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Removal of nitrate by electrodialysis: effect of operation parameters

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Abstract. We investigated the effect of applied voltage and electrolyte concentration on the nitrate removal and its energy/current efficiency during the electrodialysis. The current increased as the applied voltage increased up to 30 V showing the limiting current density around 20 V. The nitrate removal efficiency (31 to 71% in 240 min) and energy consumption (11 to 77 W·h/L) gradually increased as the applied voltage increased from 10 to 30 V. The highest current efficiency was obtained at 20 V. The increase in electrolyte concentration from 100 to 500 mM led to the dramatic increase of nitrate removal efficiency with much faster removal kinetics (100 % in 10 min).

Keywords: electrodialysis; nitrate removal; applied voltage; current efficiency; energy efficiency

1. Introduction

Nitrate (NO_3^-) contamination in surface and groundwater has gradually increased throughout the world (Koparal and Ogutveren 2002, Mueller *et al*. 1995) due mainly to the excessive consumptions of fertilizer in agricultural activities and discharge of untreated wastewater containing the animal manure (Bae *et al*. 2013, Solley *et al*. 1993). The primary health risks associated with nitrate contamination are methemoglobinemia causing blue baby syndrome and nitrosamines considering as a potential carcinogen. In addition, the ingestion of nitrate in drinking water by infants can cause low oxygen levels in the blood, a potentially fatal condition (Spalding and Exner 1993). Especially in South Korea, the fresh surface water in coastal areas and islands has been mostly obtained from groundwater which can encounter the serious problems when the groundwater is contaminated by nitrate (Choi *et al*. 2013, Kim *et al*. 2015). Thus, the Korean ministry of environment as well as the U.S. Environmental Protection Agency (EPA) has established a drinking-water standard of 10 mg/L nitrate as nitrogen (NO_3^--N) (Kim *et al*. 2015, U.S. EPA 1995) and the WHO has also set a similar guideline of 50 mg/L as nitrate (11.3 mg/L NO_3^--N) (WHO, 2001).

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There are a number of treatment technologies available for the removal of nitrate in drinking water such as ion exchange, biological and chemical denitrification, catalytic denitrification, reverse osmosis, and electrodialysis (Shapsshnik and Kesore 1997, Tanaka 2007, Bae *et al*. 2013, Strathmann *et al*. 2006, Thampy *et al*. 2011). Ion exchange generally substitutes chloride anions for the nitrate anion without substantially changing the salinity or the cation makeup of the feed water (Tanaka 2007). However, salt used for regeneration can pose a problem for waste disposal since high salt loads can adversely affect the performance of waste treatment plants. Biological treatment for nitrates is not common for drinking water applications, though it has been widely practiced in wastewater treatment. Catalytic denitrification is considered as a selective denitrification process producing nitrogen gas, but needed to provide expensive metals and hydrogen gas (Bae *et al*. 2013). The membrane processes such as electrodialysis and reverse osmosis are widely used for the nitrate reduction, since both processes can efficiently remove nitrate and result in less product wastes to be disposed (Strathmann *et al*. 2006, Thampy *et al*. 2011). However, reverse osmosis requires strict pre-treatment in comparison to the electrodialysis.

Electrodialysis is an electrically driven process that uses a voltage potential to drive charged ions through a semi-permeable membrane. This can reduce the total dissolved solids in the source water, which can produce even ultra-pure water (Turek *et al*. 2013). For areas where the salinity as well as the nitrate is high, this result in a substantial water quality improvement as compared to other nitrate removal processes (Midaoui *et al*. 2002). For waters with moderate levels of nitrate, the product of electrodialysis may be blended with feed water to achieve the desired nitrate level (i.e., < 10 mg/L NO_3^--N) (Murray 1995). It has been reported that operation temperature and flow rate can significantly influence on the nitrate removal by electrodialysis (Midaoui *et al*. 2002). Midaoui *et al*. also showed that the application of low voltage can selectively remove nitrate by electrodialysis in the presence of other anions such as Cl^-, HCO_3^-, and SO_4^{2-} (Midaoui *et al*. 2002). However, limited knowledge has been provided in the literature regarding parameters governing the design and operation of this process.

In this study, we investigated the removal of nitrate by running a lab scale electrodialysis process at different applied voltages and electrolyte concentration. The energy consumption and current efficiency also analyzed to find out an optimal condition for economic and efficient operation.

2. Experimental

Fig. 1 shows an image of the lab scale electrodialysis system in this study. The unit is mainly comprised of membrane stack, three cylindrical tanks of diluate, electrolyte and concentrate solutions, three circulation pumps, DC power supply, and three valves. The specification of the electrodialysis unit is given in Table 1. The membrane stack consisted of an alternating series of cation exchange membranes (CMX (NEOSEPTA®), Na^+ form, electric resistance: 2.5-3.5 Ohm cm^2, thickness: 0.17-0.19 mm) and anion exchange membranes (AMX (NEOSEPTA®), Cl^- form, electric resistance: 2.0-3.5 Ohm cm^2, thickness: 0.16-0.18 mm) separated by gaskets and spacers where an electrical potential difference is applied between anode and cathode. The basic unit of electrodialysis is a cell pair comprised of a diluted compartment (diluate), a concentrated compartment (concentrate), an anion exchange membrane, and a cation exchange membrane. The active area of each membrane is 50 cm^2 ((5 cm×10 cm×0.08 cm (membrane distance)), 3 pairs). The anode is made of Pt coated titanium (Ti/Pt) and the cathode is made of stainless steel. The

Table 1 Specification of electrodialysis unit

Item	Specification
Ion Exchange membrane	
-Cationic membrane	CMX Sb12
-Anionic membrane	AMX Sb10
Effective area	50 cm^2
Material of other parts	
-Gasket	EPDM
-Spacer and distributor	PE+PP
Electrodes	
-Anode	Ti/Pt
-Cathode	Stainless steel
Operation control (flow rate)	
-Diluate compartment	7 L/min
-Concentrate compartment	7 L/min
Current	5 A Max.
Voltage	50 V Max.

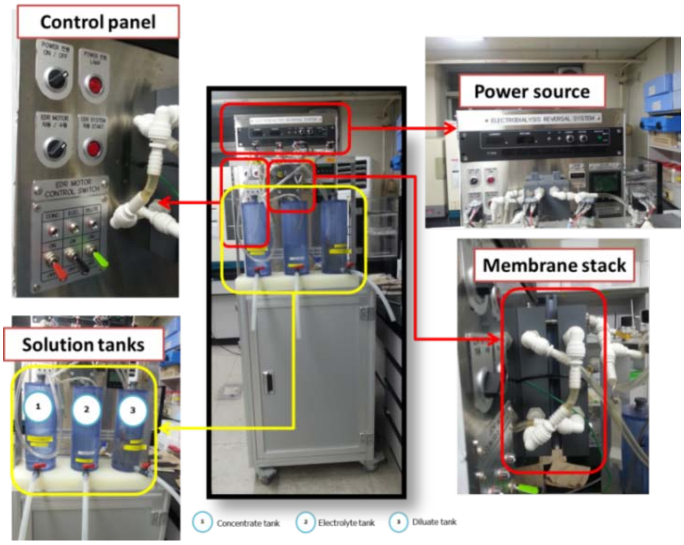

Fig. 1 Electrodialysis system used in this study

electrode solution is referred to electrolyte in this experiment. Initial nitrate concentration in this experiment was 67.7 mg/L NO_3^--N which was prepared by dissolving sodium nitrate in deionized water. We used the diluted compartment containing 1 L of nitrate solution, the electrolyte compartment containing 1 L of sodium sulfate (100 mM), and the concentrated compartment containing 1 L of deionized water. The negatively charged nitrate ions migrate towards the anode under direct current. Nitrate leaves the diluted compartment, then move through the anion exchange membrane and are stopped by the cation exchange membrane in the concentrated

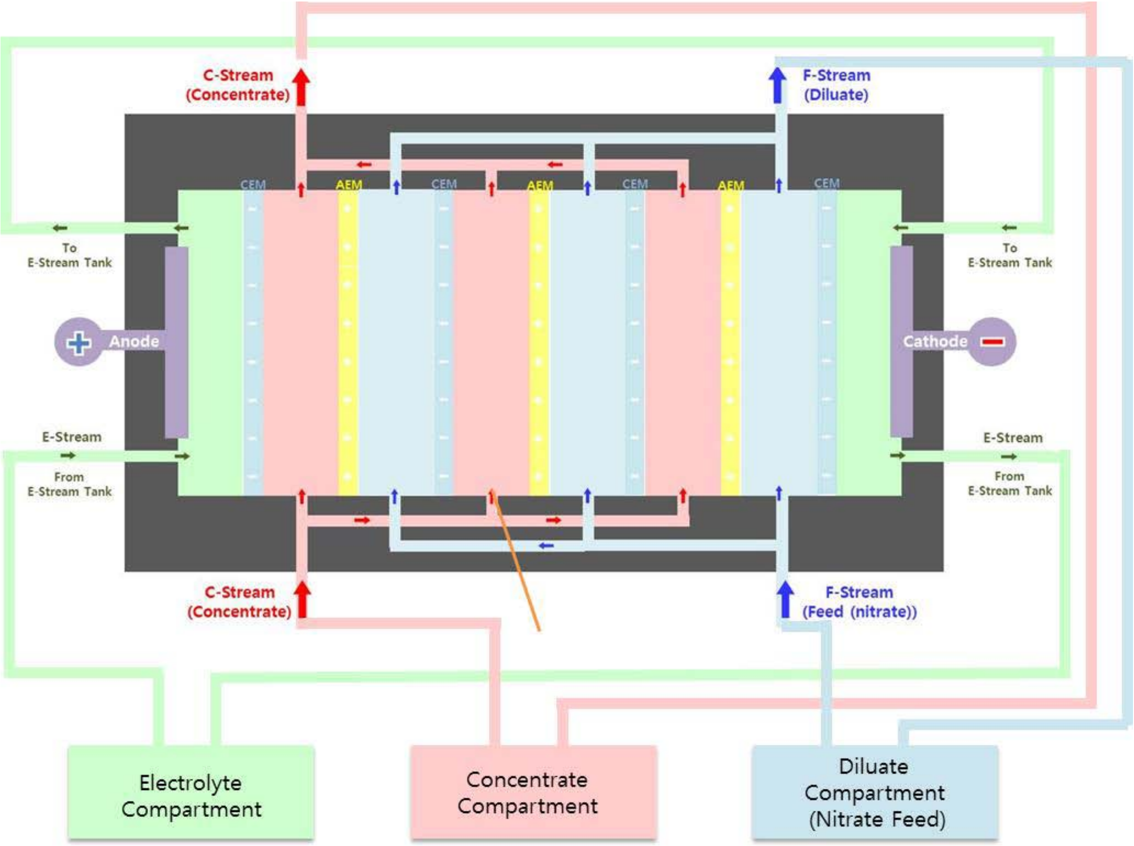

Fig. 2 The separation mechanism by electrodialysis process (AEM=anion exchange membrane, CEM= cation exchange membrane)

compartment (Fig. 2). The treated solution was circulated through the diluted and concentrated compartments by pumps to achieve a desirable concentration of nitrate. The electrolyte solution was also circulated and passed the electrodes to maintain conductivity of the membrane stack.

During the test, water samples were taken periodically from diluted and concentrated streams and the ion concentrations were determined analytically. The concentration of nitrate was determined by ion chromatography (ICS-2000, Dionex Corporation). To determine the removal efficiency (%R) of nitrate, the calculation expressed in Eq (1) was used

$$\%R = \frac{\left[NO_3^-\right]_d - \left[NO_3^-\right]_c}{\left[NO_3^-\right]_d} \times 100 \tag{1}$$

where $[NO_3^-]_d$ and $[NO_3^-]_c$ are the initial nitrate concentration in the diluted compartment and the concentrated compartment after a certain working time, respectively. In order to investigate the effect of operation parameters on nitrate removal efficiency, we used different applied voltage (10, 20, and 30 V) and electrolyte concentration (100 and 500 mM). The current efficiency was also calculated from the Eq. (2), which shows how effective ions are transported across the ion exchange membranes at a given applied current (Murray 1995).

$$e = \frac{F^* \times F_d \times \Delta N \times 100}{I \times N^*} \tag{2}$$

where F^* is Faraday's constant=26.8 A·h, F_d is the demineralized flow rate=420 L/h, ΔN is the difference between feed normality and product normality, I is the current, and N^* is the number of cell pairs=3.

3. Results and discussion

3.1 Effect of applied voltage on the nitrate removal

Fig. 3 illustrates the nitrate removal efficiency in electrodialysis process at the different voltages (10, 20, and 30 V). It has been well known that cell voltage plays a key role in electrodialysis process, since it is the driving force for separation of nitrate across the membranes (Bi *et al*. 2011, Strathmann 2010, Sahli *et al*. 2008). Nitrate concentration in the diluate stream gradually decreased (31 to 71%) as the applied voltage increased from 10 to 30 V in 240 min, while nitrate concentration in the concentrate stream gradually increased at higher applied voltages (Fig. 4). We also observed that nitrate removal efficiency at each applied voltage was dependent on operation time, indicating that increasing the operation time could decrease the nitrate remaining in the diluate streams.

3.2 Effect of applied voltage on energy and current efficiency

Although the removal efficiency of nitrate was the greatest at 30 V, the application of high voltages can cause the high energy consumption with low current efficiency. In addition, an excess

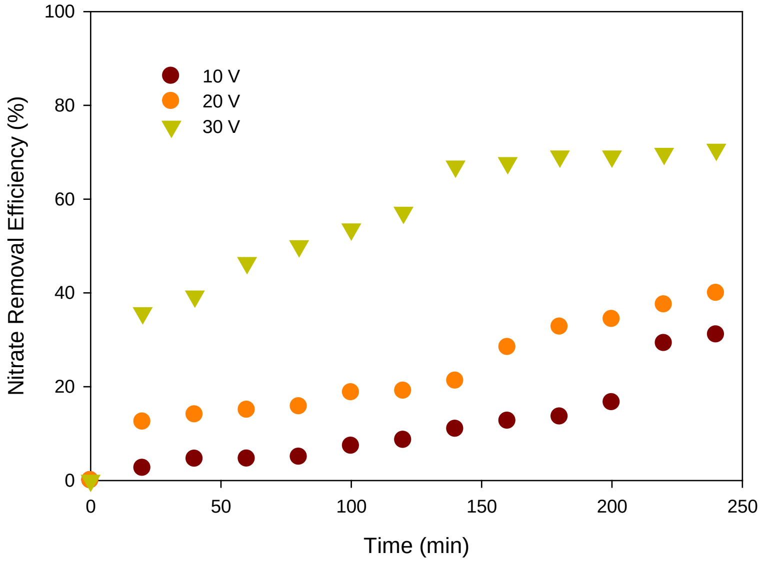

Fig. 3 Effect of applied voltage on nitrate removal efficiency

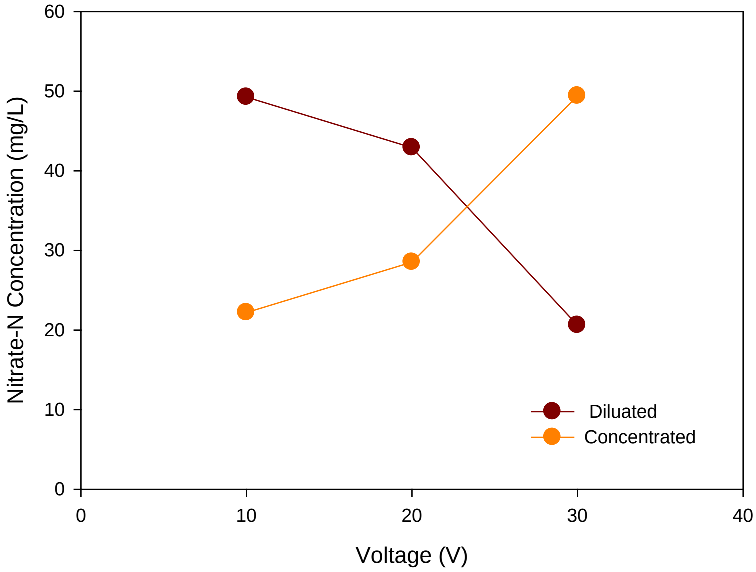

Fig. 4 Concentration of NO_3^--N in diluted and concentrated water after 240 min treatment

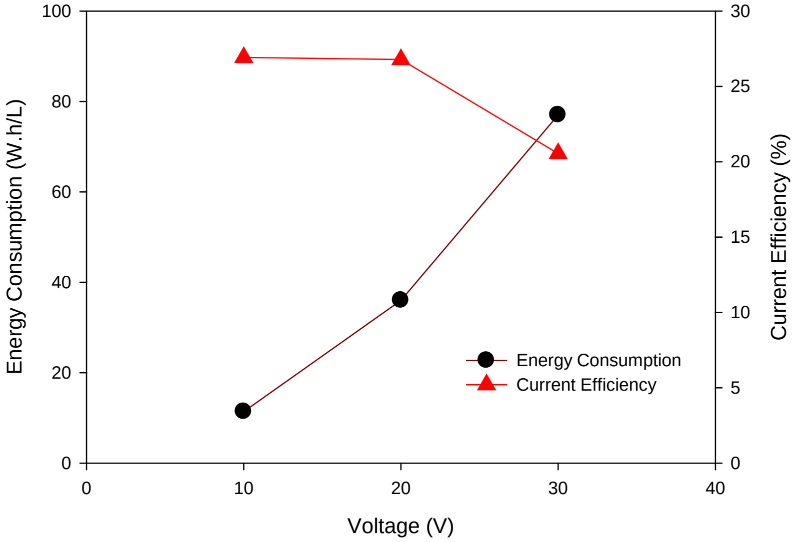

Fig. 5 Effect of applied voltage on energy consumption and current efficiency

current can melt or burn the membranes and spacers. To find out the energy and current efficiency at each applied voltage, the energy consumption obtained from the power consumption of applied voltage and the recirculation pump during the operation of the electrodialysis unit was studied (Fig. 5). Fig. 5 shows the increase in applied voltage from 10 to 30 V led to the increase of energy consumption (11.4→36.0→77.0 W·h/L), while the energy consumption per gram nitrate removal (0.77→1.66→1.63 kW·h/g NO_3^--N) showed the highest value at 20 V. In addition, current efficiency decreased from 27 to 20% when the applied voltage increased from 20 to 30 V.

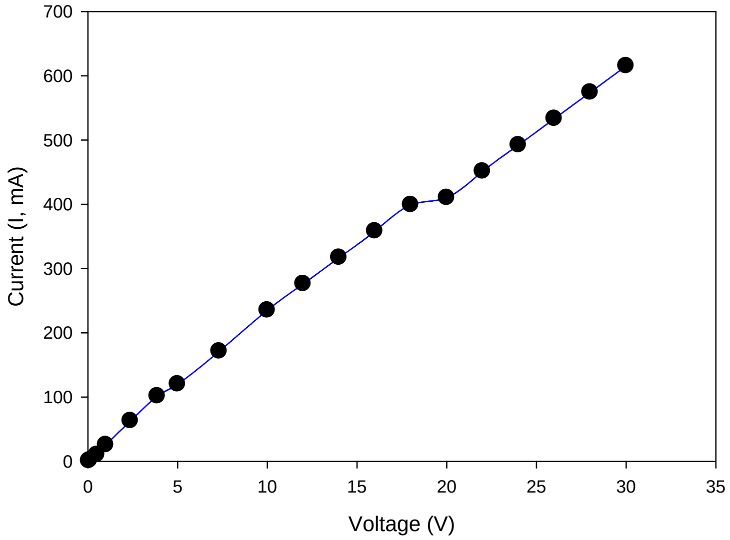

Fig. 6 Change of current with respect to voltage

These results indicate that overloaded voltage might not be economically feasible to conduct the electrodialysis process for the optimal nitrate removal. The decrease in the energy consumption per gram nitrate removal and current efficiency at 30 V may be caused by limiting current density (LCD) which can cause the concentration polarization and water dissociation in the electrodialysis process resulting in inhibition of nitrate removal efficiency (Sahli *et al*. 2008, Ali and Hamrouni 2016). To find out the LCD in this study, we recorded the change of current according to applied voltage that reveals a relationship between the limiting current and voltage to establish the polarization curve (Fig. 6). The current increased in proportion to the increase of applied voltage during the electrodialysis process. The inflection point around 20 V indicates the LCD leading to concentration polarization and water dissociation at higher voltage than the point. It should be noted that working above the LCD point can cause the higher electrical resistance or lower current utilization due to the depletion of the ions in the laminar boundary layer at the membrane surface (Lee *et al*. 2006). Therefore, we concluded that the suitable voltage was 20 V, which revealed the lowest energy consumption and highest current efficiency. The efforts to improve the nitrate removal efficiency at 20 V will be discussed in next section.

The current efficiency obtained from this study was in the range of 20-27%. The relatively low efficiency may be induced by several reasons. First, the membrane used in technical practice is not ideally selective for counter-ions, but also the co-ions can partially migrate through the membrane, which decreases membrane selectivity (Strathmann 2010, Sahli *et al*. 2006).

Another phenomena leading to current efficiency loss is backward diffusion. It is related to the diffusion transport of ions across the membrane back from concentrate to diluate. The current efficiency loss due to backward diffusion is not only dependent on the difference between the mean concentrations in diluate and concentrate, but also on the extension of the concentration polarization. Current leakage is defined as excess electric current at the electrodes that travels through an adjacent membrane, either a heavy but an excessive value or cation membrane, into higher conductivity water. The electric current passing through the external hydraulic circuits does not participate in the desalination process (salt transfer from diluted to concentrated compartment)

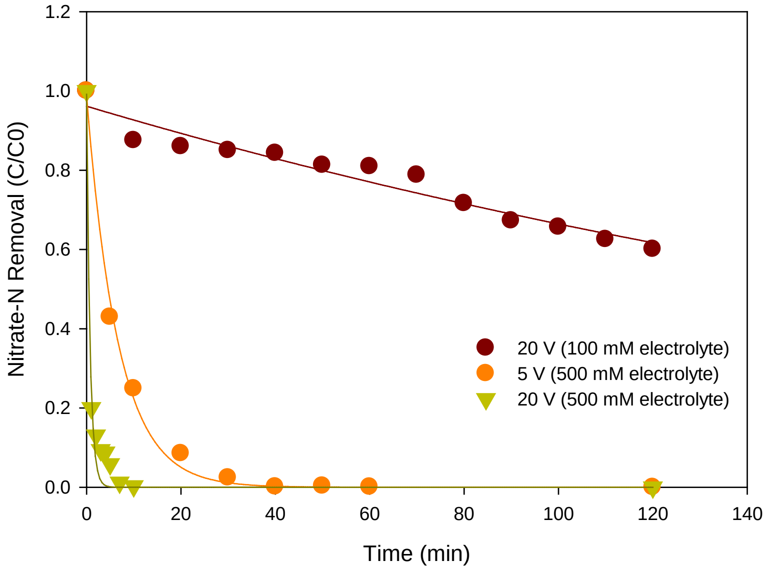

Fig. 7 Removal kinetics of nitrate at different voltage and electrolyte concentration

(Bi *et al*. 2011, Strathmann 2010, Sahli *et al*. 2008). Therefore, this portion of the total current supplied from the external current source is without any desalination effect; thus causing current efficiency loss.

3.3 Effect of electrolyte concentration on the nitrate removal

All nitrate concentration levels after the electrodialysis in Fig. 3 did not meet the drinking water standard requirement (10 mg/L NO_3^--N) due probably to the relatively low concentration (100 mM) of electrolyte used in this study. In order to improve the removal efficiency of nitrate at the suitable voltage (i.e., 20 V), we increased the concentration of electrolyte from 100 to 500 mM (Fig. 7). A complete removal of nitrate was observed in 10 min when 500 mM of electrolyte was injected into the system, while only 30% of nitrate was removed at 100 mM. The rate of nitrate removal can be described by the pseudo-first-order kinetic model (R^2>0.94). Estimated kinetic constant at 500 mM was 1.354±0.205 min^{-1}, which was 437 times higher than that of 100 mM (0.003±0.0003 min^{-1}). This indicates that the concentration of electrolyte can play an important role for the nitrate removal during the electrodialysis. To investigate the effect of electrolyte concentration against the applied voltage, we also conducted an additional experiment at 5 V with 500 mM of electrolyte. The result showed a complete nitrate removal in 40 min with the rate of 0.148±0.007 min^{-1}, which was 9 times higher than that of 20 V, indicating that the increase in electrolyte concentration can dramatically improve the nitrate removal efficiency even at low applied voltage.

4. Conclusions

We showed that drinking water contaminated by nitrate can be effectively removed by the electrodialysis process by controlling the important operation parameters, i.e., the applied voltages and electrolyte concentration. It was found that the nitrate removal efficiency can be enhanced by applying higher voltage during the electrodialysis but, an excessive value could reduce current efficiency and lead to high energy consumption, which is not economical operation. The increase in electrolyte concentration resulted in the dramatic improvement for the nitrate removal efficiency leading to the achievement of treatment goal for drinking water standard of nitrate (10 mg/L NO_3^--N). The results obtained from this study can provide the fundamental knowledge regarding the effect of operation parameters (i.e., applied voltage and electrolyte concentration) on the nitrate removal by electrodialysis process and help for the optimization of working conditions by considering the parameters to design more economic and efficient electrodialysis process.

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