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N. Kabay[a]; M. Yüksel[a]; S. Samatya[b]; Ö. Arar[b]; Ü. Yüksel[b]
[a] Faculty of Engineering, Chemical Engineering Department, Ege University, Izmir, Turkey [b] Faculty of Science, Chemistry Department, Ege University, Izmir, Turkey

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Removal of Nitrate from Ground Water by a Hybrid Process Combining Electrodialysis and Ion Exchange Processes

N. Kabay and M. Yüksel
Faculty of Engineering, Chemical Engineering Department,
Ege University, Izmir, Turkey

S. Samatya, Ö. Arar, and Ü. Yüksel
Faculty of Science, Chemistry Department, Ege University,
Izmir, Turkey

Abstract: In regions where agricultural activities are highly intensive, nitrate concentrations in ground water are usually above the permissible level for nitrate in drinking water. There are several physicochemical and biological treatment processes typically used to remove nitrate contamination from ground water. In this study, an electrodialysis-ion exchange hybrid process was used for the removal of nitrate from ground water obtained from an agricultural area in the Western Anatolia religion in Turkey. Nitrate was effectively removed from the ground water. The effect of other ionic species such as chloride and sulfates on nitrate removal by electrodialysis has also been studied using deionized water that was dosed with selected anionic and cationic species.

Keywords: Nitrate removal, ground water, water pollution, electrodialysis, ion exchange, hybrid process

INTRODUCTION

Contamination of nitrate from ground water is a significant problem in many parts of the world. The causes of high nitrate concentration in the ground water

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Address correspondence to N. Kabay, Faculty of Engineering, Chemical Engineering Department, Ege University, Izmir 35100, Turkey. Tel.: +90-232-3880016; Fax: +90-232-3741401. E-mail: nalan.kabay@ege.edu.tr

are excessive use of fertilizers, human and animal wastes, and uncontrolled land discharges of treated waste water. The consumption of water containing high nitrate can lead to health problems. Nitrate causes methemoglobinemia (so called blue-baby syndrome) when ingested by infants. In the stomach, nitrate is converted to nitrite. The nitrite in turn oxidizes hemoglobin to methemoglobin which does not carry oxygen to cell tissues (1, 2). In addition, nitrosamines are carcinogenic compounds that may be formed from nitrate. The maximum contaminant limit for nitrate in drinking water has been set at 45 mg-NO_3^-/L by EPA. A similar guideline of 50 mg-NO_3^-/L has been set by the WHO, while the European Community (EC) standards allow a maximum admissible concentration of 50 mg-NO_3^-/L and a guide level of 25 mg-NO_3^-/L (3, 4). In order to remove nitrate, several methods have been proposed in literature. These processes include ion exchange, reverse osmosis, electrodialysis, biological denitrification, and catalytic reduction (5–11). Recently, the electrodeionization process has been also developed for nitrate removal from drinking water (12, 13).

Electrodialysis is a membrane process that proved its reliability and efficiency. The main application of the electrodialysis is its utilization for the brackish water desalination. The electrodialysis is also used for the process of demineralization and deacidification in the food processing industry. Other applications in progress are the development of metallurgy, chemistry, pharmacology, biotechnology and the treatment of water and effluents. Electrodialysis is reported as one of the best separation processes for the selective removal of nitrate from water (10). Elsewhere, the selective removal of nitrate from groundwater has been carried out by coupling electrodialysis and a bioreactor (11). In this study, we investigated the performance of a hybrid process including electrodialysis and ion exchange methods for selective removal of nitrate from ground water.

EXPERIMENTAL

Materials

Inorganic chemicals were supplied by Merck and Riedel-de Haën as analytical-grade reagents. Model nitrate solutions were prepared by dissolving $NaNO_3$ in deionized water. The solutions of sulfate and chloride were prepared through the dissolution of Na_2SO_4 and NaCl respectively, in deionized water. The ground water was obtained from the agricultural field of Manisa city, Western Turkey. The characteristics of the ground water are summarized in Table 1.

A strong base nitrate selective anion exchange resin Purolite A 520E was kindly provided by Purolite Int. Ltd. This resin is a macroporous strong basic anion resin which is specially designed for the removal of nitrates from water

Table 1. Compositon of ground water (pH: 7.6)

Species	Concentration (mg/L)
Sodium	45.0
Potassium	1.7
Calcium	142.0
Magnesium	43.0
Nitrate	161.0
Chloride	49.0
Bicarbonate	20.0
Sulfate	500.0

for potable processes. This resin has the particular advantage of having more affinity with the nitrate ions than for the other anions.

Batch-mode Tests with ED Method

TS-l-10 ED equipment produced and modified by Tokuyama Co., Japan, was used for experimental studies. The layout of the experimental set-up is shown in Fig. 1. It has a stack with 10 cell pairs of Neosepta CMX (strongly acidic cation exchange) and AMX (strongly basic anion exchange) membranes having an effective area of 1 dm^2 and electrical resistance of 2.0–3.5 Ω-cm^2. Three pumps have a maximum capacity of 1.8 L/min. DC power at constant voltage (max 18 V) or current (max 3 A) is provided by a rectifier. Three solution tanks (each 1 L) are used for holding dilute, concentrated, and electrode rinse solutions. The electrodes are platinum-plated titanium (anode) and stainless steel (cathode). As defined in Fig. 2, in a typical electrodialysis cell, a series of anion and cation exchange membranes are arranged in an alternating pattern between an anode and a cathode to form individual cells. A DC supplier was connected to two electrodes. When a current is applied to the cell, the positively charged sodium ions move to the cathode, passing through the negatively charged cation exchange membrane. On the other hand, the negatively charged nitrate ions move to the anode, passing through the anion exhange membrane and are retained by the cation exchange membrane. At the end, ion concentrations increase in alternating compartments with a simultaneous decrease of ions in other compartments (14, 15). In this study, batch-mode tests were conducted using both deionized water containing 450 mg NO_3^-/L and ground water with a nitrate concentration of 161 mg NO_3^-/L. Samples were taken periodically from dilute and concentrated compartments to monitor the concentration of nitrate and other ionic species.

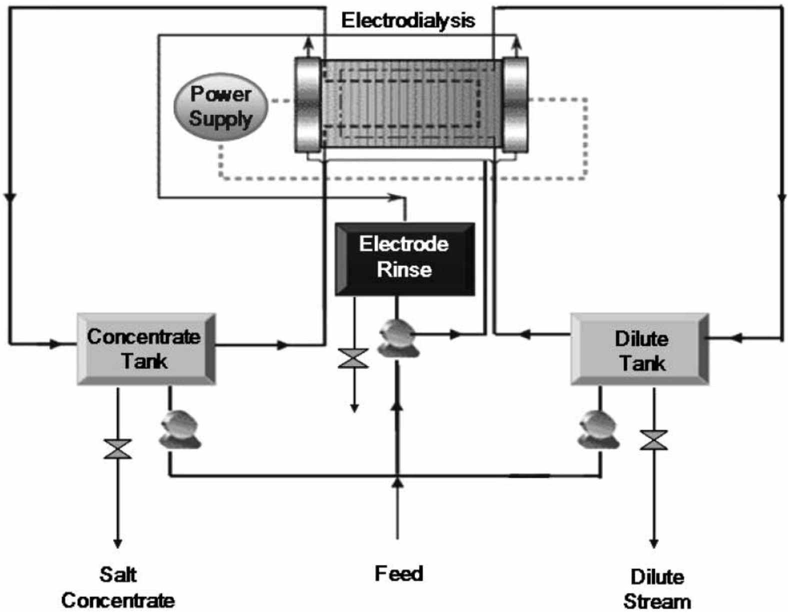

Figure 1. Batch-mode operation of electrodialysis system.

Column-mode Tests with Ion Exchange Method

The column-mode tests were carried out with a column of glass with an internal diameter of 0.7 cm. The column was packed with 0.5 mL of wet-settled volume of resin with a particle size of 0.355–0.500 mm. The effluent obtained from dilute compartment of ED system was delivered down-flow to the column at a flow rate of SV (space velocity) of 20 h^{-1} using a peristaltic pump (Ismatec). The breakthrough curves were obtained by analysis of successive 3 mL fraction of the effluent. The fractions were collected using a fraction collector (Advantec SF-2100W). The elution of nitrate from the resin was performed using 0.6 M NaCl solution at SV (space velocity) of 5 h^{-1}. The elution profiles were obtained by collecting 3 mL of fractions with a fraction collector.

Analyses of Ionic Species

The analyses of nitrate, chloride, and sulfate ions were carried out using a Shimadzu model ion chromatography equipment (Model LC 10 A*i*). The cations were determined by using atomic absorption spectrophotometer (Model Varian Plus 10 A).

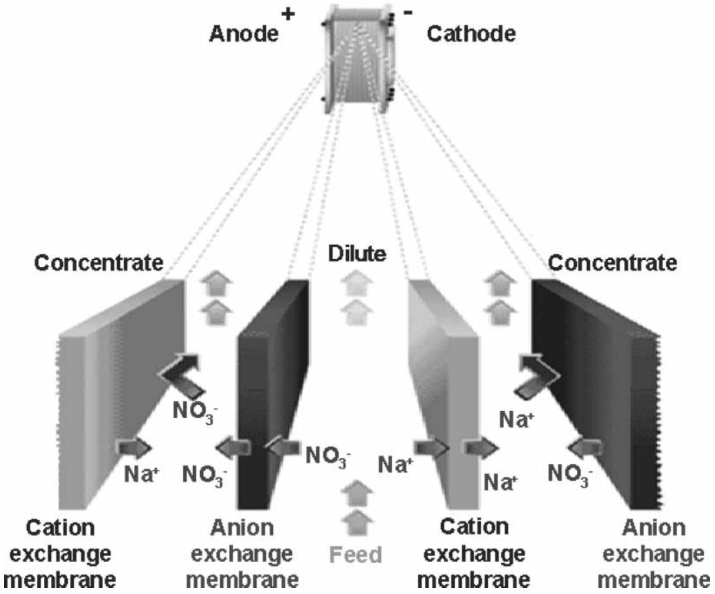

Figure 2. Principle of nitrate removal by electrodialysis.

RESULTS AND DISCUSSIONS

We have already reported that there is a remarkable influence of both chloride and sulfate ions on breakthrough curves of nitrate when nitrate selective ion exchange resins Purolite A520*E* has been used for removal of nitrate from aqueous solution (16). The electrodialysis method has been introduced as a selective method for removal of nitrate from ground water (10, 11). We also concluded that electrodialysis is an effective method for the removal of nitrate from water. But percent removal of nitrate was lower when the initial concentration of nitrate is low (17). Bearing this in mind, we considered that developing a hybrid process by combination of electrodialysis and ion exchange might be effective to remove nitrate from ground water with a high performance through the synergic effect of two separation methods.

Effect of other Ionic Species on Electrodialytic Separation of Nitrate

To investigate the permselectivity of the anion exchange membranes of TS-1-10 electrodialysis system, the separation of nitrate by electrodialysis was investigated in the presence of chloride and sulfate ions. These experiments have been performed using deionized water dosed with ionic species such as nitrate, chloride, and sulfate. The experiments were conducted with a solution containing nitrate (450 mg NO_3^-/L) paired with either chloride (257 mg Cl^-/L) or sulfate (349 mg SO_4^{2-}/L) and a mixture of three ionic species. The equivalent concentrations of all ionic species were kept the same in these mixtures. For each mixture, limiting current measurements were carried out before performance tests. The applied currents were changed keeping the solution concentration constant. The feed and concentrate solutions pumped from the same reservoir were circulated through the feed and concentrate compartments, respectively, and then recycled to the reservoir. By doing this way, the solution concentration in the feed could be maintained constant at a desired level during the experiments. If the applied current changed, the obtained voltage values will change linearly until the limiting current point. After this point, there is a sharp change in slope. This switching point is determined as limiting the current point. Applied voltage values for each mixture are given in Table 2. The feed flow rate is kept constant (1.6 L/min) during each tests. The concentrated (C) and dilute (D) streams were monitored for concentration of anions, current and conductivity values by time. Concentrations of anions in dilute and concentrated streams were measured in certain time intervals and presented on charts, in dimensionless concentrations, defined as the ratio of concentration at any time to initial concentration (C/C_o). Histories of anion concentrations at each experiments performed using different combination of ionic species are given in Figs. 3–5. According to these figures, it is seen that the operation time needed for reaching 0.01 A of current and lowest concentration of ion is almost the same for both nitrate and cloride in the mixture of nitrate-chloride species. (Fig. 3). According to Fig. 4, the time period needed to remove nitrate from the solution remained the same in the presence of sulfate ions. The operation period for sulfate ion was longer than nitrate and chloride ions. For the mixture containing three ionic species, the results agreed well with the other two. When nitrate is paired with chloride ions, the percent removal of nitrate was 98% and 99% in the presence of sulfate, respectively after 22 minutes of the operation period. The percent removal of nitrate from a mixture containing nitrate, chloride and sulfate ions was 99%.

Table 2. Applied voltage values for each mixture containing various ionic species

Ionic species in mixture	Equivalent concentration value	Flow rate, L/min
$NO_3^-:Cl^-$	1:1	1.6
$NO_3^-:SO_4^{2-}$	1:1	1.6
$NO_3^-:SO_4^{2-}:Cl^-$	1:1	1.6

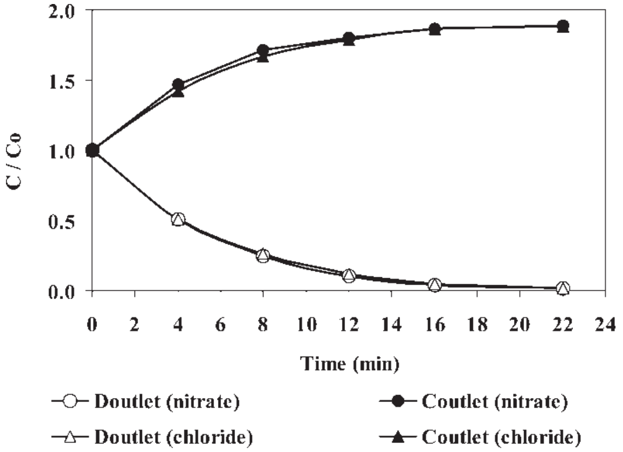

Figure 3. Removal of nitrate from a mixture containing nitrate and chloride ions at 1.6 L/min as constant flow rate and room temperature (NO_3^-:Cl^-) = (1:1) D:Dilute stream C: Concentrate stream.

The specific power consumption (SPC) values for each solution were calculated using the following equation where E is the voltage applied, I current, t time, V_D solution volume in dilute compartment (16)

$$SPC = \frac{E\int_0^t I(t)dt}{V_D}$$

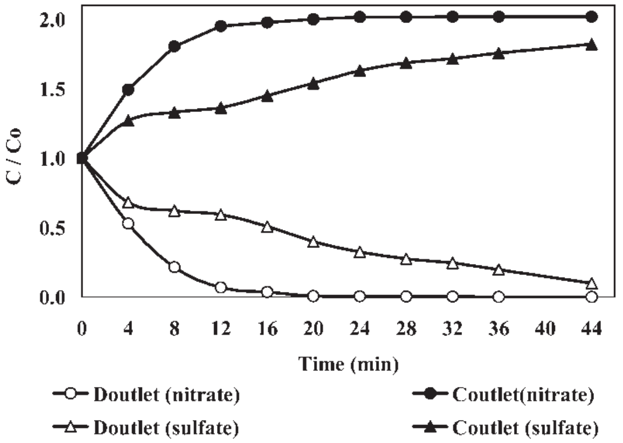

Figure 4. Removal of nitrate from a mixture containing nitrate and sulfate ions at 1.6 L/min as constant flow rate and room temperature (NO_3^-:SO_4^{2-}) = (1:1) D:Dilute stream C: Concentrate stream.

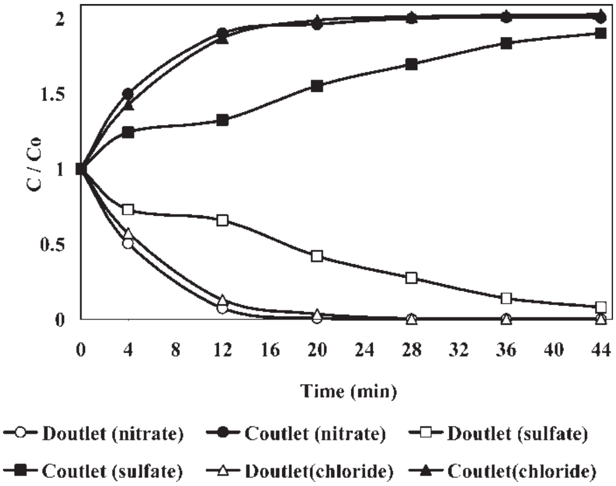

Figure 5. Removal of nitrate from a mixture containing nitrate, chloride and sulfate ions at 1.6 L/min as constant flow rate and room temperature NO_3^-: SO_4^{2-}:Cl^-) = (1:1) D: Dilute stream C: Concentrate stream.

Table 3 summarizes the calculated SPC values. According to the results obtained, one could conclude that power consumption is increased with the increase in the number of ionic species. The difference in SPC values is also due to the difference in applied voltage values.

Nitrate Removal from Ground Water by a Hybrid Process Combining Electrodialysis and Ion Exchange Processes

Limiting current measurement was carried out using a ground water sample containing 161 mg NO_3/L before electrodialysis experiment. According to the limiting current measurement, the respective voltage value for ground water was determined as 6.76 V. The electrodialytic separation of nitrate from ground water was performed using a feed flow rate of 1.6 L/min and

Table 3. SPC values for each mixture

Ionic species in mixture	Equivalent concentration value	SPC (Wh/L)
NO_3^-		0.21
NO_3^-:Cl^-	1:1	0.45
NO_3^-:SO_4^{2-}	1:1	0.35
NO_3^-:SO_4^{2-}:Cl^-	1:1	0.58

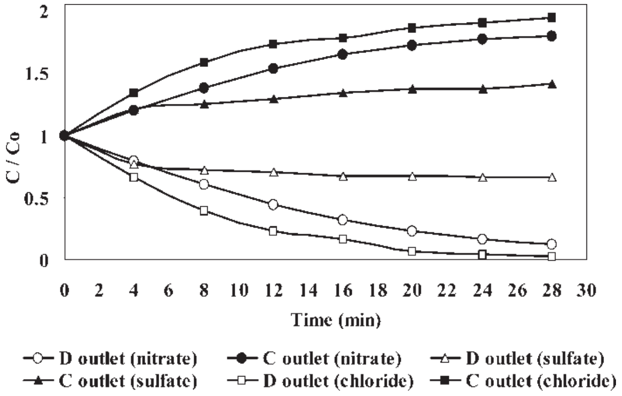

Figure 6. Removal of ionic species from ground water by electrodialysis at 1.6 L/min as constant flow rate and room temperature (D: Dilute stream C: Concentrate stream).

room temperature. Figure 6 shows C/C_o plots vs. time for removal of nitrate, chloride, and sulfate ions from ground water. When operation times were compared, the permselectivity order of anion exchange membrane of electrodialysis system has been found to be as follows: $Cl^- > NO_3^- > SO_4^{2-}$. This result agreed well with the result obtained with model solutions described above and that of the one reported in the literature (10). After 24 minutes of the operation period, the electrodialytic separation of nitrate was about 88%.

In order to remove the nitrate that remained in the dilute compartment, this effluent is passed through a column packed with nitrate selective ion exchange resins Purolite A 520. The breakthrough curve of nitrate is given

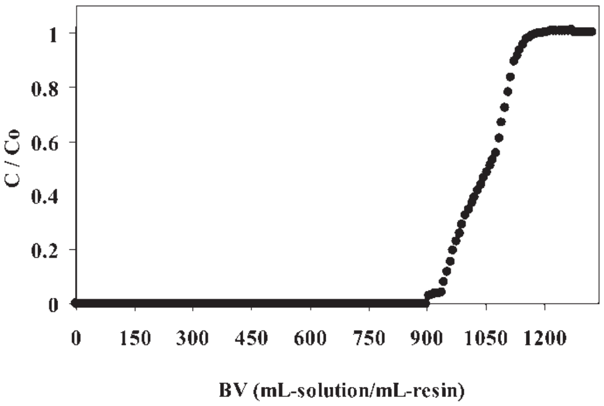

Figure 7. Breakthrough curve of nitrate obtained by Purolite A 520E using dilute effluent from ED system.

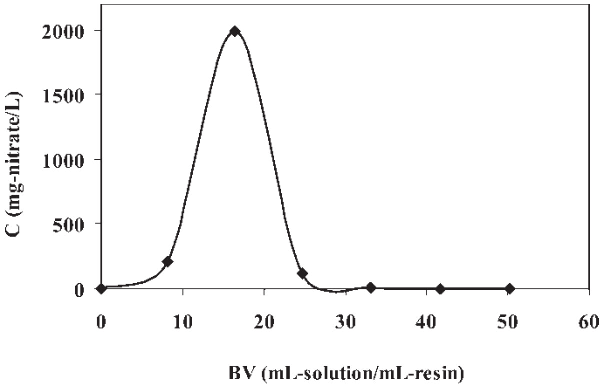

Figure 8. Elution curve of nitrate.

in Fig. 7. The respective elution curve is shown in Fig. 8. The column data obtained are summarized in Table 4. The resin Purolite A 520E exhibited a great performance for removal of nitrate remained in the effluent of the dilute compartment of the electrodialysis system. The breakthrough point at which the nitrate concentration is about 1 mg/L has been detected as 943 BV. The resin loaded onto the ion exchange resin was completely eluted with 0.6 M NaCl.

A flow sheet of a hybrid process combining electrodialysis and ion exchange processes has been given in Fig. 9. By using such a hybrid process, it was possible to obtain pure water from ground water with high process efficiency. In Table 5, a comparison has been done among three processes for nitrate removal from ground water by taking into consideration various conditions.

Table 4. The data of column-mode removal of nitrate by Purolite A 520E from diluate of ED

Purolite A 520E	
Break Point (BV) (mL/mL-R)	943
Breakthrough Capacity	
mg NO_3/mL-resin	17.00
mg NO_3/g-resin	47.59
Total BV (mL/mL-R)	1323
Total Capacity	
mg NO_3/mL-resin	18.60
mg NO_3/g-resin	52.07
Column Utilization (%)	91.40
Elution Efficiency (%)	100

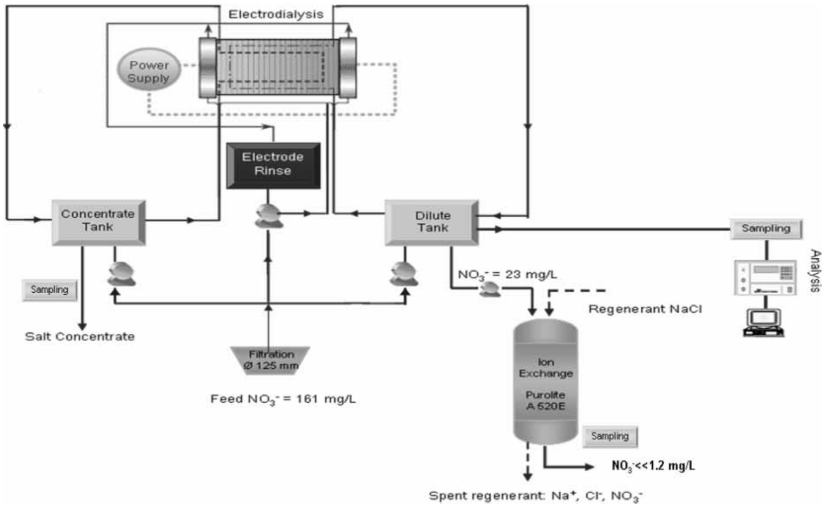

Figure 9. Scheme of the hybrid process combining ion exchange and electrodialysis processes.

Table 5. Comparison of separation processes for nitrate removal from ground water

Condition/ Process	Ion exchange (IX)	Electrodialysis (ED)	IX + ED
Post treatment	Sometimes	Sometimes	Sometimes
Chemical demand	Required for regeneration	None or low chemical demand	Required for regeneration
Post treatment	None	None	None
Waste disposal	Salt brine and rinse water	Concentrate	Salt brine and rinse water + concentrate
Feasibility/ automation	Good	Good	Good
Process start-up	Minutes	Minutes	Minutes
Cost	Low	Medium	Medium
Removal efficiency(%)	80	87	100

CONCLUSIONS

A hybrid process combining electrodialysis and ion exchange processes has been suggested for nitrate removal from ground water. It was concluded that the production of deionized water from ground water is possible with a high efficiency using an electrodialysis-ion exchange hybrid process.

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