

Groundwater treatment using a pilot scale system of integrated electrodialysis and electrolysis

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ABSTRACT

Groundwater is an important source of freshwater worldwide; however, it could include severe contaminants such as lead, arsenic, and nitrate threatening human health. This study examined the practicability of a pilot-scale integrated electrodialysis (ED) and electrolysis (EL) system for groundwater treatment in Ho Chi Minh City, Vietnam. Under circulation of the influent, the ED process exhibited a sufficient removal of arsenic and common cat(an)ions, being above 95% within 30–45 min. With fixing each 35 min/cycle (electrical conductivity <10 $\mu\text{S}/\text{cm}$), the ED had a water recovery rate of up to 83%, which sustained high contaminant removal for 22 working days. Besides, the EL system is subsequently posed for eliminating nitrogen species from the concentrated flow of ED via the denitrification. Ammonium (40 mg/L) was effectively eliminated (~100%), while nitrate (225 mg/L) was removed by 50%. The nitrate remaining was accounted to the total nitrogen concentration, which indicates that the EL effectively oxidized/reduced nitrogen-based species to nitrogen gas. These findings suggest a potential use of the proposed system for groundwater treatment with a high recovery rate and efficiency.

Keywords: Electrodialysis; Electrolysis; Groundwater; Denitrification; Heavy metals removal

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1. Introduction

Over 75% of Earth's surface is covered with water, 97.5% of which is found in the ocean and other saline sources, and the remaining 2.5% is freshwater [1]. Groundwater, a precious source of fresh water, has been exploited worldwide to serve human life. Using groundwater is preferred because it contains small amounts of contaminants, making it suitable for industrial and household use. However, groundwater is currently influenced by anthropogenic activities, whilst over-exploitation has led to a decline in quality and quantity [2]. Moreover, the penetration of heavy metals, nitrate, ammonium into groundwater poses a risk to human health [3]. Such contaminants can be increased by geochemical weathering, a process of breaking aquifer materials into finer sediments and solutes based on physical, chemical, and biological processes. For instance, the geochemical weathering releasing Ca^{2+} and Mg^{2+} and NO_3^- ions into groundwater could be enhanced by nitrification due to increased nitrogen loading for agricultural livestock in South Korea [4]. Besides, weathering causes arsenic pollution in the Mekong and Red River Deltas of Vietnam, affecting thousands of residents who use groundwater for domestic purposes [5]. Huang et al. [6] indicated undrinkable groundwater in Pearl River Delta (China) due to being high contamination of heavy metals, such as As, Ni, Ba, Se, and Hg [6]. Given the current state of groundwater quality, it is essential to select a robust and effective technology to ensure safe drinking water from groundwater.

A variety of treatment options have been reported to remove contaminants from water and groundwater. For example, the adsorption process has been conducted for the removal of arsenic [7], chromate [8], fluoride [9], etc., from groundwater. However, adsorption may not be sufficient to remove both anions and cations during desalination of groundwater completely, and contaminant accumulation certainly reduces the adsorption capacity of the sorbent. Membrane-based processes can overcome the limitations of multi-step treatment and have gained much attention in current water technologies [10]. Nanofiltration and reverse osmosis (RO) are the two most popular and effective water treatment methods for removing low molecular weight organic compounds and dissolved salts (heavy metal ions and nutrients like phosphate and ammonia) [11]. However, fouling is a critical issue in the pressure-driven membrane process, which induces deterioration in performance (i.e., water flux, recovery), the lifetime of membranes. This fact leads to an increase in the membrane cost and operating cost for maintaining the desired water production and quality [12,13]. Recently, there has been a growing interest in electrochemical processes for water desalination and treatment due to their inherent benefits of high-water recovery rate [10,13]. Electrodialysis (ED) has received research attention in wastewater treatment, brackish groundwater desalination, and salt production at laboratory and pilot scales [10]. In the ED process, ions can be separated due to a difference in electric potential. The anions pass through anion exchange membranes (AEMs), and cations pass through cation exchange membranes (CEMs). The system is therefore capable of removing cations and anions from groundwater which is characterized by low natural organic

matters. Besides, the ion exchange membranes are chemically and mechanically stable allowing ED to achieve high recovery rates (80%–90%) in the long run compared to 30%–60% for RO [14,15]. Thus, ED can reduce the volume of concentrated brines, helping to exploit groundwater resources more efficiently.

Furthermore, ED can be combined with other electrochemical processes, such as electrolysis (EL), for integrated treatment of concentrated wastewater. In this case, the EL system is an idea to enhance nitrogen removal from ED concentrated brines. The EL process can rapidly reduce nitrate and ammonia to N_2 gas, with high efficiency, no sludge generation, and relatively low investment costs [16]. Nitrate could be reduced by several reactions in the cathodic electrode. In the presence of chloride, the oxidation of ammonia to N_2 gas can be enhanced by the formation of chlorine at the anode (i.e., electrogenerated active chlorine). Moreover, to improve EL processing, a cation-selective membrane was used to separate the electrode compartments, thereby inhibiting reversible reactions. The membrane electrolysis system only allows cations (ideally protons) generated at the anode to move to the cathode side and avoids by-products such as nitrite from the cathode being re-oxidized to nitrate at the anode. Currently, however, the integrated system ED-EL for better efficiency of groundwater treatment and recovery has not been considered.

Therefore, this study investigated an integrated ED and EL system to treat heavy metals and contaminants in groundwater. The study consists of two subjects, including (i) construction of a pilot-scale integrating ED-EL system, wherein groundwater was firstly treated with the ED device and the concentrated water was then transferred to the EL device for the denitrification; (ii) evaluation of the performances of each treatment process for contaminants removal during a continuous run of the system (22 d). Moreover, the operating time, which is an important parameter affecting the efficiency of the ED process, was also examined. This study would contribute to a facile and effective solution for groundwater treatment.

2. Materials and methods

2.1. Groundwater

The health concern is with nitrate levels above 10 mg/L based on the United States Environmental Protection Agency (US EPA) and Korean Drinking Water Quality Standards (Table 1). Therefore, a survey was carried out by the authors to detect nitrate-contaminated groundwater. As a result, groundwater exceeding nitrate standards was found from a household well in Thu Duc District, Ho Chi Minh City. The nitrate concentration in this well was in the range of 13–17 mg/L. Therefore, this source was selected based on nitrate value. Groundwater was transported to the feed tank by tank truck every 2–3 d. The feed tank (5 m³) and product tank (2 m³) were made from polyethylene. However, the heavy metal concentrations were quite low to evaluate the treatment performance of the system. Therefore, several common cat(an)ions were added with groundwater for the ED process so that the final concentrations of hardness (35–40 mg CaCO₃/L), manganese (1.0–2.5 mg/L),

Table 1
Characteristics of raw groundwater

Parameters	Value	QCVN 01:2009/BYT ^a	Korean Water Quality Standards	WHO Standards	Directive (EU) 2020/2184 ^e
Nitrate, mg/L	13–17*	50	10 ^b	50	50
Iron, mg/L	0.02–0.09	0.3	0.3	0.3 ^c	0.2
Arsenic, mg/L	0.1–0.3*	0.01	0.01	0.01	0.01
Manganese, mg/L	1.0–2.5*	0.3	0.3	0.5	0.05
Ammonia, mg/L	1.4–1.8*	3	0.5	–	0.5
Aluminum, mg/L	1.5–2.0*	0.2	0.2	0.2	0.2
Total nitrogen, mg/L	15–19	–	–	–	–
Sulfate, mg/L	25–40	250	250	500	250
pH	3.9–5.5*	6.5–8.5	5.8–8.5	6.5–8.5 ^d	6.5–9.5
Hardness, mg CaCO ₃ /L	35–40	300	300	–	–
Chloride, mg/L	40–55	250–300	250	250	250

Notes:

“*” Indicates the parameters have exceeded the standard drinking water quality.

^aAccording to National Technical Regulation on drinking water quality of Vietnam;

^bAccording to the Korean and United States Environmental Protection Agency (US EPA), standards for drinking water quality;

^cDesired value for Iron according to WHO/SDE/WSH/03.04/08;

^dDesired value for pH according to WHO/SDE/WHO/03.04/12;

^eDirective (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption.

aluminum (1.5–2.0 mg/L), iron (0.02–0.09 mg/L), arsenic (0.1–0.3 mg/L), chloride (40–55 mg/L), sulfate (25–40 mg/L), total nitrogen (15–19 mg/L) and ammonia (1.4–1.8 mg/L) were maintained during the experiments. A detailed comparison of the inlet groundwater with four drinking water quality standards is presented in Table 1.

2.2. ED system

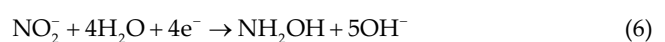
The ED system consisted of reservoirs, pumps, an ion-exchange membrane stack, power supply, electrodes, and a data acquisition system (CJ-S3, Changjo Techno, Korea). The pump capacity was 50–70 L/min (diluate), 15–20 L/min (concentrate), 7–11 L/min (electrolyte). The pump material was made of Polypropylene (magnet type). The tanks had a capacity of 100 L (diluate and concentrate each), 60 L (electrolyte). The tank material was made of polyvinylchloride.

The ED device contained cathode and anode electrodes which were made of stainless steel coated with platinum. A total of two ED cells were used. Each ED cell was packed with 24 pairs of ion exchange membranes (IEMs). Cation and anion exchange membranes were NEOSEPTA® types with a dimension of 4.75cm × 11.6 cm and were purchased from ASTOM (Tokyo, Japan). Each IEM had an effective surface area of 275 cm². The thickness of the CMX and AMX membranes was 170 and 140 μm, respectively.

2.3. EL system

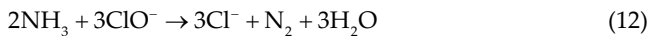
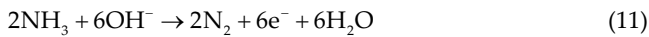
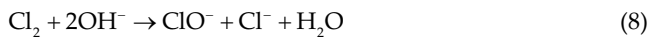
The EL system operates on a separate power supply from the ED (EX Series, Oda Technologies Co., Ltd). The TiO₂ was used as the anode, while Zn was the cathode. The surface area of the Zn, Ti plate was 150 cm² (10 cm × 15 cm), which was separated by a cationic exchange membrane

(Asahi Glass Cation Exchange Membrane, Japan). The cation exchange membrane was used as a barrier between the cathode and the anode, which allowed protons generated the anode to be transported to the cathode side. In addition, this membrane help hinder the transport of nitrite, nitrate from the cathode to the anode side and this fact facilitated to occur denitrification at the cathode side, as shown in Eqs. (1)–(6).



As reported, 1 mM of NaCl solution was added into the anode side to improve denitrification for the system [16]. At the anode side, the chloride ion can immediately react with water to form hypochlorite which then reacts with ammonia as the following equations:





2.4. Pilot-scale ED-EL system design and experimental conditions

The ED and EL systems are housed in a 10-foot container (L × W × H: 3.050 × 2.44 × 2.59 m) on the campus of the Ho Chi Minh City University of Technology. The inlet and outlet water tanks are located outside the container. The temperature of the container was kept at room temperature (about 25°C, maintained by an air conditioner) during the operation. The ED-EL system for groundwater treatment is shown in Fig. 1, wherein each component/device has functioned as below.

- TK-01 is the draw groundwater tank (5 m³), which supplies water to a TK-02 tank.
- TK-02 is the feed groundwater tank, which is used for the ED operation.
- TK-03 is the concentrated effluent tank, which is generated during the ED operation.
- TK-04 is the electrolyte solution tank, which supplies a circulating flow of electrolyte to the ED device during the operation.
- TK-05 is the diluate water tank generated from the ED treatment. This tank is equipped with a UV light to treat the remaining bacteria.
- TK-06 is the NaCl solution tank.
- TK-07 is the tank containing the concentrated water withdrawn from the TK-03 to prepare for the EL process.
- TK-08 is the treated water taken from the EL process.
- P-01 to P-06 are the pumps equipped on the system responsible for pumping water from the different tanks
- V-01 to V-05 are the valves on the pipelines, which control the direction of water flow.
- PS01 and PS02 are the electrical devices showing voltage (V) and current (A) values for the ED system respectively, while PS03 is the electrical device providing V and A values for the EL system.

All the equipment/devices in the ED-EL system were controlled using a computer system with manual- and auto-controlling functions. The operating parameters (applied current and voltage) were selected based on previous studies [17–19]. Based on the schematic diagram (Fig. 1), the working description of the ED-EL system can be summarized as follows.

2.5. ED processing system

Groundwater from tank TK-01 is pumped into TK-02 through a cartridge filter (5 μm) to remove suspended

solids that can clog IEMs pores. Then, groundwater containing cat(an)ions in the tank TK-02 was pumped by pump P-02 to the ED device. Cat(an)ions were separated from the groundwater by electrostatic force at anodes and cathodes and moved through IEMs. During the ED operation, an electrolytic solution of Na₂SO₄ was recirculated in the end plates of the ED to keep the electro dialysis running. The electrolyte solution (Na₂SO₄ 4%, tank TK-04) was pumped into the ED system by pump P-04 for enhancing the electrostatic force. The treated water was recirculated to the diluate tank (TK-02), and the concentrated stream discharged from the AEMs and CEMs went to the concentrated tank (TK-03). This process was repeated until the diluate stream containing ionic concentration reached the desired conductivity value. After the treatment was finished, the diluate flow was pumped through valve V-02 to tank TK-05 for UV sterilization.

2.6. EL processing system

Before operating the EL, NaCl solution was pumped from a tank TK-06 into the EL system. Then, the P-05 pump was opened to pump the concentrated water from tank TK-07 to the EL device. Then, the water flow was circulated several times so that ammonium and nitrate concentrations decreased to the desired level. Finally, the treated water was pumped to a tank TK-08.

The two-stage operating conditions for the ED-EL system are summarized in Fig. 2.

2.7. Analytical method

Analytical parameters for inlet and outlet water are mentioned in Table 1. The pH in groundwater was determined using a pH meter (Milwaukee Instruments, USA). The concentration of NH₄⁺, NO₂⁻, Cl⁻, SO₄²⁻, and hardness in groundwater tests were determined following the Standard Methods for Examination of Water and Wastewater. The nitrate concentration was analyzed according to the method of Vietnam Standard 6180:1996. Meanwhile, analyses of heavy metals such as arsenic, manganese, iron, and aluminum were performed using an Inductively Coupled Plasma–Mass Spectrometry (ICP-MS).

3. Results and discussion

3.1. Performance of the electro dialysis system

3.1.1. Effect of operation time

Fig. 3 shows the effect of residence time (30, 45, 60 and 80 min) on ion removal efficiency by ED in the fixed condition of applied current and voltage, examining for arsenic, nitrate, manganese and aluminum species [17]. More than 90% of ions were removed after 45 min including nitrate (93%–100%), manganese (95%–99%), aluminum (95%–99%). The results were consistent with the literature, where nitrate removal reached 100% up to 60 min of ED operation [20]. Among the four ions, the time-dependent removal of arsenic was the highest, with efficiencies ranging from 71 to ~100%. It could be reasonable due to a lower electrical force of arsenic species to ion exchange membrane at the

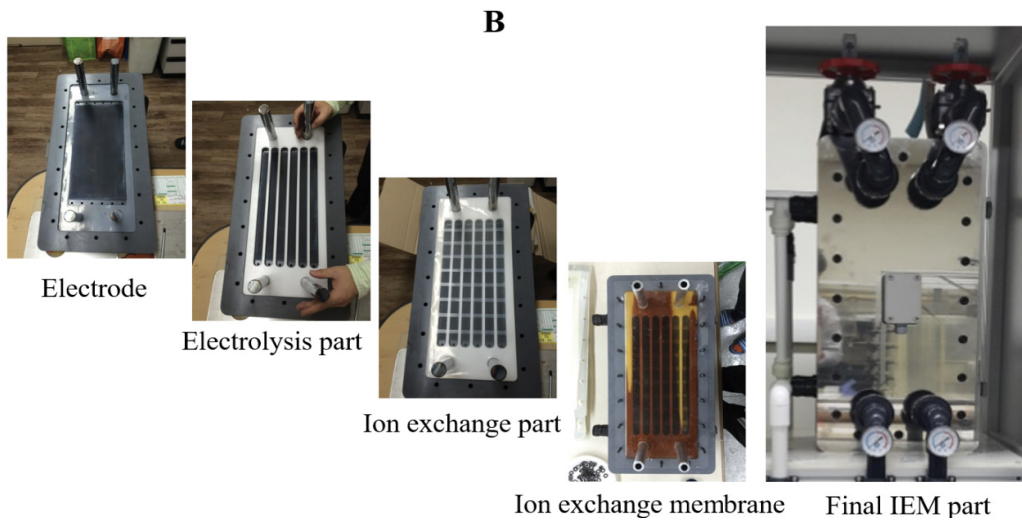
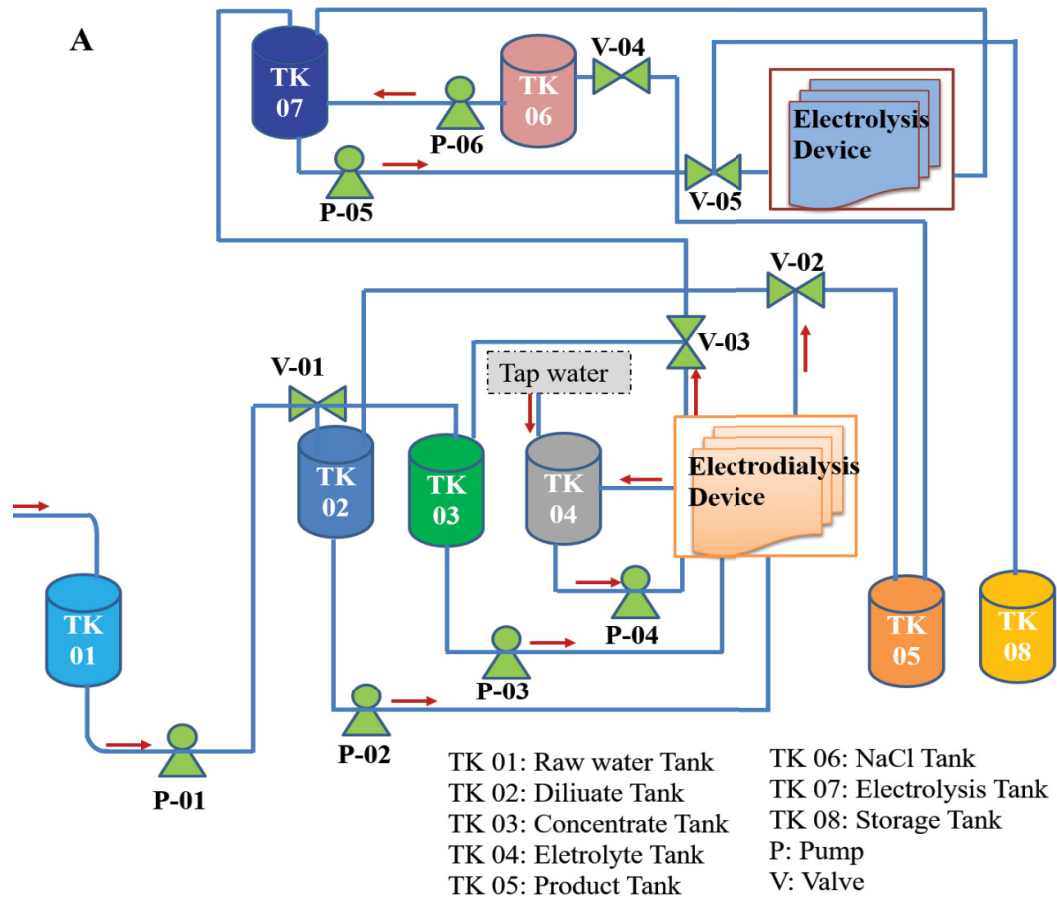


Fig. 1. (a) The schematic diagram for the integrated electrodesalination and electrolysis system and (b) each component of the electrodesalination part.

experimental conditions than others. At actual pH of ~3.9, As(V) species, mainly predominated in the form of $H_2AsO_4^-$ ion and a small ratio of H_3AsO_4 (H_3AsO_4 has $pK_{a1} = 2.2$ and $pK_{a2} = 7.1$) [7]. The electrostatic force may not occur in the presence of neutral form (H_3AsO_4), resulting in a decrease in removal. Meanwhile, the extraction of $H_2AsO_4^-$ ion through

the membranes during the circulating run could shift the reaction balance of H_3AsO_4 to produce $H_2AsO_4^-$ ion, leading to increase arsenic removal. More than 93% of arsenic after 45 min while nitrate concentrations of 13–17 mg/L were practically removed after 30 min. However, further increase in circulating time (>60 min) may be impractical

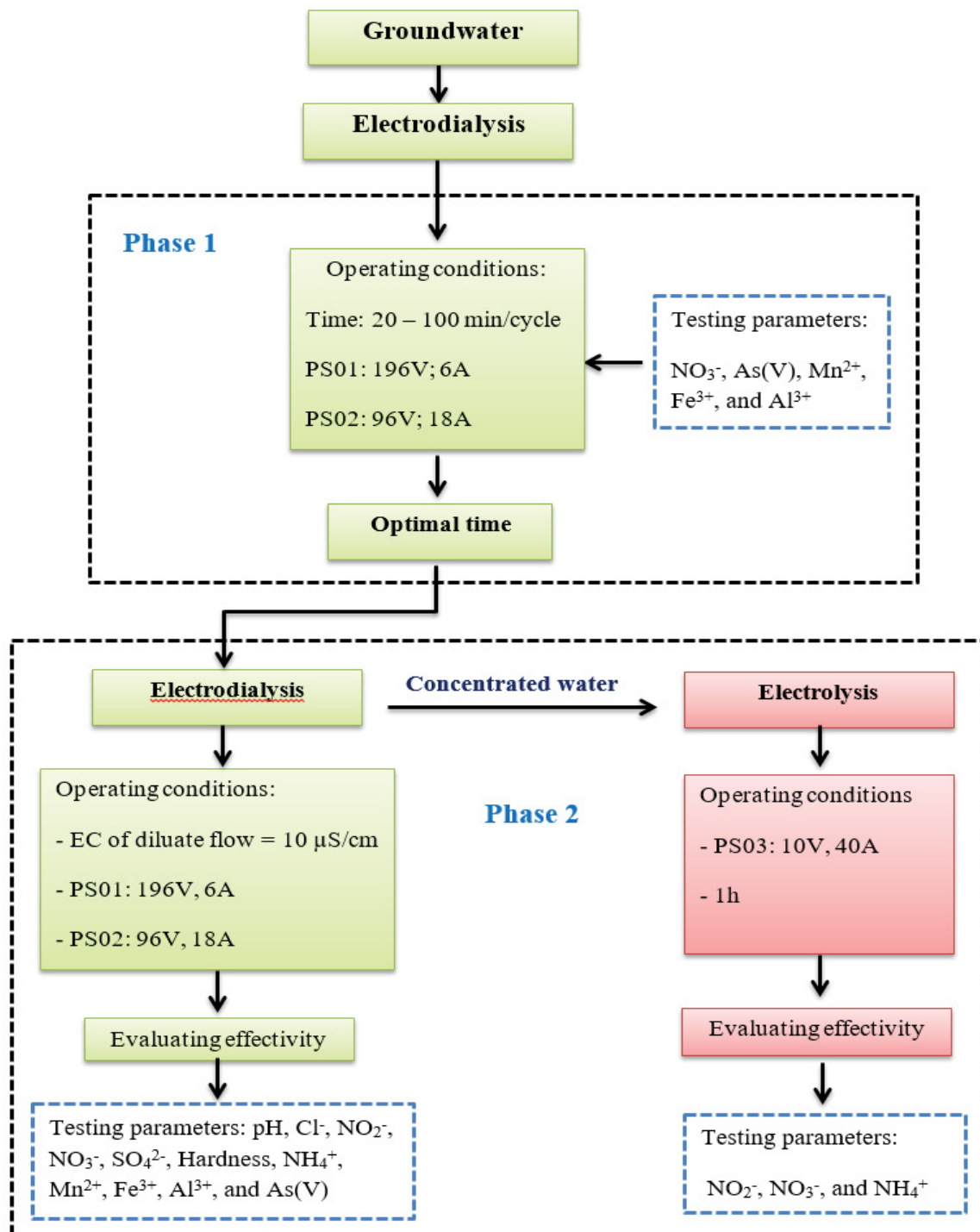


Fig. 2. Schematic diagram for evaluating pollutant removal efficiency by integrated electrodiagnosis and electrolysis system.

because elimination was not increased, even it was slightly decreased at 80 min. This could be due to an increase in the contaminant concentration in the input flow. Based on drinking water (Table 1), further ED experiments for long-term groundwater treatment were conducted at ~35 min to save energy consumption (the effluent conductivity of less than 10 $\mu\text{S}/\text{cm}$).

3.1.2. Ion separation efficiency of electrodiagnosis system

To evaluate the capability of the ED system for practical application, groundwater was continuously run for 22 d, and the concentrations of dominant ions in the diluate water (effluent) were monitored. Fig. 4 shows the changes of pH, electrical conductivity, and concentrations of cat(an)ions

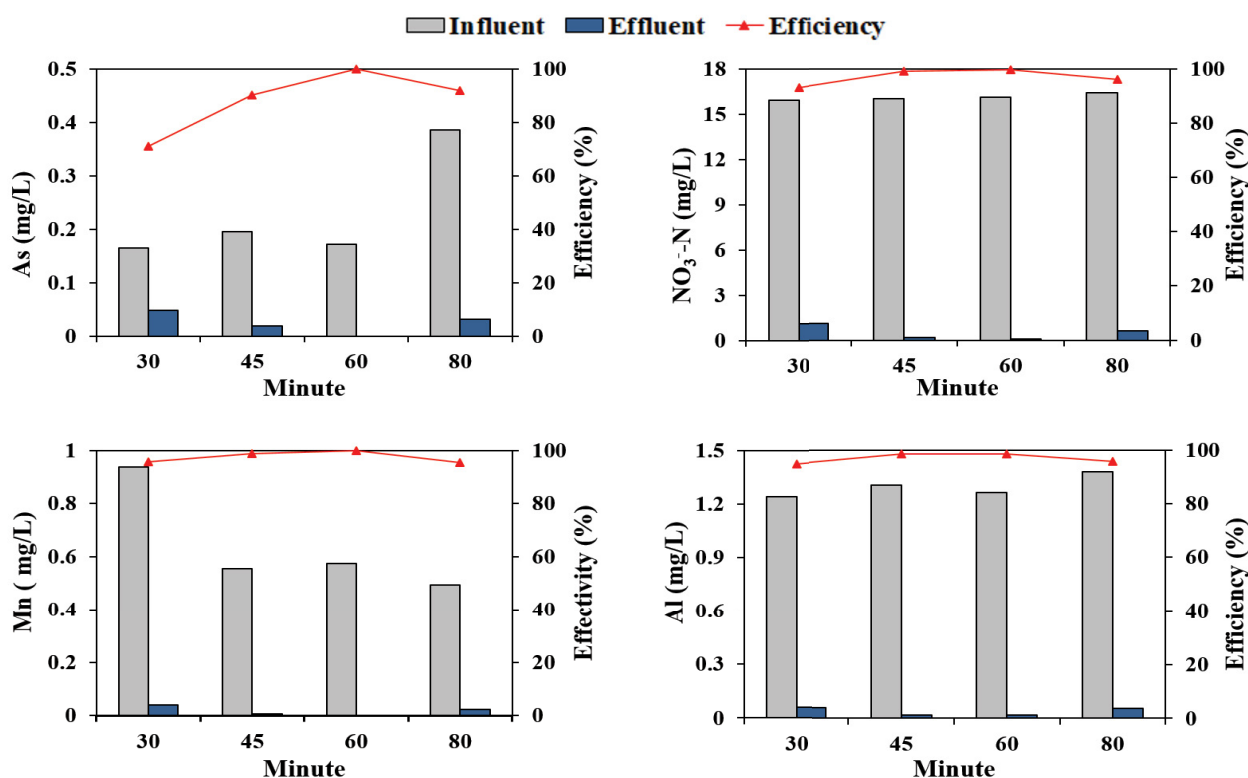


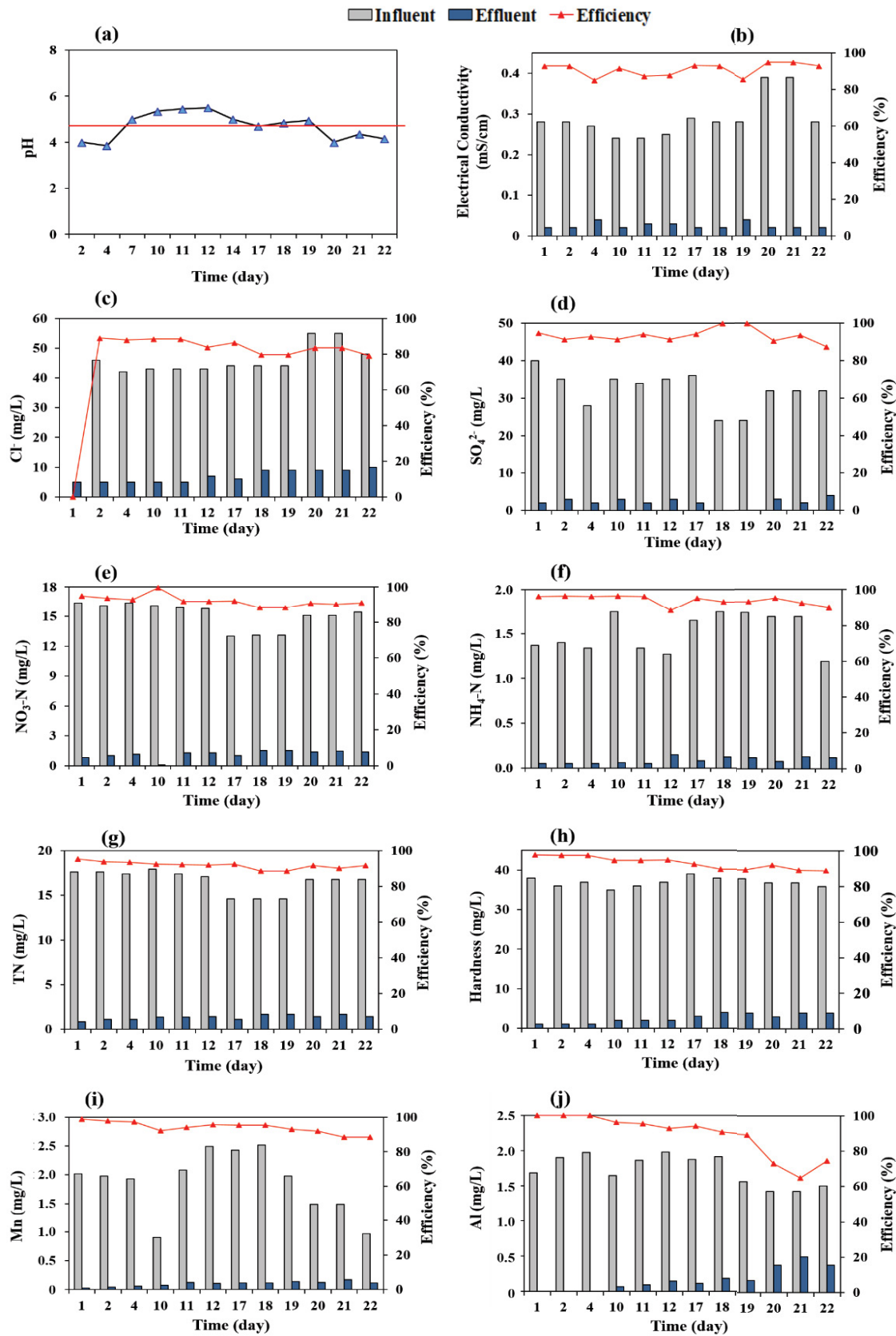
Fig. 3. Effect of residence time on the removal of nitrate, arsenic(V), manganese, and aluminum ions. The residence time varied from 30, 45, 60, and 80 min. The voltage and current were 196 V; 6 A (PS01) and 96 V; 18 A (PS02), respectively. The inlet water conductivity was 160–200 $\mu\text{S}/\text{cm}$, and the temperature was 25°C.

in groundwater during a 22-d ED operation. The removal efficiencies of these parameters were also included. The pH in the ED system ranges from 3.9 to 5.5, with an average value of 4.7 (Fig. 4a). Consequently, those ions like Cl^- , NO_3^- , H_2AsO_4^- and SO_4^{2-} , K^+ , Na^+ , Ca^{2+} , and Mg^{2+} may not have a major change in predominant species over this pH range [21]. Thus, they may act at a similar charged behavior to electrical forces produced during ED operating. Fig. 4b presents an effective removal of electrical conductivity (EC, 91.2% \pm 3.5% of reduction) during 22 d of the treatment. The EC values were dramatically dropped on each day of monitoring and ranged between 0.02 and 0.04 mS/cm (corresponding to 12.8–25.6 mg/L of TDS), which was more than 10-fold lower than the maximum allowable values guided by WHO for drinking water (0.4 mS/cm) [22]. The results, overall, indicate the effective removal of ionic contaminants. However, since low conductivity (deionization) is not preferred in drinking water, additional downstream hardness (Ca^{2+} , Mg^{2+}) could be required.

Fig. 4c–e shows the changes in chloride, nitrate, and sulfate concentrations and their removal efficiencies during 22 d of treatment. The chloride concentration in the diluate water collected during 22 d was found to be 5–10 mg/L, corresponding to the mean removal efficiency of 84.6% \pm 3.6%. Similar results were reported for chloride removal (82%–85%) from brackish groundwater treated by electrodialysis in Tunisia [23]. Nitrate (92.0% \pm 3.1%) and sulfate (94.2% \pm 3.6%) were found with a slightly better removal

than the chloride, and the diluate water contained about 0–1.5 mg/L and 0–4.1 mg/L NO_3^- -N and sulfate, respectively. These results could confirm the high capability of the ED system for trace removal of anions from groundwater. The better nitrate removal than chloride could be due to the higher chloride concentration (14.7–17.8 mg/L and 44.9–55.1 mg/L for nitrate and chloride, respectively). Kabay et al. [24] reported that the ED method could effectively remove nitrate (98%–100%) from groundwater containing co-existing chloride and sulfate ions, whereas the nitrate removal by the ion exchange process at similar conditions was 87%. Besides, a divalent ion form of sulfate was quickly attracted by electrostatic force through the AEMs. In ED, the removal of an ion can be affected by its charges and hydrated radius, wherein the dominant ion having higher charge and lower hydrated radius has a more potent driving force towards the ion exchange membranes [25]. Thus, divalent ion (SO_4^{2-}) was affected strongly by the electric force than monovalent ion (Cl^-). According to WHO guidelines, the concentration of NO_3^- -N in drinking water should not exceed 50 mg/L, and that for sulfate and chloride are 250 mg/L, respectively (Table 1). The high removal of chloride also promises a potential use of the ED method for water desalination in rural Vietnam, which is still challenging to most water treatment processes.

Like anions, the removal of common cations (except iron species) at such experimental conditions occurred similarly during the 22-day ED operation (Fig. 4f–j). Indeed,



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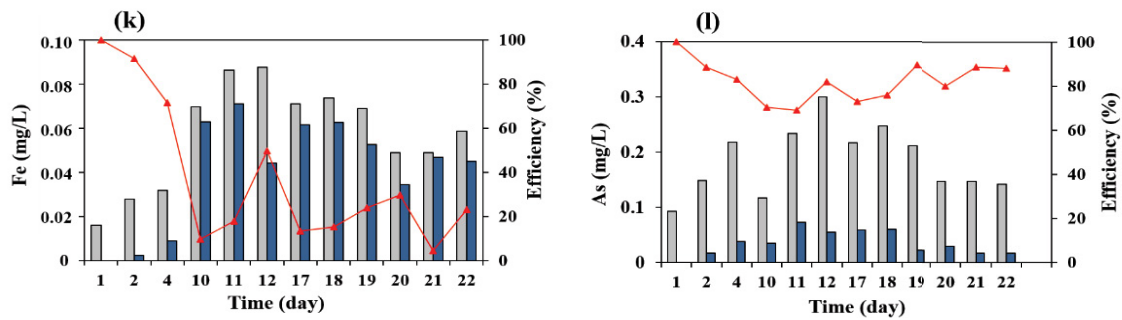


Fig. 4. Long-term treatment of ED system: (a) change in pHs, and the removal of (b) electrical conductivity, (c–e) common anions (Cl^- , NO_3^- and SO_4^{2-} , respectively), (g) total nitrogen, (f) and (i)–(k) cations (ammonium, hardness, manganese, aluminum, and iron, respectively), and (l) arsenic.

ammonium ion was effectively removed with $94.1\% \pm 2.8\%$. The NH_4^+-N concentration in the effluents was about 0.05–0.15 mg/L, be lower than the standard concentration guided by QCVN, Korean, and Directive (EU) 2020/2184 (Table 1). It should be noted that nitrate was the most predominant ion (16.25 ± 0.25 mg/L, Fig. 4e) in groundwater, which was more than 10-fold to ammonium ion (1.21 ± 0.16 mg/L), whereas nitrite concentration was almost negligible. Thus, the effective removal of both nitrate and ammonium certainly resulted in a significant reduction of total nitrogen ($92.0\% \pm 2.0\%$, Fig. 4g). Fig. 4h and i show hardness and manganese removal, achieving up to $93.5\% \pm 3.2\%$ and $94.2\% \pm 3.3\%$ during 22 days of running, respectively. The hardness and manganese concentration in the effluents were found in the range of 1–4 mg CaCO_3/L and 0.02–0.17 mg/L, respectively, which were much lower than standard allowances set by QCVN and Korean guidelines for drinking water (300 mg CaCO_3/L and 0.3 mg/L for hardness and manganese, respectively). Schaep et al. [26] reported the removal of hardness by using nanofiltration membrane, reaching about 94% of calcium rejection; however, this process faced a problem of membrane fouling. As proceeding ED at the investigated $\text{pH} < 5$ (Fig. 4a), these cations (NH_4^+ , Ca^{2+} , Mg^{2+} , and Mn^{2+}) have almost no change in the predominant forms and, therefore, were transported through the membranes by electrostatic force. To compare, the removal of aluminum (Fig. 4j) was effective up to day 19th (390% of efficiency) with the concentration in the treated water (0–0.168 mg/L), being lower than the permissive WHO guideline for drinking water (0.2 mg/L). However, the removal efficiency was strongly decreased with further treatment days (by ~20% drop on the day 20th). It is possible that there was an increase in membrane fouling with operating time [27] and the formation of less mobile aluminum hydroxo complexes or aluminates could decrease the migration toward and through the membrane [28,29]. For iron removal, ED showed a relatively low removal capacity compared with other ions, which may be related to the effect of a too low iron inlet (0–0.088 mg/L) under a pH of 3.9–5.5. Groundwater after being pumped up and exposed to oxygen, Fe^{2+} concentration can exist in a relatively small amount because Fe^{3+} precipitation will occur and separate. Ben Sik Ali et al. [30] studied the effect of various experimental parameters on the removal of iron from brackish

water using ED. There was a clear relation between the iron removal and pH solution. The removal of iron was strongly decreased at $\text{pH} > 3.7$, possibly due to the hydrolysis of iron ions to form uncharged iron hydroxides in the solution, reducing the iron transport under the applied current. In addition, the authors showed that the removal of iron was relatively low at a low iron concentration (<1.6 mg/L) and reached maximum removal at 2.4 mg/L of iron initial concentration [30]. Such results are likely coincidental for this study because the pH range of 3.9–5.5 of groundwater could significantly decrease iron removal efficiency and could be due to the competition with other cations when the iron concentration is small. Further investigation is needed to evaluate the iron removal mechanisms of the ED system

Interestingly, arsenic is the most toxic and carcinogenic element, which can be removed at an average efficiency of $82.0\% \pm 9.3\%$, wherein the lowest and largest efficiencies were 69% and 100%, respectively. However, the concentration of arsenic found in the diluate water was in a range of 0–0.072 mg/L, be higher than the standard limits of WHO and Vietnam for drinking water (0.01 mg/L) [31]. The high arsenic concentration could be due to the slow removal rate of the neutral form H_3AsO_4 under naturally acidic groundwater as previously mentioned. These results were consistent with data in Fig. 3a, which required a more extended residence time of a treatment cycle to remove arsenic than other ions effectively (e.g., 60 min/cycle run). In addition, pH value could be augmented to increase the electrical transport of arsenic species toward and through the membrane. Therefore, arsenic removal from groundwater is expected to be enhanced if pH and time conditions are adjusted appropriately. The As removal by ED is currently considered an improvement over other methods such as coagulation and flocculation (6%–74%) [32]. Meanwhile, less than 30% of As(III) and 60%–90% As(V) can be removed using nanofiltration membranes [33].

3.2. Recovery rate of the electro dialysis system

Fig. 5 presents the recovery rate of treated groundwater volume at each determined time during 22-d of ED operation. The recovery rate was high at 79%–83% up to day 11 of running, but then decreased to about 70% at day 17

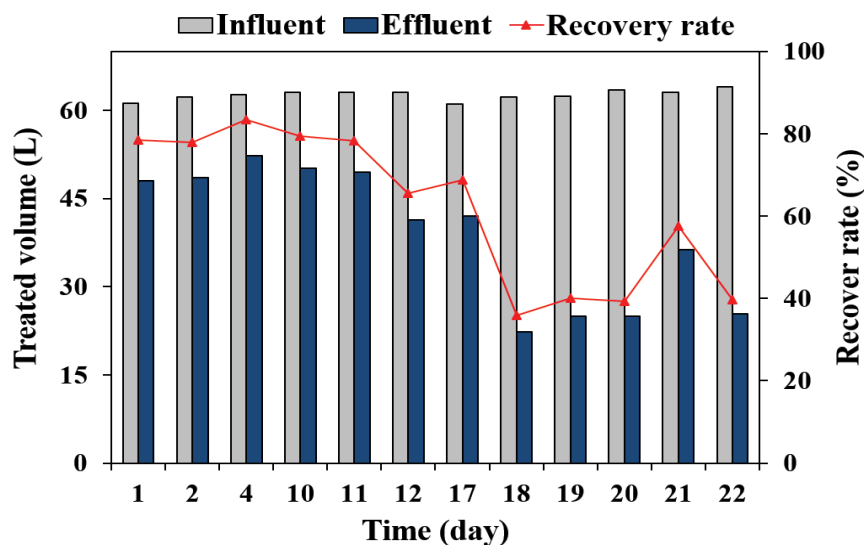


Fig. 5. Treatment efficiency of groundwater using the ED system during long-term operation.

and dramatically declined to 39% day 18 onwards. These results were well consistent with those of in Fig. 4, which showed the removal efficiencies of most cat(an)ions lowered down from day 11 (e.g., the removal decreased from 95% to 91%, 99% to 88%, and 100% to 65% for nitrate, manganese, and aluminum, respectively). Such a case could be because the ion exchange membranes were contaminated during the operation, reducing the attraction between the anode/cathode and ions in groundwater. There was a slight decrease in ion removal from day 12th for nitrate, chloride, manganese, and aluminum, which suggested that the ED performance might be slightly affected by fouling. Fouling can be produced by accumulating contaminants, organic compounds, and particulates on the membrane surface and within the pores of the membranes. Such organics can highly carry a negative charge, so AEM might show a higher degree of fouling than CEMs [10]. However, the removal efficiency of chloride and other ions was maintained at a high level (>80%) after 22 d. This finding indicated that the magnitude of the fouling effect did not appear to be large on the ions removal efficiency, but instead water recovery was impaired after day 12th. Theoretically, it can be explained that groundwater itself contains less organic pollutants and is pre-treated by the filter cartridge before being introduced into the ED, which might help reduce fouling in short term [34]. Previous research showed that fouling and scaling were negligible for short-term ED runs, offering the potential to separate salts from organic waste streams on an industrial scale [35]. Fouling can be directly related to the structure of IEMs and raw water characteristics when the operating parameters are fixed in ED, such as flow rate, voltage, current, and temperature [34]. However, the use of different IEMs structures did not seem to impact the fouling in ED. Several novel antifouling of IEMs has shown less effect on fouling and scaling tendency compared to control IEMs (e.g., IEMs fabrication, antifouling IEMs, AEMs surface modification) [10]. Thus, raw water sources can be an important factor affecting fouling in ED,

choosing a water source with low organic matter such as groundwater seems suitable for practical ED application.

3.3. Denitrification using the electrolysis system

In the EL process, contaminants can be removed by the redox reaction (oxidation–reduction) occurring at the electrode's surfaces. By applying a suitable voltage, oxidation occurs at the anode, which transfers electrons to the cathode to perform the reduction process. The principal purpose of this part was to monitor the denitrification efficiency of the concentrated water discharged from the ED system. Fig. 6 presents the changes of ammonium, nitrate, and total nitrogen values from the discharged water (from the ED device) by the EL device for 1–12 d. Note that the removal of nitrite was negligible due to its trace concentration (<0.03 mg/L). Ammonium was effectively removed, reaching up to ~100% of efficiency.

Meanwhile, nitrate ion existed at higher concentrations in the concentrated brines, and its removal reached a maximum of 50%. Indeed, the effluent $\text{NO}_3\text{-N}$ concentrations ranged from 17–181 mg/L, higher than the Vietnamese effluent standard limits (50 mg/L). As shown in Fig. 6c, the concentrations of total nitrogen in the effluents consistently matched with nitrate (Fig. 6b). It indicates that the EL process effectively transformed ammonium and nitrate ions from the influent water into a nontoxic end product of nitrogen gas. The oxidation of chloride produced chlorine at the anode, transforming ammonium into nitrogen gas. At the cathode, nitrate can be directly converted into nitrogen gas or occur through intermediates (e.g., NO_2^- , NH_3 , and NH_2OH) [16,29]. Literature reported that the removal efficiency of nitrate by the EL process could be affected by different parameters, including (i) selection of electrode materials [36]; (ii) operating conditions such as the electrical current intensity, reaction pH and operation duration [37]. For example, nitrate ions can be effectively removed at acidic and neutral pH using a zero-valent iron/activated carbon electrode.

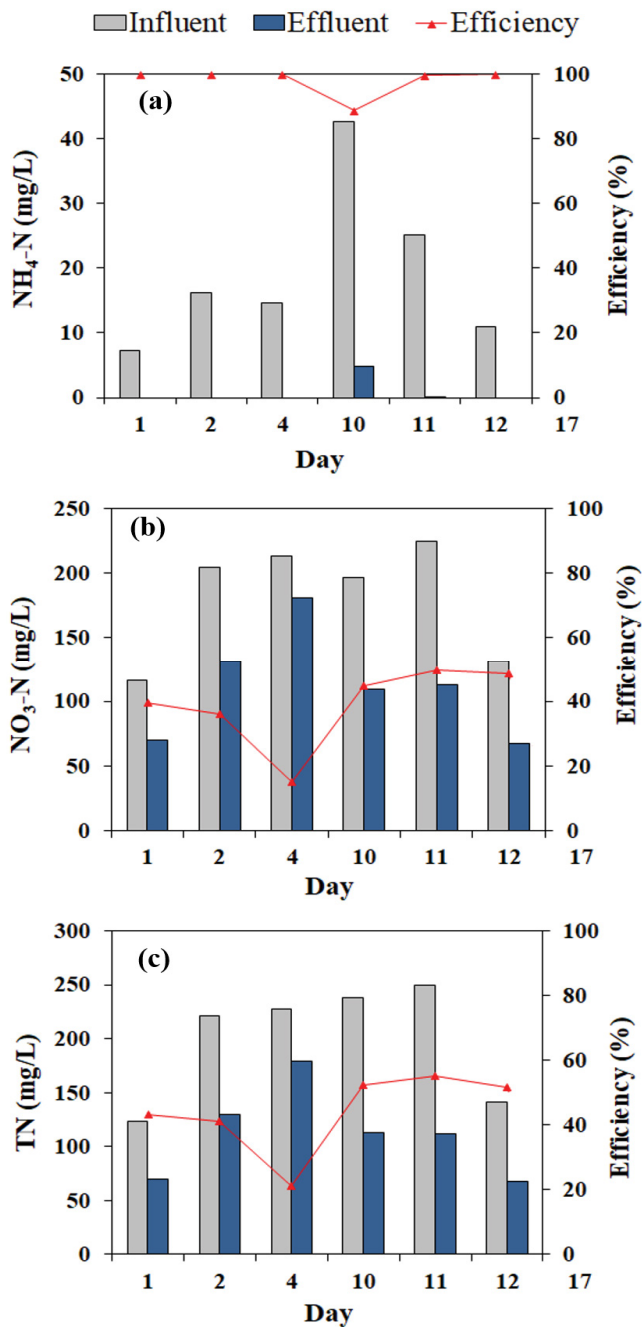


Fig. 6. Electrolysis process for the denitrification of the concentrated flow (discharged from the electro dialysis) during 12 d of operation.

4. Conclusions

The possibility of producing safe drinking water from contaminated groundwater using the integrated electro dialysis and electrolysis system was accomplished. Unlike traditional technologies, which just treat cations or anions partly, the ED method can effectively remove those contaminants from groundwater up to more than 95% of efficiency. However, the treatment of arsenic would take a longer duration time to achieve safe drinking water due

to its high toxicity and carcinogen. By equipped with an EL device, the concentrated flow discharged from the ED process can be performed for denitrification. The EL process can effectively convert ammonium and nitrate ions to a safe nitrogen gas product. However, the cathode reaction of nitrate only reached ~50% of efficiency. It raises a request for further study on alternative cathode materials or experimental conditions to efficiently remove nitrate, providing a facile system of ED-EL for groundwater treatment with good desalination efficiency and recovery rate.

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