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Groundwater treatment by electrodialysis: gearing up toward green technology

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A B S T R A C T

The performance of a tailor-made electrodialysis stack to treat groundwater was conducted and evaluated. The stack was operated at optimum experimental conditions at applied voltage of 17 V, feed flow velocity of 0.033 L/s, and desalination time of 92 min. Major cation contents of the groundwater were Na, K, Ca, Mg, and As, and anions identified were Cl, NO_3, SO_4, HCO_3, and PO_4. The average cation and anion removal efficiency were 99.15% and 100%, respectively. The oxidation-reduction potential was also recorded to increase from –162.2 to 908 mV, indicating a shift from a highly reducing to a highly oxidizing reaction. Solution pH was also noted to drop from 7.62 to 5.80 with corresponding decrease in the conductivity of 1,388–36 μS/cm. The product water can be classified as that of purified water and suitable for drinking and analytical purposes. Arsenic desalination kinetics was found to increase overtime at constant applied voltage and feed flow rate. Lower As feed concentration samples tend to achieve product water concentrations with maximum contaminant level lower than 10 ppb earlier than high feed concentration samples.

Keywords: Electrodialysis; Groundwater treatment; Removal efficiency; Green technology; Sustainable environment

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1. Introduction

One of the basic rights of the people is the access to safe and drinking water. In 2006, the United Nations General Assembly declared the periods 2005–2015 as the International Decade for Action, “Water for Life” [1]. In the first addendum to the third edition of the Guidelines for Drinking Water Quality, three important qualities are suggested to be monitored strictly, namely microbial, chemical, and radiological characteristics of drinking water.

Surface and groundwater are the two major sources of drinking water worldwide. However, the hydrogeological distribution of freshwater resources is not as even as expected throughout the world. The rapid growth in population resulted in a greater demand on the quantity of drinking water, leading to catastrophic water shortage in several areas of the world. Since only around 0.8% of the total earth’s water is fresh water [2], groundwater resources are being exploited to meet the demands of the various sectors [3]. It is projected that by year 2030, the global needs of water would increase to 6,900 billion m^3 from the current 4,500 billion m^3 [4]. Thus, about 53% increase in the amount of drinking water is needed by year 2030. Consequently, the present surface water resources will no longer be sufficient to meet the future needs of mankind, while groundwaters were mostly polluted due to natural phenomena and anthropogenic activities of man. The contamination of groundwater with metals is primarily attributed to anthropogenic activities and requires risk assessment to characterize the magnitude of the threats

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to humans and ecological receptors [5]. In addition, the natural weathering of soils and rocks also introduce traces of elements into the groundwater [6,7].

Though only a few of the chemicals that can occur in drinking water have immediate health effects to humans, priority must be given both to monitoring and remedial actions for chemical contaminants in drinking water to ensure its efficient management and avoid adverse health effects associated to prolonged period of exposure [8].

Over the years, electrically-driven membrane separation techniques are being employed to treat and remediate groundwater for drinking purposes. Electrodialysis (ED) process as an electrically-driven membrane process used in the separation of ions across charged membrane has been documented to be an efficient technology in removing chemical contaminants from industrial wastewater [9,10]. Though ED's dominant application is still in desalination, ED becomes an attractive alternative to the traditional groundwater treatment and remediation due to zero emission.

A simple ED set up required five components namely, (1) a direct current (DC) power source which will provide adequate electricity to the system, (2) membranes that will provide transport of counter ions and will block passage of coions, (3) electrodes where oxidation an reaction will occur, (4) a solvent which is used as a continuum for ion transport by filling space between electrode and membrane, and (5) an electrolyte which carries the current from cathode to anode [11]. One of the drawbacks of ED is the high cost of electricity needed for the start-up operation and to power axillary equipment such as pumps, digital flow meters, and sensors. A typical ED has three storage tanks used to hold the feed stream, the concentrate stream and the electrolyte or electrode flush solution.

Several modifications have been done over the years on the different components of ED to enhance its performance. Strathman [11] described the recent developments in ED included enhancements in the ion exchange membranes, development of new flow paths, and other design modifications. In the study of Mendoza et al. [10,12], a tailor-made ED stack with only two streams and tap water as the electrode flush solution was utilized in a recirculating batch mode is optimized to remove arsenic from groundwater. The study achieved a 97.6% arsenic separation/removal using Arsenic-spiked deionized (DI) water as simulated groundwater.

The use of ED is at present gaining popularity due to its potentials for a sustainable process. In a review about cleaner production, ED was known to be capable of simultaneously treating or recycling water and chemicals recovery [13]. Because of these abilities, ED process is also recognized to contribute to green processes. This is because upon careful consideration of the improvements in the system efficiency and design, the ED process can be an energy saving and zero waste process [14].

This study evaluated the performance of the tailor-made ED stack in treating contaminated groundwater as well as its potentials in providing potable drinking water. The study focused on ED design and process modification by using a tailor-made stack composed of only two storage tanks and used tap water as electrode flush chemical. The use of the two storage tanks and tap water as an electrode flush solution slashed the operating cost of the system and the requirement for auxiliary pumps. Though no operating cost studies were presented, the modified stack can open new design and process perspectives in producing water of different beneficial use in a stainable manner using ED.

2. Experimental

2.1. The ED stack

The tailor-made ED stack design configuration as illustrated in Fig. 1 is composed of two storage tanks. The feed tank stores feed water that enters the stack. At the start of the

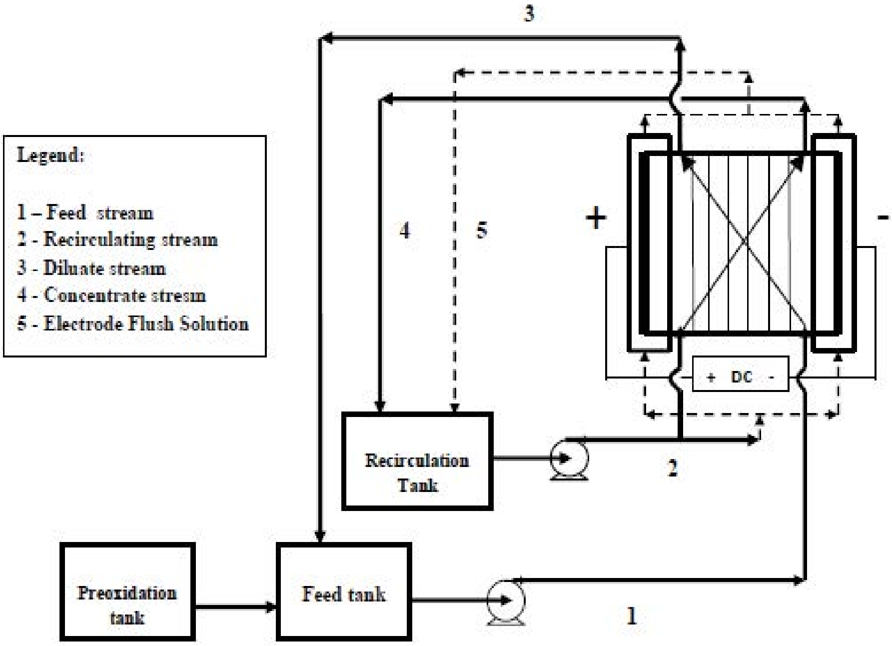

Fig. 1. The design configuration and process flow diagram of the tailor-made ED stack.

operation, the concentrate tank is filled with 6 L of tap water. The feed and the tap water were recirculated into the stack until steady state is achieved before turning on the power supply.

The stack is operated under the limiting current density and using optimum experimental parameters discussed in the previous study [13]. Primary treatment in the form of filtration through a 0.45 μm GHP was performed to remove large organic matter that may damage the ion exchange membranes. Sample pretreatment by the addition of stoichiometric amount of sodium hypochlorite was used to transform all arsenic III to arsenic V for better desalination or separation.

The cation concentrations (Na, Mg, Ca, K, Mn, and Fe) of the feed, diluate stream and concentrate stream were determined using a Perkin Elmer 2000 optima DV inductively coupled plasma – optical emission spectrophotometer (ICP-OES). The ICP-OES was equipped with a hydride generator (HG-ICP-OES) for arsenic determination. Anion concentrations in the form of nitrates, nitrites, phosphates, sulfates, and chlorides were analyzed using a Dionex DX-120 ion chromatograph (IC) equipped with a Reagent-Free Controller (RFC), carbonates were obtained by titrimetric methods and TOC by direct method for drinking water and wastewaters (Method 10129) using Hach DR 500 UV-vis spectrometer.

Groundwater samples used in this experiment were obtained from raw water source, well no. 10 of Taiwan Water Corporation water treatment plant in Beigang Township, Yunlin, Taiwan. Characteristics of the groundwater used for this study were presented in Table 1. Groundwater protocol on preservation and arsenic speciation procedures implemented in this study is the same as that of Bednar et al. [15].

2.2. Treatability experiment

3 L of contaminated groundwater was fed to the stack through the feed tank at a rate of 0.033 L/s. The concentrate tank was filled with 6 L of tap water. The flow and current steady state was initially established before the start of treatment. An applied voltage of 17 V was supplied, and the feed solution was recirculated in the stack for 92 min. Sample effluent was drawn every 10 min of desalting operation to account for the separation or removal of the cations and anions in the diluate and concentrate streams.

Table 1
Physical and chemical characteristics of the sample groundwater used in this study

Cations	Concentration (ppb)	Anions	Concentration (ppb)
Na^+	145.50	Cl^-	130.56
K^+	34.52	NO_3^-	<0.1
Mg^{2+}	18.97	SO_4^{2-}	2.29
Ca^{2+}	20.75	HCO_3^-	119.70
Mn^{2-}	0.093	PO_4^-	6.30
Fe^{tot}	<0.01	TOC	1.19 mg C
As^{tot}	232.08		

Others: E_h = –162.3 mV; pH = 7.68; T = 23ºC; and EC = 1,388 μS/cm.
tot = total.

3. Results and discussions

3.1. Feed salt concentration and ED performance

The ED performance was evaluated through the removal efficiencies of the different cations and anions in the sample. In the first 5 min of desalting, a 50% average cation removal was achieved. This is due to the adequate amount of current supplied through the applied potential and that of the ions and coions present in the stream to transport it. Figs. 2(a) and (b) indicate that the removal of cations and anions in the feed groundwater is primarily affected by the operating time. The same desalination pattern is observed on all cationic species present. The rate of desalination varies based on the charge of the cation. The cations with lower charges such as Na^+ and K^+ are separated or removed from the feed solution faster than that of Ca^{2+} and Mg^{2+}. Arsenic which is of two species (As^{+5} and As^{+3}) is removed in a relatively slower rate as compared with the other cations. The prolonged desalination of arsenic is because of the decrease in current utilization in the stack during operation due to the faster

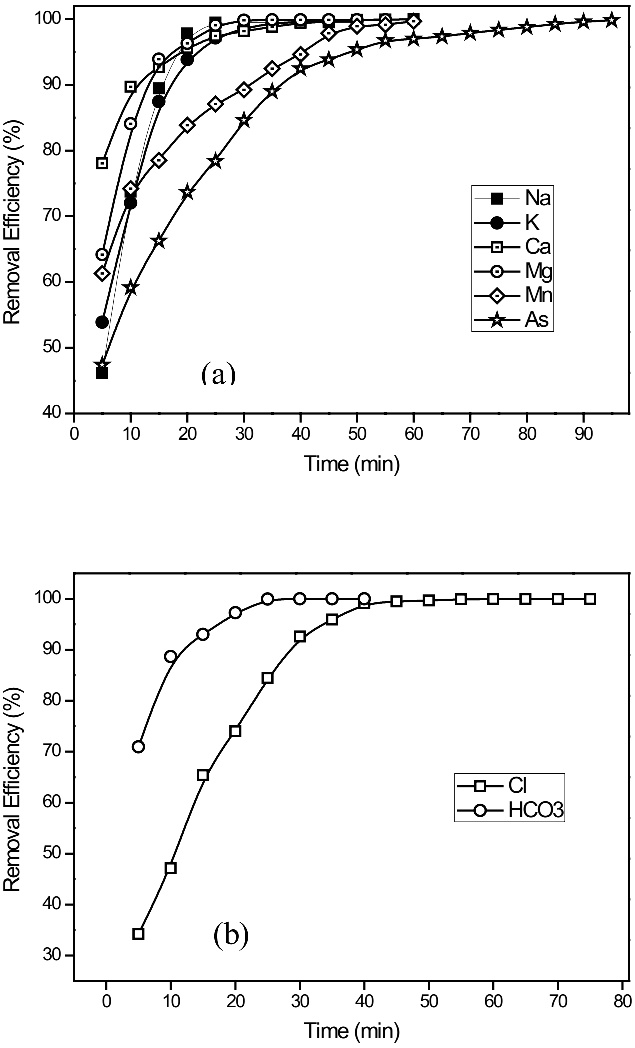

Fig. 2. Removal efficiencies (in percentage) by electrodialysis with respect to time of (a) cations, and (b) anions present in the sample groundwater.

removal of the lower charge cations. The prolonged stay of arsenic species in the low current environment also caused the reduction of some As^{+5} back to As^{+3}, which has very low membrane affinity [11].

For the anions, the ED process was found to exhibit a more superior performance than cation removal. Majority of the anions (NO$_3^-$, SO$_4^-$ and PO$_4^-$) was removed in the first 5 min of desalting time. This is attributed to the higher membrane affinity of the anions present in the feed solution, as compared with that of the cations. In general, both cation and anion removal from the sample groundwater was achieved in less than 100 min of desalting time.

3.2. The diluate and concentrate streams

The depletion of cations was achieved in the diluate stream and enrichment of cations achieved in the concentrate stream is illustrated in Figs. 3(a) and (b). Chemical analysis of the diluate and concentrate streams manifest a considerable reduction of cation and anion concentration as compared with the initial sample concentration. Cationic and anionic concentrations with respect to operating time phenomenally decreased from 5 to 20 min. Desalination becomes marginal after 30 min onward, which can be attributed to the decrease in the number of ions that supplies current to the system and possible decrease in ion exchange permselectivity [12]. The interaction of cation and anions in the solution results in the ion-pair formation. At high concentrations, the interaction between ions decreases due to shorter distance between them.

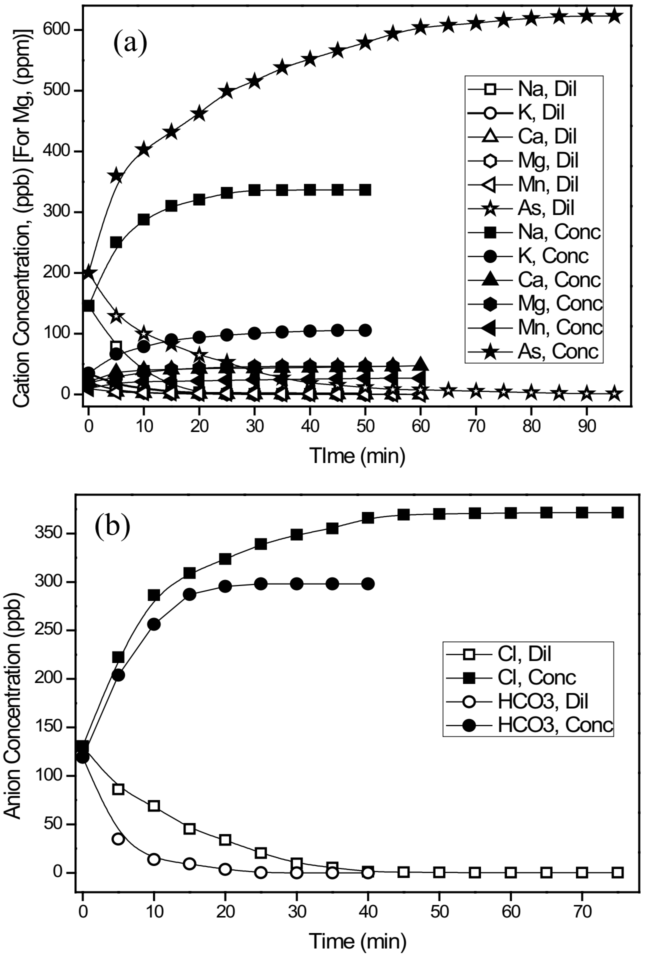

Fig. 3. Product water concentrations of the electrodialysis of sample groundwater. (a) Cation concentration and (b) anion concentration. (Dil = diluate stream, Conc = concentrate stream).

The introduction of applied voltage in the system provides supplied current in the system that is consumed by the ions. The increase in the removal rate with respect to time of the ions in the ED stack resulted in the decrease of ions and their interactions. This decreases the current transporters that reduce the ability of the solution to carry electrical current due to lower electrical conductivity (see Fig. 4).

Arsenic is the most harmful cation present in the feed solution. The presence of arsenic particularly in drinking water poses a very tremendous threat to human health and its removal from contaminated groundwater was so far the best remedy to eliminate the threat [16]. The average removal of As in the sample groundwater is at 99.81%, which leaves 0.88 ppb of Arsenic in the diluate stream. This is very low as compared with the 10 ppb maximum contaminant level mandated by USEPA and WHO [8,1]. At this concentration, the groundwater becomes safer to drink or be used for cooking or washing [17].

3.3. Arsenic desalination kinetics

The increased desalination of arsenic with its operating time is due to the efficient transport of ions in the boundary layers and across the membranes (refer to Fig. 5). As the operating time approaches optimum which is at 95 min, the current utilization was observed to approach a constant value, which signifies the depletion of ions in the boundary layer, but not polarization [18]. This is because polarization is accompanied by an increase in current utilization after the constant current region, which will commence current utilization for spitting of water in the system [19]. This means that the system is operated way below the concentration polarization region which indicates current utilization efficiency.

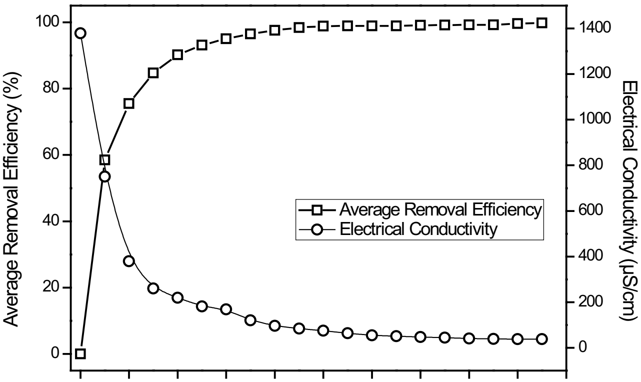

Fig. 4. Electrical conductivity and removal efficiency with respect to time of the electrodialysis of groundwater.

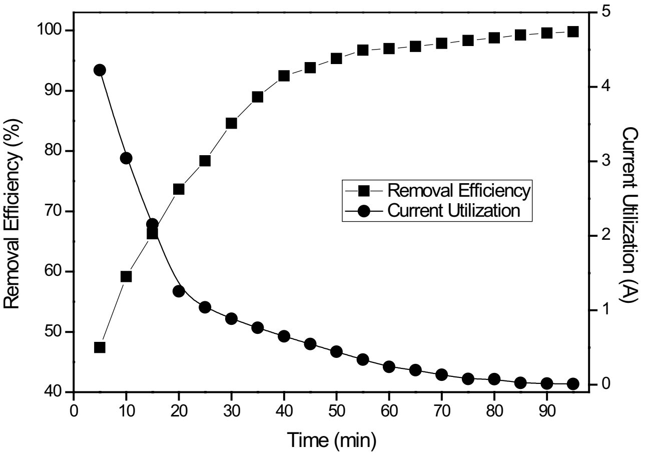

Fig. 5. Product water desalination and current utilization kinetics of the electrodialysis of sample groundwater.

3.4. *The clean product water (diluate) and process sustainability*

Some of the physical and chemical characteristics of the product diluate stream of this study as illustrated in Table 2. There is an observed considerable reduction in the cationic contents of the groundwater sample from its feel solution characteristics to the final product water, indicating the huge potential of ED as a process to yield potable drinking water. The purity of the product diluate stream was determined by comparing it to purified water's physical characteristics. It was observed that product diluate stream produced by electrodialysis competes with that of purified water.

The high pH (5.68) of the product diluate stream further attests to its purity. At high purity, waters rapidly pick up contaminants such as CO_2 from air, which affects its (low) conductivity and pH and can affect the accuracy of the pH meters. The adsorption of just a few ppm of CO_2 can cause the pH of water to drop to as low as 4.5 though water is still in high purity [18]. In addition, the collecting tanks for the diluate stream are uncovered which might facilitate atmospheric CO_2 adsorption, in addition to the carry-over of contaminant due to the recirculation process.

The oxidation-reduction potential was also recorded to increase from –162.2 to 908 mV, indicating a shift from a highly reducing to a highly oxidizing reaction that will enhance easier immobilization of toxic metals present in the system.

Table 2
Physical and chemical characteristics of the diluate

Cations	Concentration (ppb)	Anions	Concentration (ppb)
Na^+	0.77	Cl^-	0.04
K^+	1.23	NO_3^-	ND
Mg^{2+}	0.003	SO_4^{2-}	ND
Ca^{2+}	0.009	HCO_3^-	ND
Mn^{2-}	ND	PO_4^-	ND
Fe^{tot}	ND	TOC	ND
As^{tot}	0.88		

Others: E_h = 908 mV; pH = 5.80; T = 24ºC; EC = 36 μS/cm; TDS = 1.02 ppb. ND = none detected.

Table 3
Comparison of the physical characteristics of purified water and the product water (diluate stream) of this study

Parameters*	Purified water [19]	Product water (this study)
Electrical conductivity (μS/cm)	1–50	36
Electrical resistivity (MΩ cm)	0.02–1.0	0.034
pH	6.6–7.6	5.8
TDS (ppb)	1.4	1.02

*Measured at T = 25°C.

The concentrate stream, on the other hand, has very high ionic concentrations can be reprocessed for ion/salt recovery for commercial and even pharmaceutical utilization. For instance, the very high amount of arsenic in the concentrate stream which is around 600 ppb (from Fig. 3(a)) in the concentrate stream is an ideal concentration for the recovery of pharmaceutical grade arsenic trioxide (As_2O_3) which was used as treatment for acute myeloid leukemia [20] approved by the USA FDA as Trisenox in 2000. The other cations and anions in the concentrate stream also share the same fate. With the production of potable drinking water through the diluate stream and the great possibility of cations reclamation of the concentrate stream, this ED process becomes a zero-waste generating process.

4. Conclusion

The performance of a tailor-made ED stack using only two storage tanks and tap water as an electrode flush solution is evaluated. The cations and anions present in the feed solution was successfully separated from the diluate stream at 99%–100% removal efficiency under optimum experimental conditions. The product diluate stream's physical and chemical characteristics were observed to be within that purified water. With proper process control and optimization, two possible beneficial use of the product water is at hand; (1) the production of potable water, and (2) production of a high purity water for laboratory and analytical preparation. The recovery and reclamation of the ions in the concentrate streams provide avenues to produce some significant pharmaceutical substances such as arsenic trioxide into Trisenox. Thus, the ED process sustainability goes a long way down to its potential to be a zero-waste process which is major criteria for green technologies.

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