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Nitrate Removal by Electrodialysis from Brackish Groundwater: Effects of Process Parameters

Juan T. Medina Collana[a,*], Luis A. Carrasco Venegas[a], Carlos A. Ancieta Dextre[a], Oscar J. Rodriguez Taranco[a] ,Jorge A. Montaño Pisfil[a] , Denis Gabriel Hurtado[a]

Universidad Nacional del Callao, Facultad de Ingenieria Quimica ,Pablo II 306 Avenue, Bellavista 07011, Peru
jtmedinac@unac.edu.pe

A large part of the world's population is supplied with drinking water from subway sources. During the last few years, groundwater nitrate concentrations have increased considerably. This work proposes the removal of nitrates from brackish groundwater and a model solution by electrodialysis. To evaluate their effect on nitrate removal and energy consumption, three factors were selected with three levels for each: nitrate ion concentration (50, 200 and 500 mg/L), applied electrical potential (5, 10 and 15 V) and feed flow arrangement (A, B and C). The results showed that the most influential variable was the electrical potential, the increase of the potential (15 V) led to a considerable increase in nitrate removal (92.5 %). The best conditions for nitrate removal from the synthetic solution were at an electrical potential of 15 volts, initial nitrate concentration 200 mg/L and the flow arrangement (C) achieving an average nitrate removal of 80%. Nitrate removal increased moderately with the addition of the Venturi tube and even more with the addition of an air flow. In addition, a nitrate removal of 44.43% of brackish groundwater has been achieved during 120 minutes of treatment with an electrical potential of 15 V and the addition of air. Energy consumption varies between 0.2 and 3.17 kWh/m3 of solution. In conclusion, its effectiveness as a desalination and denitrification process and its environmental advantages over conventional methods are highlighted.

1. Introduction

In recent decades, high nitrate levels in drinking water have become a serious environmental problem in many parts of the world(Verma et al., 2023). The main sources of nitrate pollution are considered to be agricultural production, industrial production and domestic wastewater(Fang et al., 2023). The contribution of nitrogen to the ecosystem is due to human activity through the fertilizers used (ammonium nitrate, potassium nitrate, urea), which have grown exponentially since the 1905s, following the invention of the Haber Bosch process in the synthesis of ammonia (NH_3). The World Health Organization has established a maximum concentration limit of 50 mg/L (as nitrate) or 11.3 mg/L (as nitrogen) for drinking water(Ward et al., 2018). Nitrates are an important indicator of surface water quality, and high levels play a key role in water eutrophication, which is a serious threat to the safety of aquatic ecosystems(Davidson et al., 2014). Nitrate in drinking water can also cause blue baby syndrome due to the conversion of hemoglobin to methemoglobin, which is unable to carry oxygen(Richard et al., 2014). Nearly half of the nitrogen fertilizers used are drained from farmland and contaminate available water resources, including surface and groundwater(A. Verma et al., 2023). The high solubility of nitrate in water favors its easy leaching into groundwater and surface water after discharg(Singh et al., 2022). [2]. Researchers have proposed many methods for removing nitrate ions, including: electrocoagulation(Aliaskari & Schäfer, 2021). nanofiltration(Reig et al., n.d.). ion exchange resins(Hekmatzadeh et al., 2012). photocatalysis(Wang et al., 2021). adsorption(Rahdar et al., 2021). electrodialysis(Ali et al., 2010a, 2010b).. Electrodialysis (ED) is an electrochemical process based on ion exchange membranes (IEM) that separates or accumulates ions by applying electric current through the cell. In its simplest form, a conventional electrodialysis cell consists of two metal electrodes (anode and cathode), cation exchange membranes (CEM), anion exchange membranes (AEM), both immersed in an electrolyte solution (dilute compartment and concentrated compartment) and externally connected to a DC power source. This device may have only one pair of membranes or several cation

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and anion exchange membranes usually placed alternately. Cation exchange membranes (CEM) with negatively charged functional groups allow the passage of cations and block the passage of anions, while negatively charged anion exchange membranes (AEM) allow the passage of anions and reject the passage of cations(Alshebli et al., 2023).Compared to conventional adsorption, filtration and ion exchange technologies, ED is a mico-free method with high ionic separation efficiency, low pressure requirements and low sludge production; therefore, it has both technical and economic advantages(Tekinalp et al., 2023).The objective of this work was to investigate the performance of the newly constructed electrodialysis cell on the percentage removal of nitrate ions from a model solution of similar nitrate concentration in brackish water. The effect of the initial nitrate concentration, the applied electrical potential, and the arrangement of the inlet to the dilution, concentrate, and electrode washing compartments on the percent nitrate removal and specific energy consumption was studied. The best conditions were selected and applied to a real brackish groundwater sample.

2. Materials and Methods

2.1 Water samples

In this research work, synthetic solutions of nitrate ions and real brackish groundwater have been used to validate the DE process. Three solutions of concentrations 50, 200 and 500 mg L-1 of $NaNO_3$ were prepared. Brackish groundwater samples were extracted from a well located in the district of Lurin, Lima, Peru.

2.2 Chemicals and solution chemistry

The nitrate solution was prepared by dissolving $NaNO_3$ (purity > 99 %) in distilled water. 7.2 g/L sodium sulfate solution (purity >99.5 %, Merck, Germany) was used as a washing solution for the electrodes (cathodic and anodic chambers). 0.5 N sodium chloride solution was prepared by dissolving analytical grade NaCl (99.9%) to soak the membranes prior to application. Thirty liters of solutions of nitrate concentrations (10 L of 50 mg/L, 10 L of 200 mg/L and 10 L of 500 g/L) were prepared respectively

2.3 Analytical methods

The concentrations of NO3- , Cl^-, $SO4^{2-}$ ions in the actual brackish groundwater, as well as in the diluted compartment were analyzed by ion chromatograph, mark thermo scientific, ICS-3000. The concentrations of the cations (Ca2+, Mg2+, Na+, K,) in the actual brackish water were measured using the following equipment ICP Thermo scientific model ICAP 6000. The nitrate concentrations in the model solution were analyzed by Sonda HQD Intellical of the series ISENO3181 Hach. The conductivity values were measured using a portable digital multimeter HQ40D.Nitrate concentration, conductivity levels were measured every 30 minutes in the dilute and concentrate compartments.

2.4 Ion exchange membranes

Heterogeneous cation exchange (MK-40) and anion exchange (MA-41) membranes (Shchekinoazot, Pervomaisky, Russia) is their manufacturer. The main characteristics of the two membranes are summarized in Table 1. Before use, the membranes were immersed in a 0.5 M NaCl solution for 24 h, then the membranes were washed with deionized water until a constant level of electrical conductivity of the wash water was reached.

Table 1. Physical-chemical characteristics of the membranes used adapted from (Tekinalp et al., 2023)

Membrane / Characteristic	MK-40	MA-41
Electric resistance (Ω.cm2)	2	<11
Ion-exchange capacity (meq/g dry membrane)	2	1.6
Transport number	>0.98	0.98 ± 0.02 in 1 M NaCl
Thickness (μm)	520	530 ± 20

2.5 Design of experiment by Taguchi method

The design contemplated the effect of three factors at three levels for each variable to evaluate the removal of nitrate ions from a synthetic aqueous solution and energy consumption. The three operating variables and the levels considered are presented in Table 2, an L9 orthogonal array was used in which a total of 9 experiments were carried out. Tests were conducted in duplicate and average values were reported.

Table 2. Experimental process parameters and levels.

Factors	Notation	Units	Levels		
			Low	Medium	High
Electric potential	X1	V	7	10	15
Initial nitrate concentration	X2	mg/L	10	200	500
Feed flow arrangement	X3	…….	A	B	C

A: without the presence of the Venturi tube and air flow. B: A 1/5 inch Venturi tube has been integrated into the inlet hose to the diluent, concentrate and electrode wash compartment, respectively. C: Using a compressor, air has been injected through the throat of the Venturi tube.

2.6 Data analysis

The removal efficiency (R) is an indicator to evaluate the amount of nitrate ions that are removed by the electrodialysis cell Removal is calculated by Eq. (2).

$$R = \left(\frac{\Delta C}{C_0}\right) x100\ \% = \left(\frac{C_0 - C_t}{C_0}\right) x100\% = \left(1 - \frac{C_t}{C_0}\right) x100\% \quad (1)$$

Where, R is the removal efficiency (%) C_0 and C_t are the initial concentration and the concentration of the diluted solution at time t in (mg/L).

The consumption of electrical energy is an economic parameter of great importance in the electrodialysis process. Is directly proportional to the applied electric potential, to the treatment time, to the electric current intensity and inversely to the volume used. In this study, the specific electrical energy consumed (SEC) is defined as the amount of electrical energy per cubic meter, was calculated by (Gherasim et al., 2014; Wu et al., 2022) (Bejjany et al., 2017) equation (3).

$$SEC\ \left(\frac{kW.h}{kg}\right) = \frac{U \int_0^t Idt}{V_d x 10^{-3}} \quad (2)$$

where SEC refers to speciic electricity consumption, U refers to the voltage, I refers to the electric current (A), t refers to the time (h), V_d (L) correspond to the volume of dilute solution and 10−3 is the numerical coefficient for converting L to m^3

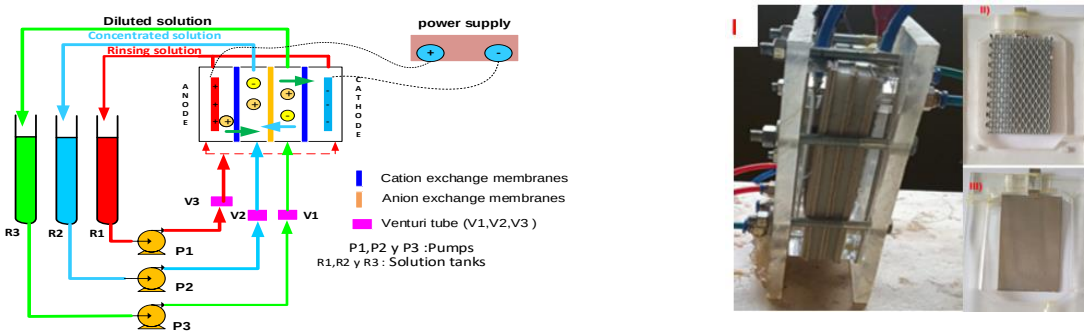

Figure 1. Schematic diagram of the experimental setup used for the electrodialysis study

2.7 Experimental equipment

Figure 1 shows the experimental ED system used in the tests, which includes two cation exchange membranes and one anion exchange membrane. The cell configuration is " MK- MA- MK" as shown in Figure 1. The effective membrane area of each memebrane is (80 mm × 120 mm). The anodes were made of titanium coated with ruthenium oxide and iridium oxide (Ti-RuO2 -IrO2), the cathode was of pure titanium, both electrodes have an effective area of 50cm^2. The concentrated, diluted and rinsing solutions of the electrodes were placed in three cylindrical containers of acrylic material with a volume capacity of 1000 mL (R1, R2 and R3). The solutions were recirculated through the diluted, concentrated and electrode washing compartments by means of pumps (P1, P2 and P3) with a flow rate of 900 mL/ min tests. 5 L of electrode washing solution (7.2 g/L Na_2SO_4) was used with the same flow rate used in the diluted and concentrated compartments in order to avoid pressure differences in the compartments. Anode and cathode were connected to the positive and negative output of a digital power supply (DC 0-32 V, 5 A UNI-T UTP). The intensity of the electric current has been read on the power supply indicator every 5 minutes. Samples of the diluted and concentrated solutions were taken every 30 min and analyzed for nitrate ion concentration (NO_3^-) and conductivity. The temperature of the solutions was maintained at 20 ± 1°C in all experiments.

3. Results and discussion

3.1 Results of Brackish Groundwater

Figure 2 (A) shows the initial concentrations of ions (Na1+ , Ca2+ , Mg2+) , anions (Cl- , SO4-2) , and silica contained in the brackish water and the changes in concentrations in the diluted compartment during 90 minutes of treatment. A nitrate ion concentration of 279.5 mg/L was observed in the electrodialysis cell feed. A nitrate removal of 44.43% was achieved by applying an electrical potential of 15 V and adding air in the feed streams of the dilution, concentrate and electrode washing compartments. Other previous studies reveal results of ion concentration removal in percentages similar to those of our work (Gahlot et al., 2017). A progressive decrease in the concentration of all ions is observed as a function of treatment time. Likewise, the percentage of removal of monovalent anions (chloride and nitrate) is greater than 40% and the sulfate ion reaches 33.42%. This is consistent with previous studies (Aliaskari & Schäfer, 2021; Karimi & Ghassemi, 2016). It is also observed that the variation in silica concentration is not significant (3.6%), a fact that is attributed to the lack of electrical charge of the substance. The changes in nitrate concentration versus treatment time are shown in Figure 1(B). The decreasing trend of nitrate ion concentration in the diluted compartment was similar to the increasing concentration in the concentrated compartment. However, a more significant increase in nitrate concentration in the concentrated compartment was observed in the last minutes of the treatment. It was found that 44.43% of the nitrate ion concentration was eliminated after 120 minutes of treatment. Previous studies reveal results of removal of ion concentrations in percentages similar to those of our work (Gahlot et al., 2017)

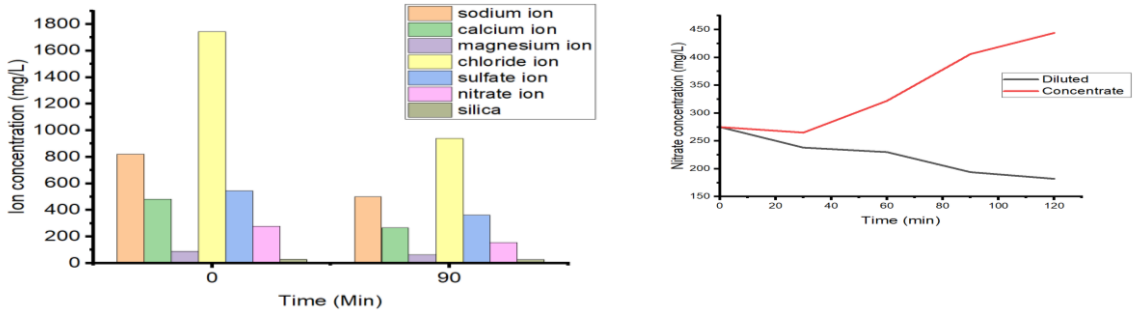

Figure 2. Concentration of brackish water ions in the diluted compartment in 90 minutes of treatment at 15 Volts with Venturi tube and air inlet.

3.2 Results of the synthetic solution

Table 3 presents results of descriptive statistics on the percentage of nitrate removal and specific energy consumption. Table 3 shows the mean of the 9 tests for nitrate removal is 77.14 % and the mean for specific electricity consumption is 1.022 kWh/m3.

Table 3. Mean nitrate removal percentage and energy consumption

Response	N	Mean	Standard error	Desv.Est	Variance	Minimum	Maximum
Nitrate removal rate	9	77.14	4.16	12.48	155.65	59.59	93.88
Energy consumption	9	1.022	0.306	0.918	0.843	0.2	3.17

Figure 3 shows the conductivity of the diluted solution as a function of treatment time for the nine experimental runs. As can be seen, the electrical conductivities of all solutions decrease with treatment time. Figure 3 shows the variations in the percentage of nitrate ion removal as a function of treatment time. It is observed that the maximum removal (92%) is reached when the electrical potential applied to the cell is 15 volts and the lowest nitrate concentration (50 ppm) and air is incorporated through the Venturi tube. Also, the lowest removal obtained is at 7 volts and a nitrate concentration of 50 ppm and the feed configuration without the presence of the Venturi tube and air.

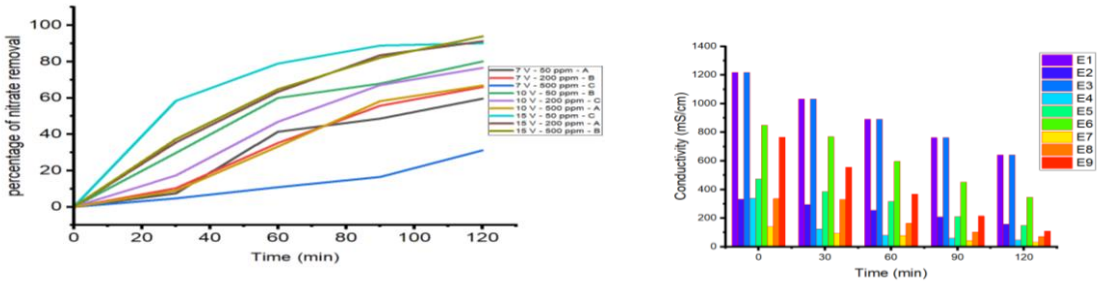

Figure 3. Variation over time of the percentage of nitrate removal according to the experimental design and conductivity evolution in dilute compartment .

Figure 4 (A) shows the effects of the factors versus the percentage of nitrate removal. From the figure it can be seen that the most influential factor in the removal of nitrate ions was the electrical potential applied to the electrodialysis cell. The most suitable levels for maximum removal efficiency were at an electrical potential of 15 volts, an initial nitrate concentration of 200 mg/L and a Venturi tube inlet configuration with an air flow. With these conditions, the calculated removal efficiency was 92%. As shown in Figure 4 (B) , the energy consumptions are in direct relation to the applied electric potential and the initial concentration of nitrate ion for the high levels studied (15 Volts and 500 mg/L of nitrate). Previous studies have pointed out the same trend in energy consumption in relation to the factors mentioned above (Abarkan et al., 2021).

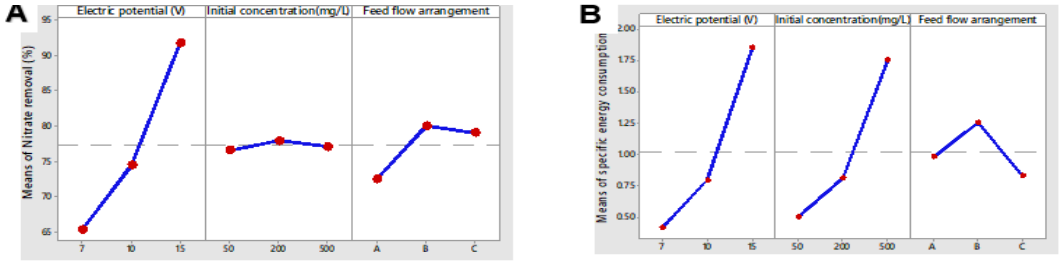

Figure 4. Mean nitrate concentration removal rates (A) and mean specific energy consumption(B)

4. Conclusions

The present work investigates the implementation of a batch electrodialysis process for the removal of nitrates from brackish groundwater and a model solution for the removal of nitrates from brackish groundwater. The effect of applied electric potential (7, 10 and 15 V), initial nitrate ion concentration (50, 200 and 500 mg/L) and flow arrangement in the cell feed (A, B and C) on nitrate ion removal performance was studied. It has been observed that nitrate removal across ion exchange membranes is significantly influenced by the electrical potential applied to the cell. A strong decrease in nitrate concentration (44.43%) in the actual groundwater was achieved within 90 minutes. Removal of anions from actual brackish water followed the order $Cl^- > NO_3^- > SO_4^{2-}$; cations $K^+ > Ca^{2+} > Na^+ > Mg^{2+}$. The best conditions for nitrate removal from the synthetic solution were at an electrical potential of 15 volts, an initial nitrate concentration of 200 mg/L and the flow arrangement (C) achieving an average nitrate removal of 80%. The nitrate removal power consumptions were 0.42 kW.h/m³ for 7 V and 1.8 kW.h/m³ for 15 V electric potential applied.

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