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Removal of nitrate from groundwater using the technology of electrodialysis and electrodeionization

Jingjing Bi, Changsheng Peng*, Huizhen Xu, Abou-Shady Ahmed

College of Environmental Science and Engineering, Ocean University of China, Qingdao, China
Tel./Fax: +86 (532) 66782011; email: pcs005@ouc.edu.cn

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ABSTRACT

In this paper, the technical capabilities of a lab-scale electrodeionization (EDI) process and its basic technology electrodialysis (ED) process that used for removing NO$_3^-$ from nitrate-contaminated groundwater were investigated. The EDI unit with three chambers (anode, diluted and cathode) was used; it utilized electricity to regenerate ion-exchange resins instead of chemicals. At first, the voltage-current (V-I) characteristic curves about the ED and EDI processes were studied, and then chose the optimum operating voltage which based on the curves. The effects of operational parameters (voltage, water flow rate and initial NO$_3^-$-N concentration) on nitrate removal rate and concentration effect of ED and different ion-exchange resins, the proportion of anion and cation resins and the voltage used for regeneration of EDI were investigated. The results of ED showed that NO$_3^-$-N concentration could be reduced from initial 50–300 mg/l to 1–6 mg/l, with the removal rate 99% and the conductivity could be reduced to less than 10 μs/cm. Under the conditions of equal (1–8 l/h) and unequal (1:1,2,3,4,5,6,7,8 l/h) water flow rate between concentrated and diluted water, the concentrated water could be reached to 2–5 times more than the initial water. The current efficiency and energy consumption was 17–34% and 0.–1.7 W·h/l, respectively. It was shown that ED was effective to NO$_3^-$ removal and concentration. As to EDI process, the results showed that continuous electrodeionization could regenerate the resins effectively from simulated nitrate-contaminated water. Under the condition of 50 V as the regenerate voltage, after 90 h, the regeneration rate was as high as 60%. In addition, the NO$_3^-$-N concentration of the diluted water was reduced to 5 mg/l from initial 50 mg/l. As a fundamental technology of in-situ remediation for groundwater contamination, the process was proved to be feasible and provided foundation for further research.

Keywords: Nitrate contamination; Electrodialysis; Electrodeionization; Water reuse; Regeneration

1. Introduction

Nowadays, nitrate contamination of surface and ground waters has become a main environmental problem in many countries. Due to it is related to a number of health hazards; nitrate contamination has aroused more and more concern. Around 1960, 200 infants living in a village that located on the border of Germany and Austria had been found that approximately half of the infants suffered from “Methemoglobinemia”, known as “Blue baby syndrome”, among which one third died and one third appeared the symptom of oxygen lack [1]. The World Health Organization’s recommendation on the maximum contaminant level (MCL) in drinking water is 10 mg/l NO$_3^-$-N [2], while in our country the drinking water standard of the GB/T 14848-93 has set the maximum contaminant level at 20 mg/l NO$_3^-$N [3]. Early in

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*Corresponding author.

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the 1960s, some northern region of China, such as some areas of Liaoning, Jilin and Hebei provinces, had been reported the problem of "fertile groundwater" [4]. At present, nitrate contamination in soil and groundwater has became a big problem and cursed extensively concern in China. Zhao Tongke [5] found that the average content of NO_3^--N (11.9 mg/l) in groundwater and about 34.1% exceeded the standard of WHO according to evaluate drinking water quality in 7 provinces of north China such as Beijing, Hebei, Henan, Shandong, Liaoning, Tianjin and Shanxi. Pan Yongzhang [6] analyzed the contents of nitrate in soils and groundwater samples from the vegetable cultivation areas and found that the concentration of NO_3^--N in groundwater was 0.13–49.84 mg/l, some of the samples exceeded the standard of China. Chen Gan [7] found that the nitrate contents exceeded 20 mg/l in half areas of Nanfeihe River Basin of Hefei City. Zhao Xiuchun [8] analyzed the contents of nitrate in groundwater from several areas of Qingdao and found that the samples of 353 monitoring sites exceeded the standard of China.

The sources of nitrate contamination include agricultural fertilizers, the leakage of wastewater treatment plants and domestic sewage, landfills, the reuse of sewage etc [9]. Currently, there are several technologies used for treating nitrate-contaminated water, including chemical precipitation, distillation, ion-exchange, reverse osmosis (RO), electrodialysis and biological denitrification [10]. As the treatment of nitrate-contaminated water, these technologies have their own advantages, but there are also many disadvantages, such as the contamination causes by the regenerate solution of the ion-exchange resins, the strict pre-treatment requirement for RO and the secondary contamination of biological denitrification. In addition, the biological processes are only suitable for large-scale applications [2].

Permeable reactive barrier (PRB) and Electrokinetic remediation (EKR) technologies were emerged at the end of the 20th century as in-situ remediation technologies of the soil and groundwater contamination. Since there is no need to pump polluted groundwater above ground, PRB can be cheaper and faster than other methods, schematic PRB currently being developed for the management of heavy metal and petroleum-contaminated effluent from tips that are situated in coastal areas [11]. EKR has been proven that it is effective for removing heavy metals from polluted soils [12]. Though there are many advantages about the PRB and EKR technologies, for treating nitrate-contaminated water, there are still disadvantages. Seunghee [13] utilized the nanoscale zero-valent iron (1–100 nm) to remove the nitrate in the water environment, within a period of 30 min with little intermediates and the end product was not ammonia but N_2 gas, but the iron was too fine and the cost was high. While the disadvantage of EKR was that the processing cycle was very long and sometimes needed several mouths or years.

The aims of this research are to evaluate the feasibility of combining the PRB and EKR technologies and to choose an optimal material as the reactive material according to compare two kinds of ion-exchange resins. As to the ED process, the effects of operational parameters (voltage, water flow and initial NO_3^--N concentration) on nitrate removal rate and concentration effect were studied. Column experiments with the ion-exchange resins were carried out to ascertain the initial exchange capacity of different anion exchange resins (201×7 and D407) and the influences of different proportions between anion and cation exchange resins. A lab-scale unit with three chambers (anode, diluted and cathode) was used, the feasibility of utilizing electricity to regenerate ion exchange resins instead of chemicals and the effects of different ion exchange resins were examined.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

(1) Ion-exchange resin

Previous study about "removal of nitrate from water by ion-exchange resin" has finished. According to the results, it was considered that 201×7 (Amberlite IRA-400, USA) and D407 (PuroliteA520E) had good adsorption-desorption properties to NO_3^-, which could be used for nitrate removal [11]. In this experiment, two kinds of anion and cation ion-exchange resins were examined. The D407 was obtained from (Jiangsu Suqing Water Treatment Engineering Group Ltd., China) and the other three resins used in this paper were obtained from (Anhui Sanxing Resin Technology Ltd., China). The main properties of the ion-exchange resin were shown in Table 1.

Table 1
Main properties of the ion-exchange resin

Resi	201×7	001×7	D407	D001
Type	anion	cation	anion	cation
Matrix	Styrene	Styrene	-	Styrene
Porosity	Gel	Gel	Macroporous	Macroporous
Moisture holding capacity, %	42~48	46~52	52~60	45~55
Total exchange capacity, (mmol/g)	3.6 (dry)	4.5	1.2	4.35

(2) Chemicals and instruments

Different concentrations of nitrate-contaminated water were prepared by diluting the stock solution which was made by sodium nitrate (NaNO3) with tap water. Nitrate concentration was monitored by UV-visible spectrophotometer (UV-2600, Unico (Shanghai) Instrument Ltd., China). A pH meter (PHSJ-4A, Shanghai Precision & Scientific Instrument Ltd., China) was used to obtain the pH measurements; the conductivity was determined by a conductivity meter (DDSJ-308A, Shanghai Precision & Scientific Instrument Ltd., China). All the chemicals used for the chemical analysis were from Sinopharm Chemical Reagent Ltd. with analytical grade.

2.2. Experimental apparatuses

2.2.1. Electrodialysis

The ED system consisted of electrodialyzer, tubes, pumps, water flow meters etc. The membrane stack was packed with 110 pairs of cation and anion exchange membranes and two carbon electrodes (anode and cathode) which were made of carbon. The area of each electrode and membrane was 260 mm×140 mm. Fig. 1 lists the experimental set-up of ED.

2.2.2. Ion-exchange

To identify the initial exchange capacity of different anion exchange resins (201×7 and D407) and the influences of different proportions between anion and cation exchange resins, column experiments with the ion-exchange resins were carried out. The nitrate-contaminated (200 mg/l NO_3^--N) water was pumped through the ion-exchange column and the flow rate was 10–12 ml/min. The experimental set-up of this part is shown in Fig. 2.

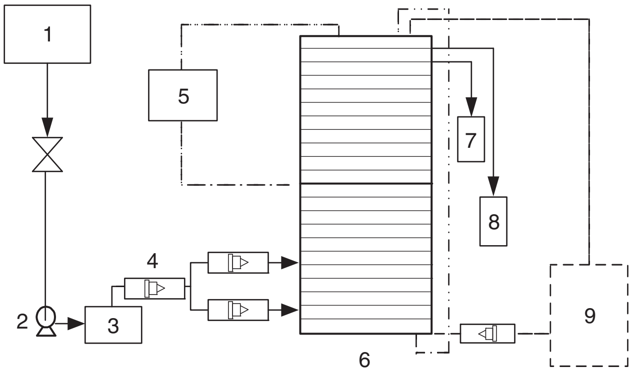

Fig. 1. Schematic representation of the electrodialysis system. 1-Raw water tank; 2-Pump; 3-Filtration; 4-Flow meter; 5-Power; 6-Membrane stack and electrodes; 7-Tank (diluted water); 8-Tank(concentrated water); 9-Tank(rinse water).

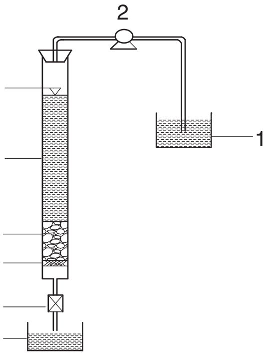

Fig. 2. Ion-exchange experiment set-up.
1-raw water tank; 2-peristaltic pump; 3-liquid level; 4-exchange cartridge; 5-ion-exchange resin; 6-porous stone; 7-valve; 8-effluent tank.

2.2.3. Combination process

For the combined process of PRB and EKR, the experimental set-up of this part is schematically shown in Fig. 3. The unit consisted of three separate chambers: an anode chamber, a cathode chamber and a center chamber, each chamber had the same size (180 mm × 50 mm × 80 mm). The ion-exchange resin was packed in the center chamber. The electrode chambers and the center chamber were separated by an anion exchange membrane (AEM) and a cation exchange membrane (CEM) respectively. In addition, ion-exchange membrane (Shanghai Chemical Ltd., China) used in this apparatus was characterized as low permeability, with an effective area of 90 cm^2 (180 mm × 50 mm). The spacing between the AEM and CEM was 5 mm. Ti/Ru electrodes that had the same effective area as the membrane were utilized as the positive and negative charges. A power supply (TPR-6420D, Hongkong, Longwei Ltd., China) was used to provide a constant

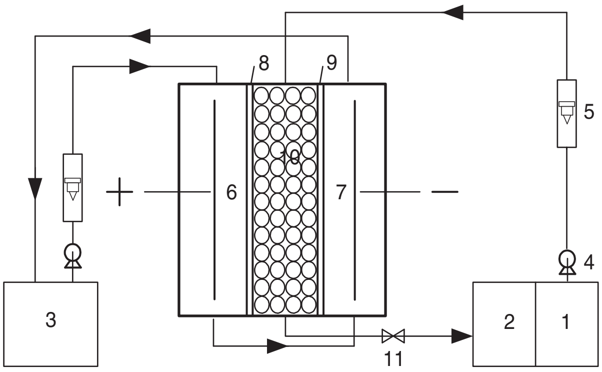

Fig. 3. Schematic representation of electrodeionization.
1-tank(inlet); 2-tank(outlet); 3-the electrode tank; 4-water pump; 5-flowmeter; 6-the anode chamber; 7-the cathode chamber; 8-AEM; 9-CEM; 10-the center chamber (filled with resins); 11-valve

DC voltage. The flow rates of diluted and concentrated water of the unit were 12 ml/min and 3 l/h respectively. The diluted chamber was filled with 1300 ml resins and the column ratio of anion and cation exchange resins was 2:1.

3. Results and discussion

3.1. Electrodialysis

The influences of cell voltage, flow rate and initial nitrate concentration on the diluted water, energy consumption and current efficiency were studied. In this experiment, the simulated nitrate-contaminated water was fed into the membrane stack and the effluent water samples (diluted and concentrated) were taken at certain intervals.

3.1.1. Effect of cell voltage

Cell voltage was the driving force of ED process, for it determined the migration speed of NO_3^- across the membranes. As shown in Fig. 4, the polarization curve was recorded in order to establish the limiting current. At the beginning of ED, the current raised linearly with the increase of the applied voltage. There were two inflection points at 35 V and 40 V, suggesting that the concentration polarization and water dissociation may happen when the voltage was higher than 30 V. As shown in Figs. 5 and 6, from 30 V to 40 V, the NO_3^--N concentration of diluted water was reduced to below 1.5 mg/l, the conductivity was below 20 μs/cm, and the removal rates of nitrate were all above 98%. The increasing cell voltage resulted in a linear increasing of energy consumption and slumping of current efficiency obviously that can be seen in Fig. 7. Based on an overall analysis, we chose 30 V as the operating voltage.

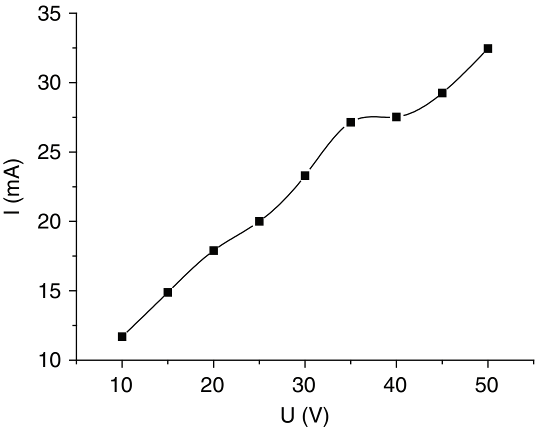

Fig. 4. Voltage-current curve.

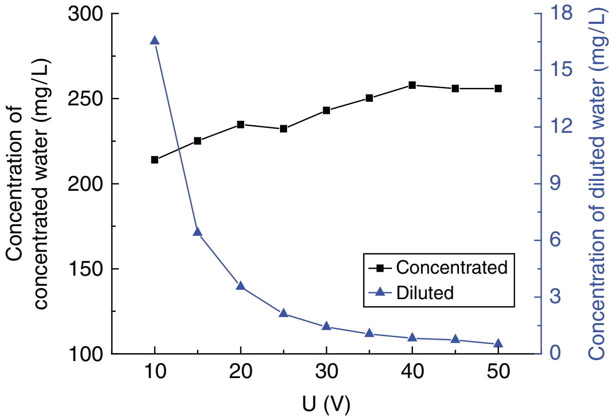

Fig. 5. Effect of cell voltage on nitrate concentration.

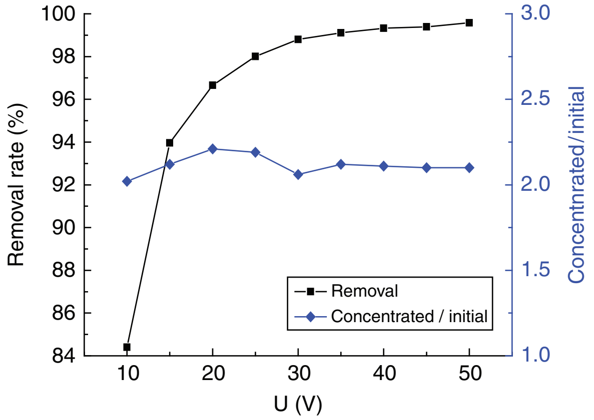

Fig. 6. Effect of cell voltage on nitrate removal and enrichment factor.

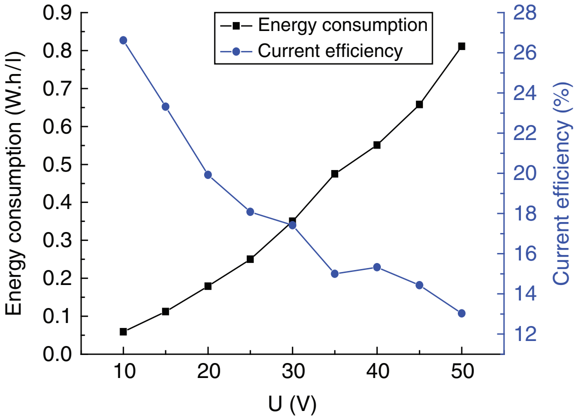

Fig. 7. Effect of cell voltage on energy consumption and current efficiency.

3.1.2. Effect of flow rate

Reuse rate of water was defined as ratio of diluted water to the total input. To know the influences of flow rate on nitrate removal rate and energy consumption, two kinds of water flow rate: equal and unequal water flow rate between concentrated and diluted water were studied.

3.1.2.1. Equal flow rate. The voltage and initial concentration of NO_3^--N was 30 V and 100 mg/l respectively. The flow rates of diluted and concentrated water were 1, 2, 3, 4, 5, 6, 7 and 8 l/h, respectively.

Curve R_1 of Fig. 8 showed that with the increasing of flow rate, the nitrate removal rate increased firstly. Due to along with the flow rate increased, more NO_3^- ions could be treated and then the concentration decreased; on the other hand, if the flow rates were too fast, the residence time of the ions in the membrane became short so that parts of the NO_3^- were discharged before treated. Finally, all these resulted in the concentration increased. Increasing water flow rate reduced the thickness of turbulent layers beside the surface of membranes and lowered the resistance of the membrane stack, which increased current efficiency (curve CE_1) and decreased the energy consumption (curve E_1).

3.1.2.2. Unequal flow rate. In order to enhance the recycle rate of diluted water, the flow rate of diluted water could be higher. So the diluted water flow rates were 1–8 l/h, while the concentrated was fixed as 1 l/h. The voltage and initial concentration of NO_3^--N were also 30 V and 100 mg/l respectively. Curve C_2 of Fig. 8 illustrated that the concentration and enrichment factor of concentrated water increased fast from 1 l/h to 6 l/h but lightly after 6 l/h. Since the flow rate of diluted water increased, there were more NO_3^- ions transferring to the concentrated compartments in comparison with equal flow rate. So enrichment could be much higher. Curve E_2 of Fig. 9 illustrated that energy consumption decreased sharply and current efficiency increased fast with the increasing of diluted flow rate. For NO_3^--N concentration of 100 mg/l, the optimum water flow rate of concentrated and diluted were 1 l/h and 8 l/h respectively. Under this condition, the concentration of diluted water was reduced to 2 mg/l, the conductivity was 30 μs/cm, while the concentration of concentrated water could be enriched to 460 mg/l, the enrichment factor was as high as 4.8 times, and the water reuse rate was 88%.

3.2. Ion-exchange

3.2.1. Initial exchange capacity

The results of the initial exchange capacity experiment were shown in Fig. 10a. Comparing the two anion exchange resins (201×7 and D407), it can be found that when there was only anion exchange resin (100 ml), after 12 h or so, the saturated adsorptive capacity of 201×7 and D407 were 59.40 and 24.79 mg NO_3^-/ml resin respectively; when the volume ratio of anion and cation resins was 1:1, after 6 h or so, the saturated adsorptive capacity of 201×7 and D407 were 63.60 and 25.74 mg NO_3^-/ml resin respectively. As shown in Fig. 10b, it was evident that Resin 201×7 had a larger overall exchange

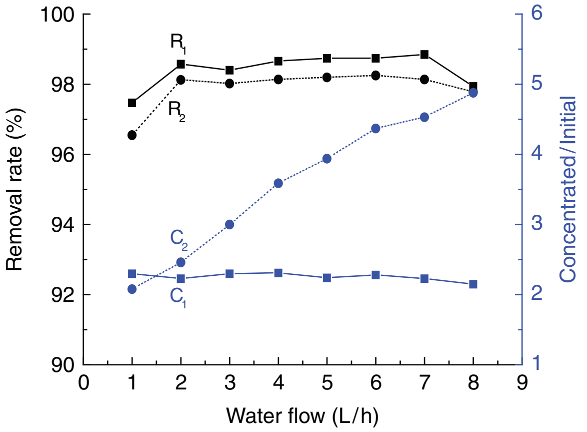

Fig. 8. Effect of water flow rate on nitrate removal and enrichment factor.
R_1, R_2: Nitrate removal rate of diluted water under the equal and unequal water flow rate
C_1, C_2: Enrichment factor of concentrated water under the conditions of equal and unequal water flow rate.

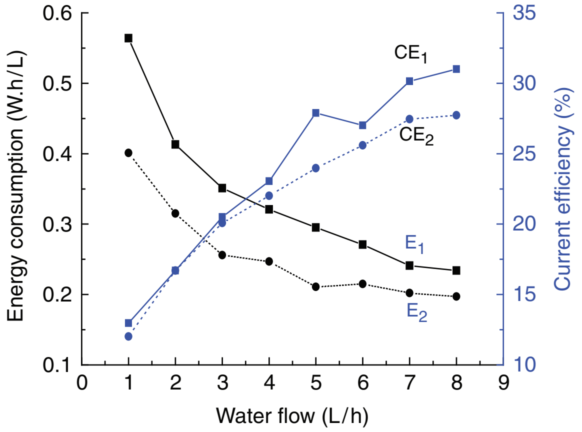

Fig. 9. Effect of water flow rate on energy consumption and current efficiency.
E_1, E_2: Energy consumption under the conditions of equal and unequal water flow rate
CE_1, CE_2: Current efficiency under the conditions of equal and unequal water flow rate.

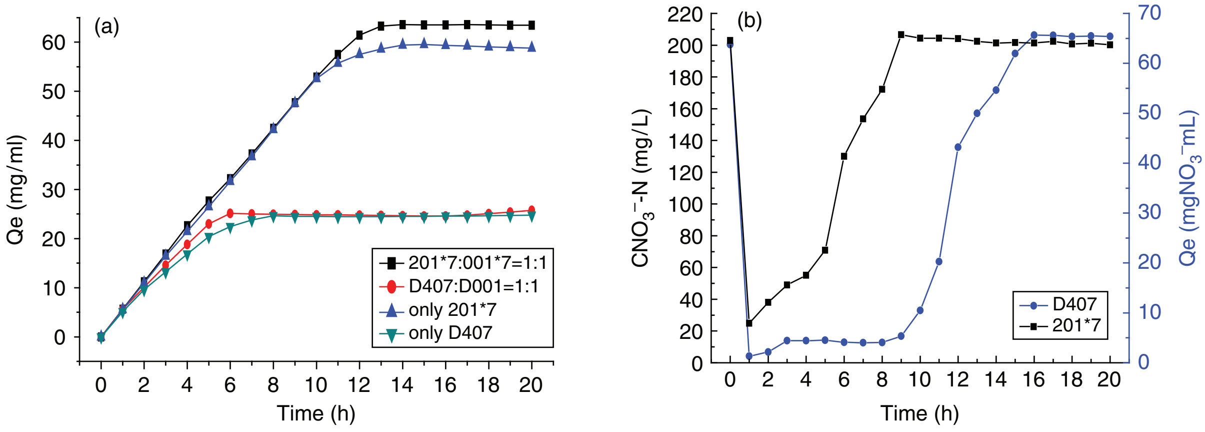

Fig. 10. (a) Adsorption quantity of two resins versus time (b) The NO_3^--N concentration of effluent versus time.

capacity and lasted a long time before achieved the breakthrough than Resin D407. Also, the existence of cation exchange resin hardly had effect on the exchange capacity of anion exchange capacity.

3.2.2. The influences of different proportions between anion and cation exchange resins

Different volume ratios (1:1, 6:4, 2:1 and 7:3) between 201 × 7 and 001 × 7 were examined. The volume of anion exchange resin was 100 ml and the volumes of cation exchange resin were 100 ml, 67 ml, 50 ml and 43 ml respectively. The results of this part, comparing different volume ratios between anion and cation exchange resins, were shown in Fig. 11, it can be found that within 2 h at the beginning of the adsorption experiment, the nitrate of the raw water was adsorbed almost completely and the NO_3^--N concentration of the effluent water was reduced to less than 1 mg/l from initial 200 mg/l. Fig. 11 also presented that the breakthrough of different volume ratios were achieved after 9–12 h adsorption, the saturated adsorptive capacity of different volume ratios between 201 × 7 and 001 × 7 were 63.33, 60.64, 58.38, 58.77 and 58.79 mg NO_3^-/ml resin respectively. The results indicated that different volume ratios hardly had effect on the exchange capacity of anion exchange capacity, but had effect on the pH of the effluent water evidently in Fig. 12. If there was anion exchange resin only, the pH of effluent water increased rapidly and then decreased until it became neutral; as filled with anion and cation exchange resins, the pH of effluent water decreased sharply and then increased until the effluent water became neutral.

3.3. Combined process

3.3.1. V-I characteristic curve

The voltage-current curve in the experiment was shown in Fig. 13. During the whole experiment, the electrical

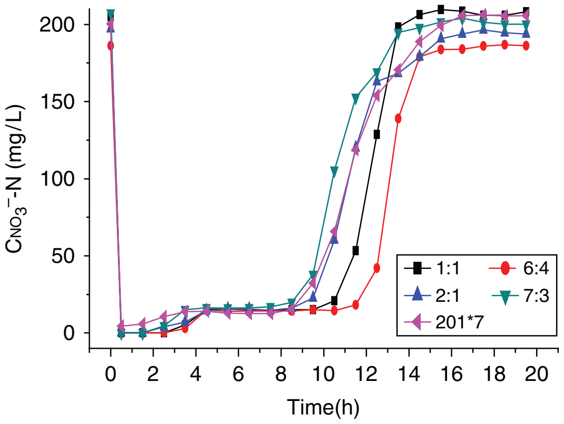

Fig. 11. NO_3^--N concentration of effluent water versus time.

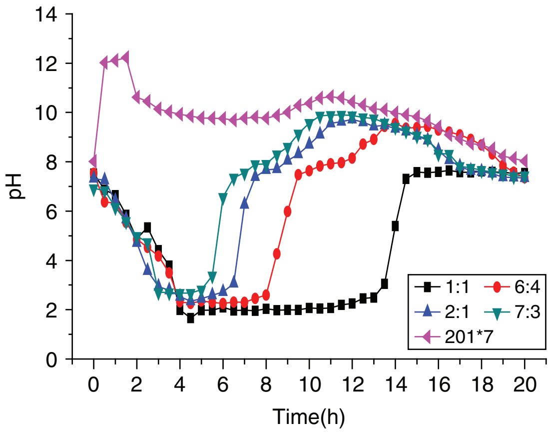

Fig. 12. Effluent pH of different volume ratios between anion and cation resins.

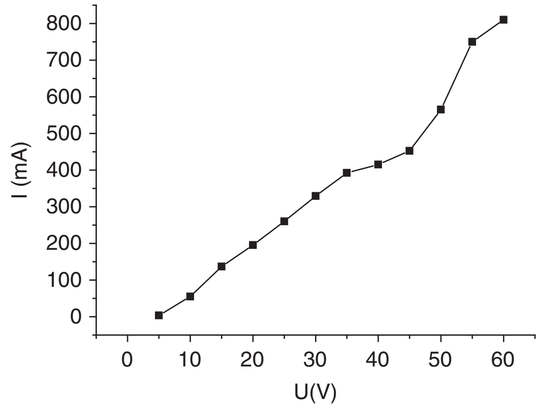

Fig. 13. Voltage-current curve (201 × 7:001 × 7 = 2:1).

current of the unit increased more rapidly than the voltage. The curve could be fall into three segments, as the voltage from 5 V to 35 V, the current increased linearly as the voltage increased and there was no polarization point, due to there were sufficient ions in the diluted chamber to ensure the need of the current; at the stage of 35–45 V, comparing to the previous segment, it was evident that the current increased slowly and appeared a inflection point, which can be found according to the pH of concentrated water that was shown in Fig. 14. For as the voltage increased, there was no enough ions affording the current in the diluted chamber, so the water dissociation took place in the diluted compartments and a significant amount of H^+ and OH^- ions were produced, the H^+ and OH^- ions could regenerate the saturated resins and renew the ion- exchange capability of the resins. From the inflection point, the current increased linearly as the voltage increased like the first segment but more quickly. The third segment was appeared at the voltage of 55 V, the increased rate of the current became slowly.

3.3.2. Quality of diluted water and effect on concentrated water

After 90 h operation at constant applied voltage of 50 V and steady feed quality (50 mg/l NO_3^--N), the results were shown in Fig. 15, the resins were saturated with sodium nitrate solution before regeneration. It can be found that the NO_3^--N concentration of effluent water from diluted chamber gone up rapidly in a very short period of time after electrifying, mainly duo to the saturated resins arise regeneration under the influence of an electric field, the adsorptive NO_3^- were released and caused the NO_3^--N concentration of diluted chamber go up quickly. Along with the electric regeneration, the regenerative NO_3^- transferred to the concentrated chamber and caused the NO_3^--N concentration of concentrated chamber go up continuously. Fig. 15 illustrated when filled the mixed resins of 201 × 7 and 001 × 7, after 10 h regeneration the NO_3^--N concentration of diluted water reduced to lower than 20 mg/l and satisfied the standard of China; about 20 h or so, the NO_3^--N concentration reduced to lower than 10 mg/l and satisfied the standard of WHO. After 85 h regeneration, the NO_3^--N concentration of diluted chamber began go up slowly, Fig. 16 showed that the NO_3^--N concentration of concentrated chamber increased hardly, which illustrated that the regeneration had gone on no longer. For the concentration difference between diluted and concentrated chamber was too big, it caused ion reverse osmosis performance that made the NO_3^--N concentration of diluted chamber go up slowly. Fig. 16 also showed that after 90 h regeneration, as filled the mixed resins of 201 × 7 and 001 × 7 in the diluted chamber, the NO_3^--N concentration of concentrated chamber could achieved 720 mg/l; while filled the mixed resins of D407 and D001 in the diluted chamber, the NO_3^--N concentration of concentrated chamber could achieved 530 mg/l.

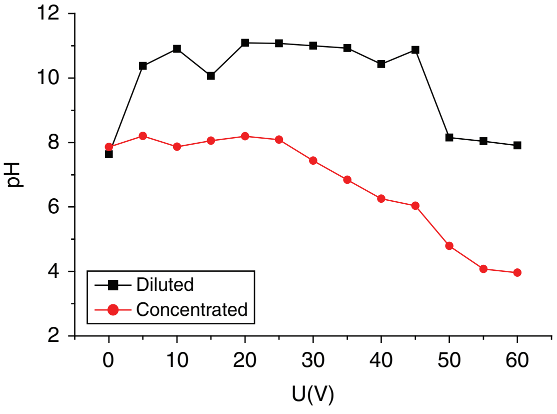

Fig. 14. Effect of voltage on the pH of diluted and concentrated water.

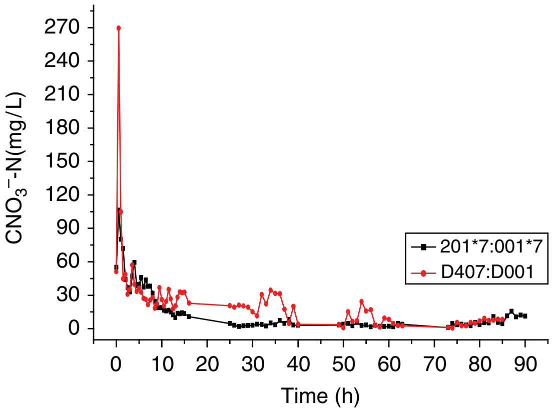

Fig. 15. NO_3^--N concentration of the diluted water versus time.

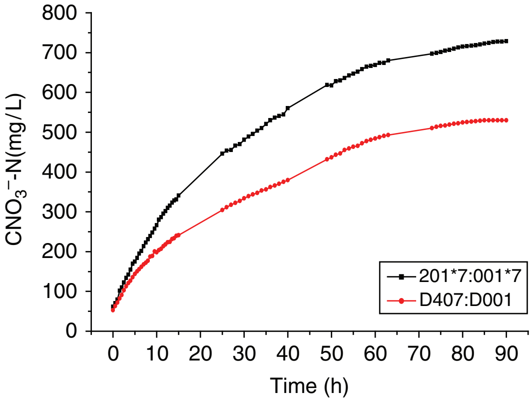

Fig. 16. NO_3^--N concentration of the concentrated water versus time.

4. Conclusions

The results of ED process showed that NO_3^--N concentration was reduced from initial 50–300 mg/l to 1–6 mg/l, with the removal rate 99% and the conductivity could be reduced to less than 10 µs/cm. Under the conditions of equal (1–8 l/h) and unequal (1:1, 2, 3, 4, 5, 6, 7, 8 l/h) water flow rate between concentrated and diluted water, the concentrated water could be reached to 2–5 times more than the initial water. The current efficiency and energy consumption was 17–34% and 0.–1.7 W·h/l, respectively. It was shown that ED was an effective treatment for NO_3^- removal and concentration.

According to the column experiments, when there was only anion exchange resin (100 ml), after 12 h or so, the saturated adsorptive capacity of 201×7 and D407 were 59.40 and 24.79 mg NO_3^-/ml resin, respectively. When the volume ratio of anion and cation resins was 1:1, after 6 h or so, the saturated adsorptive capacity of 201×7 and D407 were 63.60 and 25.74 mg NO_3^-/ml resin, respectively.

The combination process that filled ion-exchange resins in the diluted chamber showed that the ion removal was not an additive process when ion-exchange and ED technologies were combined. The results indicated that the role of the resin was only to maintain the dilute compartment conductive throughout the process [14]. The EDI with mixed bed of different kinds of anion and cation exchange resins (2:1) was effective to remove NO_3^-, the NO_3^--N concentration of effluent water from diluted chamber gone up rapidly in a very short period of time after electrifying, could be reduced to lower than 10 mg/l and satisfied the standard of WHO. So utilizing electricity to regenerate ion-exchange resin instead of chemicals was proved to be feasible and the regeneration efficiency of the resins was as high as 60% after 90 h. As a fundamental technology of in-situ remediation for groundwater contamination, the process was proved to be feasible and provided foundation for further research.

Acknowledgement

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