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Simultaneous removal of nitrate and hardness ions from groundwater using electrodeionization

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ABSTRACT

Nitrate concentrations in groundwater frequently exceed permissible levels for potable water in intensive agricultural regions. It is critical to develop highly efficient techniques for the removal of nitrate at low cost, without the addition of chemicals. In this study, we report on an advanced and efficient approach, referred to as electrodeionization (EDI), for effectively removing and concentrating nitrate with low energy consumption. An additional merit of this process was that hardness ions, such as Ca^{2+} and Mg^{2+}, were also simultaneously removed from the dilute compartment and recovered in concentrate compartment. Furthermore, the limiting current was systematically investigated and the impacts of different applied currents, water flow rates, and ratios of cationic and anionic exchange resins on the performance of nitrate removal were studied. When treating actual groundwater samples, the EDI system exhibited an excellent removal rate for all ions (>90%) under a low and constant cell voltage. The results confirmed that the EDI process is suitable for the continuous and highly efficacious removal and recovery of nitrate and hardness ions in ground water.

1. Introduction

Increased levels of nitrate in surface water and groundwater have become a significant environmental problem on a global scale. Contamination with high nitrate concentrations is the result of industrial activity, wastewater treatment plants, domestic sewage, landfills, agricultural fertilizers, as well as human and animal wastes, etc. [1]. One of the primary health hazards regarding nitrate is that it is reduced to nitrite within human body, which reacts with red blood cells to cause methemoglobinemia (also known as blue-baby syndrome). Nitrite oxidizes hemoglobin to methemoglobin, which impacts the capacity of blood to transport oxygen to cells and tissues [2,3]. In addition, due to their low gastric acidity, infants are particularly sensitive to the nitrate contamination. Therefore, it is critical to develop an effective approach for nitrate removal from potable water. According to the Guidelines for Canadian Drinking Water Quality, as well as World Health Organization's recommendation, the maximum acceptable concentration (MAC) in drinking water has been set at 10 mg/L NO_3^--N [4], which corresponds to 45 mg/L of nitrate.

In order to remove nitrate from water, several techniques have been proposed: biological processes [5–7], chemical precipitation [8], reverse osmosis [9,10], ion exchange [11,12], electrodialysis [13–16] and catalytic reduction [17]. Among them, biological denitrification has been previously successfully utilized for the treatment of municipal and industrial wastewater. However, large installations are required and biological processes are quite slow. Moreover, since bacterial responses for nitrate transformation are very sensitive, ambient parameters such as pH and temperature must be maintained within a certain range. Conventional ion exchange resins have also been employed for the removal of nitrate. Advantages of this strategy include the acquisition of very low nitrate concentrations, low operating cost, reduced time consumption, and relative insensitivity to temperature fluctuations, in comparison to biological denitrification [18]. However, this is a non-continuous operation as the resins become exhausted, which necessitates their regeneration using concentrated acidic or basic solutions, which create secondary chemical wastes, as well as increased operational costs [19]. Membrane processes such as electrodialysis (ED) have proven their reliability and efficacy when large volumes are to be treated. This is an electrochemical separation process that combines an electric field with ion exchange membranes to separate ionic species from aqueous solutions. Nevertheless, the limitation of electrodialysis is that high levels of energy are consumed, in conjunction with low ion removal efficiencies, once ion concentrations become too low [20].

A hybrid ion-exchange resin/electrodialysis process is referred to as electrodeionization (EDI) [21–24]. This synergistic

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combination allows EDI to overcome the inherent drawbacks of these two technologies when they are applied on their own. Systems that integrate EDI have the capacity to continuously treat solutions with low conductivity due to the incorporation of ion exchange resins between the membranes that are contained within the dilute compartment of the electrodialysis system. The ion exchange resins are continuously regenerated by the applied electric field, which can dissociate water in situ to form H^+ and OH^-, thus no additive chemicals are required [25]. Further, added ion exchange resins provide supplementary conductivity to the dilute compartment, which leads to more rapid, energy efficient, and extensive separation [26]. Electrodeionization was initially investigated in 1956 by Walter et al. [27], and in the late 1950s, Glueckauf conducted theoretical investigations into these hybrid processes [28]. Currently, EDI is widely used for the generation of high-purity water, removal and recovery of heavy metals, organic compound separation, and rinse water for the microelectronics industry [29–36].

Very few researchers have investigated the removal of nitrate using EDI to produce potable water [14,24,37,38], and actual water streams typically contain hardness ions such as Ca^{2+} and Mg^{2+}. The aims of this investigation were to evaluate the impact of the presence of hardness ions on the removal of nitrate and energy consumption, and to determine the optimal operating parameters of EDI technologies for the purification of groundwater. In the present work, we have explored EDI as an advanced approach for the continuous removal of nitrate and hardness ions. UV–Visible spectroscopy was applied to monitor nitrate concentrations, while Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used to determine Ca^{2+} and Mg^{2+} concentrations in mixed solutions. Furthermore, the effects of different operational parameters (e.g., current density, water flow, and ion exchange material ratios) have been systematically investigated. Meanwhile, in this study, we have improved the configuration of the EDI membrane stack, which might be employed to simultaneously separate and recover other cations and anions.

2. Experimental

2.1. Materials

A strong acidic macroreticular cation exchange resin (Amberlite® 200C Na) and a strong basic macroreticular anion exchange resin (Amberlite® IRA900RF Cl) were purchased from Rohm and Haas Co. Cationic exchange membranes (CMI-7000S) and anionic exchange membranes (AMI-7001S) were provided by Membranes International Inc. (The properties of the membrane are listed in Table 1). Inorganic chemicals were supplied by Sigma Aldrich as analytical grade reagents, and standard nitrate solutions were prepared using $NaNO_3$. Solutions containing Ca^{2+} and Mg^{2+} were prepared through the dissolution of $Ca(NO_3)_2$ and $Mg(NO_3)_2$, respectively. The 0.1 M H_2SO_4 electrolyte was prepared from ACS reagent grade H_2SO_4 (95.0–98.0% purity). The water used in the preparation of all the solutions was purified by a Nanopure® Diamond Water System (18.2 MΩ cm), and all of the experiments were carried out at 20 ± 2 °C.

2.2. Instruments for measurements

Nitrate concentrations in solutions were monitored by a UV–Visible spectrophotometer (Cary 50) with a 4 cm^3 quartz cuvette, whereas the Ca^{2+} and Mg^{2+} concentrations in solutions were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (Varian Vista Pro). A pH meter (Oakion Acorn®) was applied to measure the pH of solutions. The current–voltage curve and time–voltage curve were recorded by a Voltalab (PGZ 402 Universal Potentiostat) and the conductivity experiments were carried out using a multimeter (Oakton).

2.3. Ion exchange materials pre-treatment

All of the ion exchange materials were treated accordingly prior to the EDI process in order to minimize any inaccuracies due to the initial exchange capacities of resins and membranes. Specifically, the anion and cation membranes were immersed in 0.1 M NaOH and 0.1 M H_2SO_4 for 24 h, respectively, before use, and subsequently rinsed with deionized water to remove any excess reagents just prior to their installation into the EDI cell system. The anion exchange resins (Amberlite® IRA900RF Cl) were treated with 0.1 M NaOH and stirred for 1 h while the cation exchange resins (Amberlite® 200C Na) were immersed in 0.1 M H_2SO_4 and stirred for 1 h, subsequent to being rinsed twice with pure water and separated from the water via filtration and complete drying at 60 °C [21].

2.4. Electrodes for EDI cell

The EDI process was carried out in a custom-fabricated electrochemical cell utilizing a stainless steel plate (6 cm × 10 cm) as the cathode, and $Ti/Ta_2O_5–IrO_2$ (6 cm × 10 cm) as the anode. Our previous work has verified that $Ta_2O_5–IrO_2$ coatings possess robust electrical and electrocatalytic properties as an anode material [39,40].

In order to fabricate the $Ti/Ta_2O_5–IrO_2$ electrode, a thermal decomposition technique was employed. Briefly, a pure Ti mesh substrate with area of 6 cm × 10 cm was initially immersed in acetone in an ultrasonic bath for 15 min, rinsed with pure water, then etched in a 18% HCl solution at 85 °C for 15 min, and then rinsed again with ultrapure water. According to an established protocol published by our group [41], the $Ta_2O_5–IrO_2$ coating was prepared by combining tantalum and iridium precursor solutions. The tantalum precursor solution contained 0.13 g of $TaCl_5$ dissolved in 7.5 mL of isopropanol, while the iridium precursor solution was prepared by dissolving 0.30 g of $IrCl_3·3H_2O$ in 2.5 mL of ethanol. Subsequent to mixing both the tantalum and iridium precursor solutions, the Ti substrates were manually painted with the coating solution using a brush. This process was repeated until an oxide coating load of 30 g/m^2 was attained. The fabricated $Ti/Ta_2O_5–IrO_2$ electrodes were then annealed at 450 °C for 1 h.

2.5. Description of the EDI cell and experimental scheme

The experiments were performed with a laboratory EDI cell, as shown in Scheme 1, which is a plate-and-frame module with ion

Table 1
Properties of anionic and cationic exchange materials.

Materials	Cationic resin	Anionic resin	Cationic membranes	Anionic membranes
Name	Amberlite® 200C Na	Amberlite® IRA900RF Cl	CMI-7000 Membranes International Inc.	AMI-7001S Membranes International Inc.
Matrix	Styrene DVB copolymer	Styrene DVB copolymer	Gel polystyrene crosslinked, DVB	Gel polystyrene crosslinked, DVB
Functional groups	-SO_3^-	-$N^+(CH_3)_3$	-SO_3^-	-$N^+(CH_3)_3$
Total exchange capacity (Eq/L)	>1.7 (Na^+ form)	>1.0 (Cl^- form)	1.6	1.3