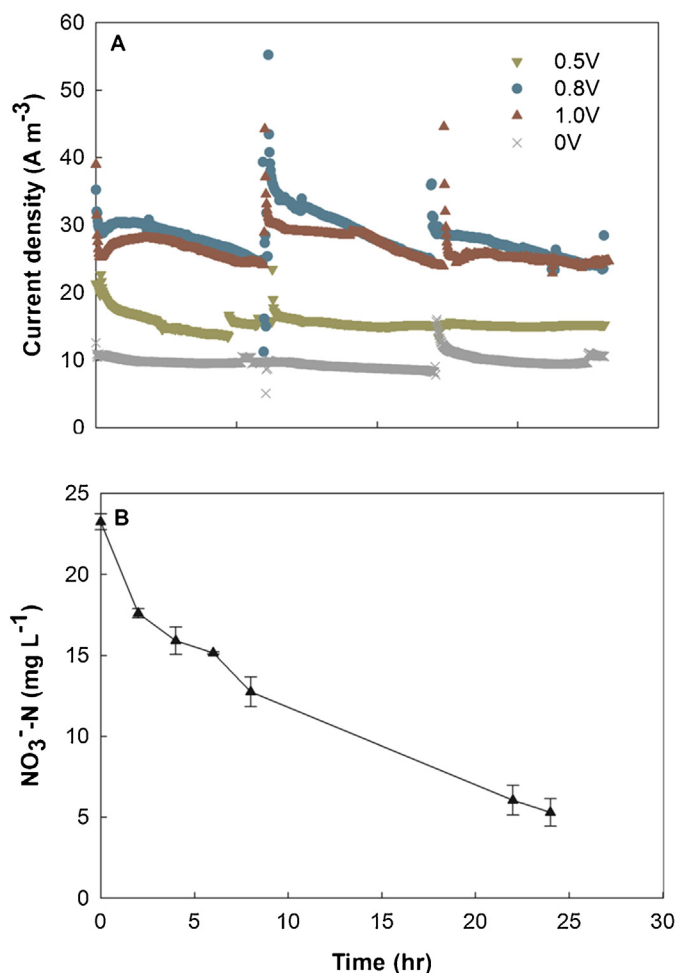

Fig. 2. Current production in the BES under different operating conditions (A), and the nitrate concentration variation in the synthetic groundwater under an applied potential of 0.8 V (B).

the use of a phosphate buffer solution, the pHs of the anolyte and the catholyte were maintained at 7.2 ± 0.1 and 7.4 ± 0.0, respectively. The COD concentration in the anolyte was about 550 mg L^{-1} at the end of a batch, resulting in 66.9 ± 7.7% removal within one cycle; we found that 15.7 ± 1.6% of COD was converted into electricity. Nitrate nitrogen in the synthetic groundwater was removed by 77.3% within 24 h (Fig. 2B). The anode effluent contained a very low concentration of nitrite (below 0.1 mg L^{-1}) and almost no nitrate. The theoretical nitrate removal rate in the BES was 208.2 ± 13.3 g NO$_3^-$-N m^{-3} d^{-1}.

It was observed that the decrease in nitrate concentration in the synthetic groundwater was greater in the first 10 h and then relatively slowed down, likely affected by current generation, which was related to the activity of electrochemically-active microbes and organic supply. The consumption of organic compounds in the anode compartment was mainly by electricity generation (electrochemically-active microbes), denitrification (denitrifying bacteria), and other microbial processes [31]. With the nitrate removal from the synthetic groundwater, more and more nitrate ions migrated into the anode compartment and increased the competition of organic compounds among those microbial processes. As a result of this and other continuing consumption of organic compounds over time, the electrical current became smaller and the electrical force for continuing nitrate removal became weaker. Consequently, the nitrate removal from the synthetic groundwater became slower. Given the fact that there was still a certain

Table 1
The nitrate removal rate and Coulombic efficiencies under different operating conditions. CE_C is the Coulombic efficiency based on organic substrate, and CE_N is the Coulombic efficiency based on nitrate.

	0 V	0.5 V	0.8 V	1.0 V
Nitrate removal (g NO_3^--N $m^{-3} d^{-1}$)	154.2 ± 24.4	172.1 ± 9.1	208.2 ± 13.3	181.1 ± 17.5
CE_C (%)	4.6 ± 0.5	8.0 ± 1.0	15.7 ± 1.6	13.8 ± 0.1
CE_N (%)	14.6 ± 0.2	22.6 ± 1.5	34.2 ± 0.8	36.2 ± 5.0

amount of organic compounds at the end of a batch, to ensure an efficient nitrate removal from groundwater, the activity of the electrochemically-active microbes must be further improved (*e.g.*, to improve Coulombic efficiency).

To further understand the effect of the operating conditions, the BES was examined in the MEC mode with 0.5 or 1.0 V, and in an MFC mode without any additional potential. As shown in Fig. 2A, the MEC mode with 0.8 or 1.0 V produced higher current densities than that with 0.5 V while the MFC mode ("0 V") generated the lowest current. Accordingly, the highest nitrate removal rate (208.2 ± 13.3 g NO_3^--N $m^{-3} d^{-1}$) was obtained with 0.8 V and the lowest one (154.2 ± 24.4 g NO_3^--N $m^{-3} d^{-1}$) was in the MFC mode (Table 1). Statistic analyses confirmed that the MEC mode with 0.8 V achieved the highest nitrate removal rate, while there was no statistic difference in nitrate removal rates between the 0.5 V and the MFC mode. The MEC mode also significantly improved the Coulombic efficiencies based on either organics or nitrate (Table 1). Better performance with 0.8 V than 0.5 and 0 V was because a higher energy input increases current generation, as observed in other MEC studies [30,32]. However, the 1.0 V condition did not lead to more current production than 0.8 V; the exact reason is not clear at this time. Surprisingly, there was a substantial nitrate removal with a nitrate removal rate of 158.5 ± 4.2 g NO_3^--N $m^{-3} d^{-1}$ under an open circuit (no electricity generation), and while in the absence of the cathode chamber, the anode alone achieved a nitrate removal rate 135.0 ± 3.9 g NO_3^--N $m^{-3} d^{-1}$, suggesting that other factors, likely ion exchange, played an important role in nitrate transport from the groundwater into the anode compartment. In the presence of an anion exchange membrane (surrounding the anode compartment) and a nitrate concentration gradient across the anion exchange membrane (higher in the groundwater and lower inside the anode compartment), nitrate ions could be exchanged by the anions such as chloride ions, phosphate ions, and acetic ions in the anolyte. Chloride ions would likely be one of the major exchange agents because of their large quantity. In addition, the Coulombic efficiency based on the nitrate consumption was less than 40% (Table 1), indicating that the movement of some nitrate ions across the anion exchange membrane was not associated with electricity production.

3.2. Effects of ion exchange

The nitrate removal from the synthetic groundwater under an open circuit condition (without electricity generation) intrigued us to investigate the effect of an ion exchange on the nitrate transport. The anode compartment contained an anion exchange membrane that allows the movement of anions such as nitrate ions driven by a concentration gradient. In the present study, the anolyte contained 50 mmol L^{-1} of a phosphate buffer solution that provided anions (*e.g.*, phosphate ions) to exchange nitrate ions from the synthetic groundwater. We found that the phosphate concentration in the synthetic groundwater reached 36.0 ± 3.1 mg L^{-1} under the open circuit condition or 28.4 ± 2.3 mg L^{-1} in the absence of the cathode chamber (Fig. 3). When we decreased the phosphate buffer concentration to 1 mM in the anolyte, the concentration of phosphate ions in the synthetic groundwater also notably decreased under the open circuit condition (Fig. 3). At an applied potential of

0.8 V, electricity was generated and we observed a significantly lower concentration of phosphate ions (3.8 ± 2.1 mg L^{-1}) with an initial 50 mmol L^{-1} phosphate buffer. The use of the 1 mmol L^{-1} phosphate buffer in the anolyte resulted in a non-detectable concentration of phosphate ions in the synthetic groundwater under 0.8 V. Those results indicated that electricity generation inhibited the migration of phosphate ions from the anode compartment into the synthetic groundwater; however, without electricity generation, the activity of the ion exchange became relatively stronger.

According to those results, we propose different mechanisms of nitrate transport from the synthetic groundwater into the anode compartment in the absence or presence of electricity generation. When there is no electricity production, the nitrate ions are exchanged by the anions (*e.g.*, phosphate ions) in the anode compartment; thus, the anion movement across the anion exchange membrane is in dual directions to maintain a neutral ionic change: the nitrate ions move into the anode and the anodic anions migrate into the synthetic groundwater. Phosphate ions could be a major anion for such exchange at a high initial concentration of the phosphate buffer (*e.g.*, 50 mmol L^{-1}). When the phosphate buffer is at a low initial concentration (*e.g.*, 1 mmol L^{-1}), other anions in the anolyte such as bicarbonate and chloride ions would act as exchange agents (unfortunately we did not monitor the concentrations of other anions). When electricity is produced, the movement of some anions including nitrate ions across the anion exchange membrane is in a single direction: the nitrate ions move into the anode compartment. To keep electric neutrality in the synthetic groundwater, additional anions need to move in or cations in the groundwater will move out; in this case, we think cations move out into the cathode compartment driven by an electric potential. That matches the principle of electricity generation in an MDC, in which anions move into an anode while cations migrate into a cathode. The co-existence of ion exchange with electricity generation also results in some dual-direction anion movement. Although the
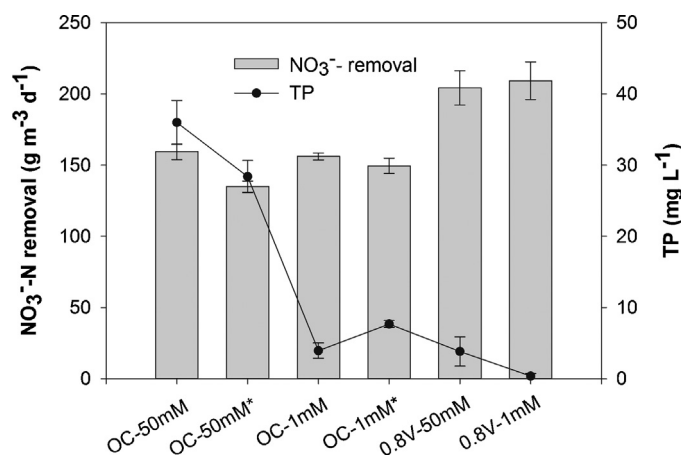

Fig. 3. Nitrate removal rate in the BES and the phosphate concentration (TP) in the synthetic groundwater under open circuit or 0.8 V with different phosphate buffer concentration in the anolyte. "OC-50 mM" means the open circuit condition with 50 mmol L^{-1} phosphate buffer solution. The "*" indicates that there was no cathode compartment in the groundwater during the test.
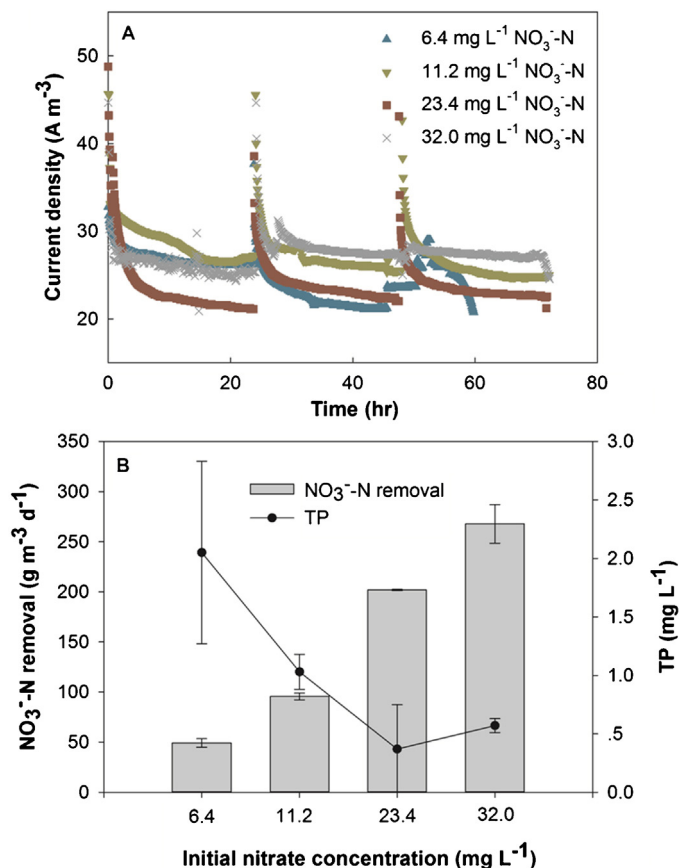
Fig. 4. Current production in the BES (A), and the nitrate removal rates and the phosphate concentrations (TP) in the synthetic groundwater (B) at different initial nitrate concentrations. The applied potential was 0.8 V and the initial phosphate buffer in the anolyte was 1 mmol L^{-1}.

Fig. 5. Current production in the BES with the actual groundwater.

nitrate was removed in both conditions, we think the electricity-generating condition is more desirable, because it enhances the nitrate removal rate and prevents unfavorable anions from entering the synthetic groundwater (avoiding potential contamination).

3.3. Effect of nitrate concentrations

The concentration of nitrate in groundwater affects the conductivity and consequently the electricity generation and ion exchange in the present BES. The US federal NO$_3^-$-N threshold in groundwater is 10 mg L^{-1} while in some states this value can be as high as 45 mg L^{-1}; therefore, we examined a series of nitrate concentrations, including 6.4, 11.2, 23.4, and 32.0 mg L^{-1}, with 0.8 V applied. The current generation exhibited a batch profile (Fig. 4A), and the four concentrations resulted in the produced coulombs of 176.2 ± 12.6, 200.1 ± 8.8, 177.0 ± 2.7, and 205.3 ± 8.2 C, respectively. Accordingly, the Coulombic efficiencies based on nitrate removal are $118.3 \pm 13.5\%$, $67.6 \pm 5.2\%$, $28.3 \pm 0.5\%$ and $24.8 \pm 1.4\%$. This suggests that as the initial C/N ratio decreases (with an increasing nitrate concentration), electricity generation played a weaker role in moving the nitrate out of the synthetic groundwater, likely due to a stronger activity of denitrification in the anode compartment that competed for electrons with the anode electrode and a stronger ion exchange activity.

We observed an unstable current generation with 6.4 mg NO$_3$-N L^{-1}, which was not shown with higher concentrations of nitrate; while the change in the phosphate concentration in the synthetic groundwater exhibited the largest variation at 6.4 mg NO$_3$-N L^{-1} (Fig. 4B). Those two phenomena could have a
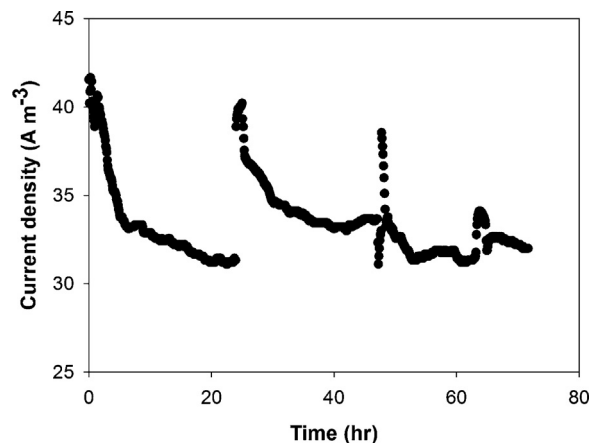
correlation, which needs further investigation. Higher concentrations of nitrate might stimulate ion exchange activities, resulting in higher nitrate removal rates: the nitrate removal rate of 267.78 ± 19.28 g NO$_3^-$-N m^{-3} d^{-1} with 32.0 mg L^{-1} was more than five times the one (49.25 ± 4.21 g NO$_3^-$-N m^{-3} d^{-1}) with 6.4 mg L^{-1} (Fig. 4B). There was almost a linear relationship between the nitrate removal rate and the initial nitrate concentration ($Y = 63.9X$, $R^2 = 0.9492$), suggesting a nitrate removal process behaving similarly to a first-order reaction in the present BES (while the actual removal mechanisms involve physical processes such as ion exchange, and biological reactions).

3.4. Nitrate removal from actual groundwater

The actual groundwater contains a nitrate concentration of $\sim$18 mg NO$_3$-N L^{-1}. The current generation in the BES exhibited a similar profile as those from the synthetic groundwater (Fig. 5). The nitrate removal rate was 130.0 ± 12.2 g NO$_3^-$-N m^{-3} d^{-1}, similar to that of the synthetic groundwater with a nitrate concentration between 11 and 24 mg L^{-1}, and also fit into the linear relationship developed with the synthetic groundwater. The average current density was 33.4 A m^{-3}, higher than those with the synthetic groundwater (23.7 A m^{-3} with 24 mg NO$_3^-$-N L^{-1} and 27.3 A m^{-3} with 32 mg NO$_3^-$-N L^{-1}); as a result, the total coulomb production was 244.7 ± 9.1 C, much higher than those with the synthetic groundwater, likely due to other ionic species present in the actual groundwater that promoted ion transport across the ion exchange membrane and thus current generation.

3.5. Perspectives

The present BES provides a promising approach for *in situ* nitrate removal in groundwater remediation. It takes advantage of bioelectricity generation to attract nitrate ions out of groundwater and thus avoids the addition of other compounds for remediation (*e.g.*, to stimulate microbial activities in groundwater bioremediation). The configuration of the separated anode and cathode improves the flexibility of the BES construction and operation and makes it possible to modify the components more conveniently (for example, modifying the anode/cathode or adding more units without affecting other units). Although the bioelectrochemical reactions in the anode and the cathode may affect the pH of adjacent groundwater *via* proton production/transport, this influence is minor due to a large volume of groundwater compared with much smaller volumes of the anolyte and the catholyte.

To further develop the present BES for *in situ* nitrate remediation, we must address several challenges. First, a proper anode

feeding solution should be selected: the use of purified organic compounds may increase the expense of remediation, while the low-cost substrates like wastewater must be used with caution to avoid introducing other contaminants into groundwater *via* the ion exchange processes. Second, the nitrate removal in the presence of other competing anions should be investigated: the competition could decrease the nitrate removal; on the other hand, the system may also remove other undesired ions (such as heavy metals into the cathode compartment) from groundwater. Third, the long-term performance of the BES with actual groundwater under a non-laboratory condition should be examined: the influence of environmental conditions (*e.g.*, temperature and pH) on the BES performance is a key factor to its successful operation, and some issues such as fouling of ion exchange membrane due to ionic deposition require a long-term operation of the system. Fourth, the BES needs to be scaled up to an applicable size: the scaling up is always a challenge to the development of bioelectrochemical systems, and an advantage of the present BES for groundwater remediation is that it does not require a very large scale system like that for wastewater treatment, thereby making scaling up relatively feasible. Last but not least, we should properly evaluate this system from the aspects of capital investment, operating expense, and advantages/disadvantages compared with other *in situ/ex situ* nitrate remediation approaches once the BES is enlarged to a certain scale.

4. Conclusions

This study has demonstrated the feasibility of using a bench-scale bioelectrochemical system to remove nitrate from groundwater. The BES effectively attracted nitrate out of groundwater driven by electricity generation and reduced it to nitrogen gas in the anode compartment *via* heterotrophic denitrification. Applying an external electric force improved the nitrate removal, and it was found that 0.8 V resulted in the highest nitrate removal rate. In addition to electricity generation, ion exchange was another major mechanism of nitrate migration into the BES anode, and there was competition between electricity-driven and ion exchange-driven nitrate movement, in which an electricity-driven process could inhibit the ion exchange process. The ion exchange process was also affected by the ionic concentration in the anolyte. The nitrate removal rate linearly increased with the increasing nitrate concentration in groundwater. The BES also achieved successful nitrate removal from actual groundwater sampled from a well in the state of Wisconsin. Further development of the BES for *in situ* nitrate removal from groundwater must consider the challenges such as the selection of anode substrates, the competition between nitrate and other anions, the long-term system performance, the reactor scaling up, and the economic evaluation of this approach.

Acknowledgements

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